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# Obtaining and characterizing bioplastic films obtained from passion fruit (*Passiflora edulis* Sims) waste

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**ABSTRACT**

**Objective**: Obtaining films from a vegetable biopolymer from the peel (a by-product) of passion fruit (*Passiflora edulis*) (BPM) and contribute to reduce the environmental pollution generated by the consumption of petroleum-derived plastics.

**Design/methodology/approach**: By acid hydrolysis at four concentrations of citric acid (0, 1, 2, and 3%), pectin was extracted of passion fruit peels, making a paste mixture with glycerol. The obtained biofilms with an approximate 1 mm thickness were characterized by transformed Fourier infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with coupled elemental analyzer (EDS).

**Results**: XRD diffractograms revealed that passion fruit bioplastic had a semi-crystalline structure and a calculated crystallinity index of 74.6%. Its value reduced by the half as the citric acid increased concentration, the samples with lower concentration with greater flexibility (1%). FTIR analysis suggested alterations in the BMP structures and a decrease of methoxyl groups in the polymeric chains with the increasing in citric acid content.

**Limitations/implications**: SEM micrographs showed homogeneity in the films, although with some granular irregularities and folding.

**Findings/conclusions**: The increase in citric acid concentration decreased the degree of gelation in the writing of the obtained biofilms, suggested by EDS and FTIR results, with a consequent reduced flexibility of the GMP films.

**Keywords**: Passion fruit, bioplastics, agro-industrial waste, physicochemical characterization.

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## INTRODUCTION

Plastics are among the most widely used commodities in the world. According to recent data, their global plastic production is of about 335 million t $yr^{-1}$, from which more than 95% are petroleum-based plastic (Xin-Chan *et al.*, 2021; Rivero *et al.*, 2017).

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For many years, these synthetic materials have been used in a variety of applications in everyday life, such as in food and beverage packaging, automotive, healthcare, electronics, and communication industries (Goncalves *et al.*, 2017). Plastics became indispensable due to their versatility, aesthetic qualities and low cost. However, it is estimated that these constitute 10% of household waste and most of it is dumped in landfills. Plastic waste has several effects on human health and ecosystems. Mismanagement of landfills leads to the release of waste containing chemicals. Its impact on humans and the ecosystem is due to toxic microfragments that easily leach into the surrounding ecosystems (Devasahayam *et al.*, 2019).

The fossil fuels depletion, the energy crisis, the deteriorating environmental conditions and climate change have spurred the development of sustainable technologies derived from renewable sources. In this context, the abundant available biomass represents a potential alternative to manufacture essential products for everyday life. The utilization of biomass such as fiber, cellulose and starch to produce bioplastics and the replacement of fossil materials is a widely accepted strategy to establish a more sustainable society (Karan *et al.*, 2019).

About $3.7 \times 10^{9}$ t of agricultural residues are annually generated worldwide, which contributes to the problem of waste disposal in landfills, as these are burned, generating greenhouse gases (Grewal *et al.*, 2020). Therefore, valorising these agro-industrial wastes to manufacture new products is essential in the development of a circular economy and combating dependence and reduction of fossil fuels.

The maracuya (*Passiflora edulis* f. flavicarpa) (*Passifloraceae*) is a native species of the American tropics. There are more than 400 species of *Passiflora*, 50 of which are edible and two are commercially cultivated. Maracuya or passion fruit as *P. edulis* is known, is one of the most appreciated exotic fruits in the international markets, mainly for its organoleptic and nutritional properties and the large amount of pectin it contains. Pectin is an additive with no limitations or reserves of use and is a main hydrocolloid in food processing, which modifies the texture of compotes, jams and jellies. Due to its characteristics, passion fruit is a very versatile fruit, used in the cosmetic industry, confectionery, non-alcoholic beverages and particularly in the gastronomic sector (Arias-Domínguez *et al.*, 2019).

For Colombia, passion fruit cultivation is important for its economy, because it is a source of income and employment in the region. In 2020, 19,853 ha were cultivated, with a production of 200,920 t, and a yield of 13.30 t $ha^{-1}$ (DCAF, 2020). In the department of Meta, where the Agroindustrial Center (SENA-Hachón) is located, the producer municipalities Vista Hermosa, Mesetas, Granada, Fuente de Oro and Puerto Lleras are founded, which cultivate 1,320 ha, with an average yield of 15 t $ha^{-1}$, harvesting approximately 19,800 t, of which only 35% is used (pulp and seeds); the remaining 65% are harvest residues, so in 2020 there were 12,870 t of residues, available for use. Therefore, this research focuses in obtaining films of bioplastic from passion fruit residues (peel), manufactured with citric acid at different concentrations, by the analysis of results acquired with XRD (X-ray diffraction), FTIR (Fourier infrared spectroscopy) and SEM-EDS (scanning electron microscopy - coupled elemental analyser) methods to characterize their crystallinity, functional groups and intermolecular interactions in their structure and morphology.

## MATERIALS AND METHODS

The passion fruit residues (peels) were supplied by the Department of Meta, Villavicencio, Colombia and processed at the Meta Agroindustrial Center (SENA-Hachón). In the pectin extraction stage, the following procedure was carried out (Figure 1): (1) the peels were washed with tap water, with the purpose of eliminating contaminant remains present in the raw material, (2) extraction of the pectin by the method of acid hydrolysis, with a citric acid solution ($C_6H_8O_7$) at concentrations of 0 (without additives), 1, 2, and 3% (BPM0, BPM1, BPM2, BPM3, respectively), (3) the peels were immersed in the citric acid solutions for 90 min, at 90 °C and removed from the water, (4) once cooled, the mesocarp was separated with the aid of a spatula. The mesocarp obtained was ground in a stainless steel industrial blender to form a homogeneous paste, which was passed through a sieve with a mesh size of 250 $\mu$m to ensure its homogeneity.

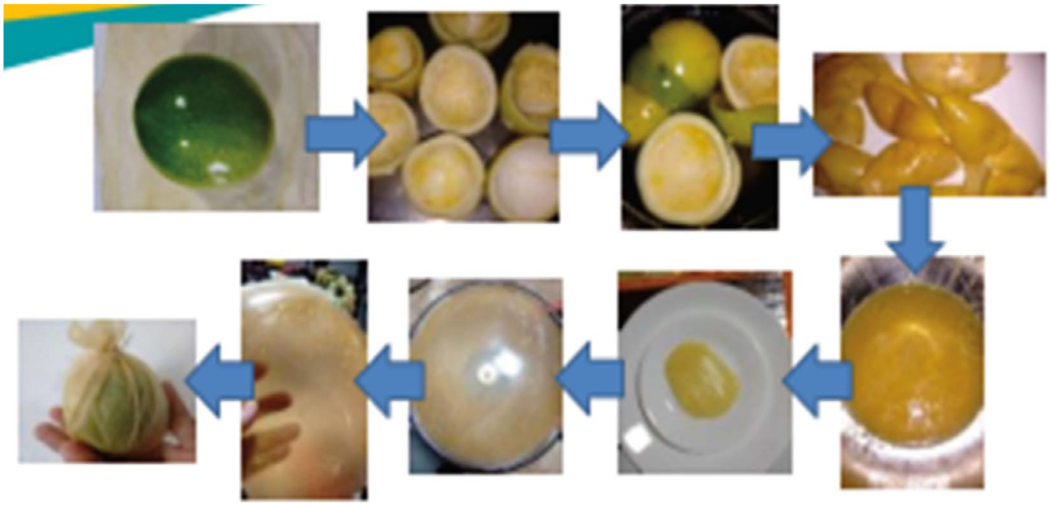

**Figure 1**. Process of the extraction of the mesocarp from passion fruit residues and its hydrolysis (Henao, 2016).

The elaboration of the passion fruit bioplastic films (BPM) was carried out by the following procedure: the paste obtained from the mesocarp was mixed with glycerol at a concentration of 5%, used as a plasticizer; a portion of the mixture was poured onto smooth expanded polystyrene plates covered with a non-stick plastic film (film), spreading the mixture with the help of spatulas to form thin films. The bottom of the plates were then gently tapped to break air bubbles formed during the pouring or the spreading of the biofilms and were placed in a convection drying oven (ECOSHELL brand) at a temperature of 60 °C for 24 h. Once the drying process was completed, the films were carefully peeled off, avoiding breakage, and were stored in hermetically sealed bags to avoid environmental humidity until their subsequent use.

## Characterization methods

*Infrared spectroscopy* (*FTIR*)

The determination of the functional groups of the passion fruit bioplastic samples was carried out using the Fourier Transform infrared spectroscopy technique with a Nicolet Magna Protegé 460 FTIR infrared spectrophotometer in the absorbance mode, with a resolution of 4 $cm^{-1}$ and 100 scans. The 1 mg samples were mixed in 100 mg KBr.

*Scanning Electron Microscopy* (*SEM-EDS*)

The morphology and elemental composition of the bioplastic were determined by scanning electron microscopy (SEM) with an integrated elemental analyzer (EDS), Bruker D8 Advance. The samples were coated with a gold deposit (thickness less than one micron).

*X-ray Diffraction* (*XRD*)

The crystallinity of passion fruit mesocarp was determined by X-ray diffraction spectra, powder method (PXRD), using a Siemens D 5000 Diffractometer equipment, CuK$\alpha$ spectrum ($\alpha$=1.5418 Å and energy 8.047 keV).

The percent crystallinity was calculated by the method of Segal *et al.* (1959) Eq. (1):

$$X_c\% = 100\left[1-\left(\frac{I_1}{I_2}\right)\right] \qquad \text{Eq. (1)}$$

where: $I_1$ is the intensity of the minimum peak and $I_2$ is the maximum intensity of the crystalline peak, respectively.

## RESULTS AND DISCUSSION

### Fourier Transform Infrared Spectroscopy (FTIR)

Fourier infrared spectroscopy was performed to characterize the molecular interactions in the passion fruit bioplastic (PMB) film. The interferograms of the PMB films, manufactured with different concentrations of citric acid (0, 1, 2 and 3%) are shown in Figure 2 a, b, c and d. The broad absorption area between 3600 and 3000 $cm^{-1}$ was assigned to O—H stretching vibrations, due to inter- and intramolecular hydrogen bonds, characteristic of the pectin structure (Nizar *et al.*, 2019). The absorption band around 2925 $cm^{-1}$ corresponds to the stretching of C—H bonds, involved in CH, $CH_2$ and $CH_3$ groups of stretching and bending vibrations (Lorevice *et al.*, 2016).

The bands around 1616 $cm^{-1}$ and 1734 $cm^{-1}$, corresponding of carbonyl groups (COOH) and acetyl groups ($COOCH_3$) of pectin, confirm the high degree of esterification and the presence of high methoxyl pectin in the passion fruit mesocarp. The free and esterified carboxyl groups are useful for the identification of high and low methoxyl pectins (Manrique, 2002). The pronounced elongation at 1616 $cm^{-1}$ corresponds to the COO— carboxylate ion symmetric strain vibration band. The peaks at 1318 and 1517 $cm^{-1}$ are attributed to the C—O—H bond stress vibration band. On the other hand, the peaks near 1260 $cm^{-1}$ belong to the asymmetric strain vibration band of the C—O—C bond, and indicate the abundance of methoxyl groups (—O—$CH_3$).

The strong peak at 1061 cm$^{-1}$ suggests the strain vibration band of the symmetric C—O—C group, which also confirms the high degree of esterification and the presence of high methoxyl pectin (Chasquibol *et al.*, 2008). The interferogram corresponding to the BPM1 sample (bioplastic with 1% citric acid, Figure 2b) shows a similar behavior to that of the film in the absence of citric acid (Fig. 2a).

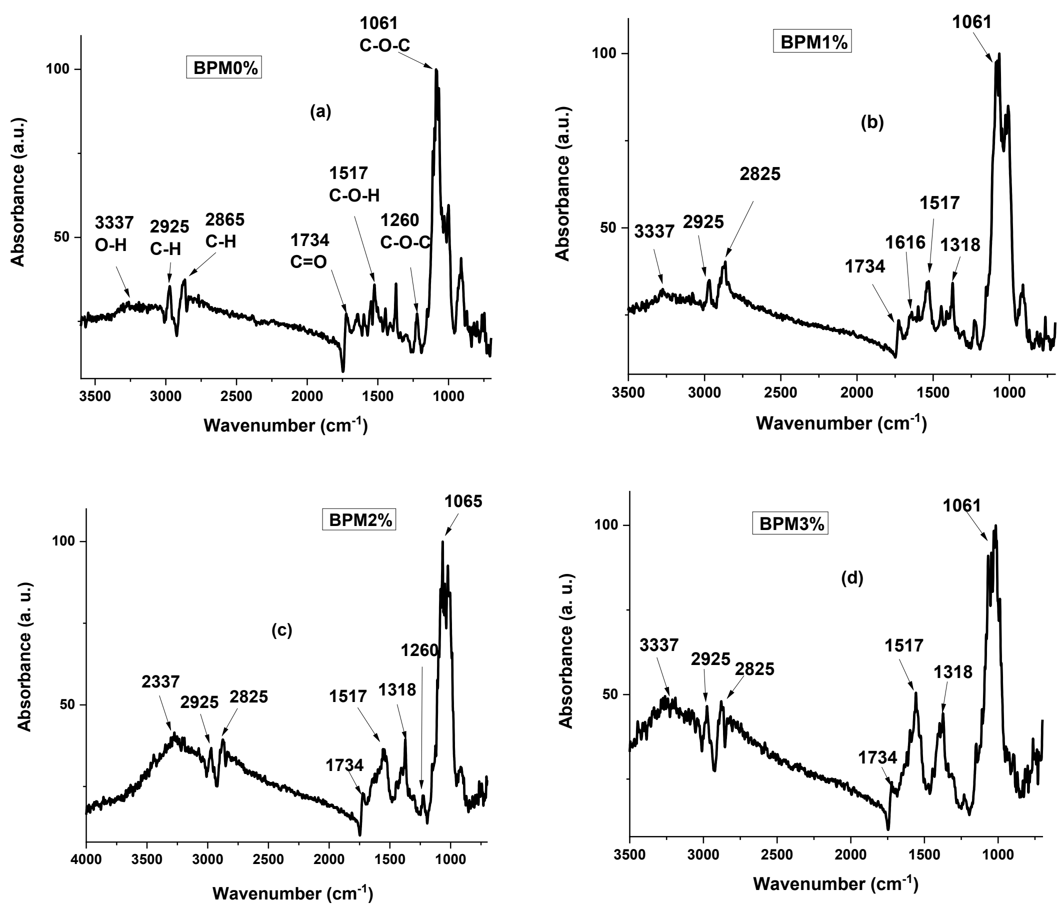


**Figure 2**. FTIR spectra of passion fruit bioplastic (BMP) films prepared with different concentrations (%) of citric acid: a) BPM0, b) BPM1, c) BPM2 and d) BMP3, e) BPM3, f) BPM3, g) BPM3, h) BPM3 and i) BPM3.

The interferograms corresponding to 2 and 3% citric acid (Figure 2c and 2d) were very similar to each other. However, it should be noted that increased acidity (lower pH, 2 and 3% citric acid) affected the methoxyl content of the extracted pectin, the corresponding band at 1734 cm$^{-1}$ (Figure 2c and 2d). The absence of a pronounced elongation in this band, corresponding to the esterified carboxylic groups, places this pectin as having a low methoxyl content (Vázquez *et al.*, 2008). Pectin forms colloids par excellence (Willats *et al.*, 2006), so it has the property of absorbing large amounts of water. These colloids belong to the family of oligosaccharides and polysaccharides of high molecular mass and contain long chains of 1,4-$\alpha$-D-galacturonic acid (GalpA) units. According to one report (Willats *et al.*, 2006), it has been possible to separate and characterize three pectic polysaccharides (homogalacturonan, rhamno galacturonan-I and substituted galacturonans) and all contain GalpA acid in a greater or lesser amount.

*Scanning electron microscopy with integrated elemental analyzer* (*SEM-EDS*)

The microstructure of the passion fruit bioplastic film is influenced by the inter-spatial organization of its components, as well as the way they have interacted during the drying process. Figure 3a shows that the films of BPM0 bioplastic (prepared without citric acid) showed a smooth microstructure in general, compact and continuous without pores, although with some irregularities such as folding and granules, compared to the surface of BPM2 (Figure 3b). Elemental analysis (EDS) (Table 1) suggests that the main elements are C and O, in the presence of traces of other elements (N, Mg, P, Cl, K and Ca), part of the chemical composition of passion fruit peel (León and Riveros, 2014).

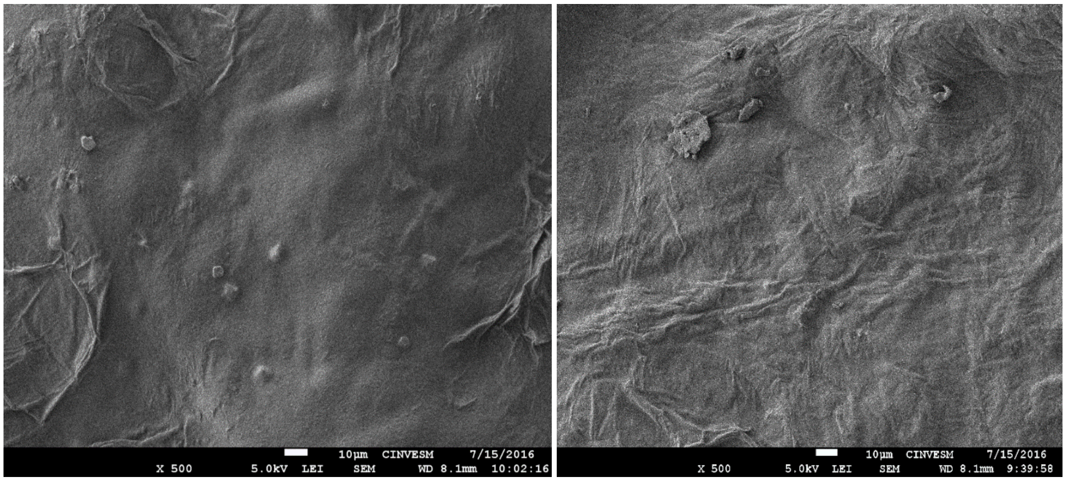


**Figure 3**. SEM micrographs of passion fruit bioplastic BMP films: a) BPM0 (0% citric acid) and b) BPM2 (2% citric acid).

The high percentage of calcium compared to the other BPM0% minerals (Table 1) is due to the clearly structural role of its metal ion for maintaining the integrity of the membranes of the middle lamella and cell walls, binding to the free carboxyl groups of the uronic acid of pectin in the form of pectates (Simmonds, 1980). The calcium ion induces crosslinks involved in the cell adhesion and tissue texture (Fisher & Bennet, 1991).

**Table 1**. Elemental analysis (EDS) of passion fruit bioplastic films BMP0 and elaborated with 2 % citric acid (BPM2), SEM.

| Samples | Element | C | O | N | Mg | P | Cl | K | Ca | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| BPM0% | Mass (%) | 52.3 | 39.34 | 3.63 | 0.35 | 0.95 | 0.43 | 2.54 | 0.38 | 100.00 |
| BPM2% | Mass (%) | 44.73 | 51.91 | | 0.19 | 0.29 | 0.43 | 2.26 | 0.20 | 100.00 |

Note* The EDS analysis of BPM3 is not presented because it shows similar results to BMP2.

When a higher concentration of citric acid was used in the elaboration of the BPM films, the microstructure was slightly altered (Figure 3b) and caused an irregular configuration.

This fact is possibly due to the decrease of esterified carboxylic groups, transforming into a low methoxyl pectin, as can be confirmed by FTIR of BPM2% and BPM3% (Figure 2c and 2d). It has been reported that the gelation power depends also on the concentration of calcium ions that influence the texture of the formed gelatin (Devia, 2003). The ability of calcium to form complexes with pectin is associated with the free carboxyls in the pectin chains. It has been considered that there is an increase in gel formation as the degree of esterification decreases (Anyas and Deuel, 1950). This is corroborated by FTIR analysis (Fig. 2c and 2d), by the absence of a pronounced elongation in the esterified carboxyl groups (band 1750 $cm^{-1}$). EDS elemental analysis of BMP2% citric acid (Table 1) reveals that the calcium concentration decreased by the half compared to BMP (prepared in the absence of citric acid, Table 1).

*Powder X-ray diffraction* (*XRD*)

XRD diffractograms (Figure 4) were analyzed to characterize the crystal structure of the BMP bioplastic. Peaks at 2=12.7, 16.3, 18.40, 25.3 and 40.1° are related to pure pectin (Nizar *et al.*, 2019). A broad peak at 16.3°, as well as a peak of higher intensity at 25.3°, confirmed the presence of some crystalline structure (Figure 4a). In Figure 4b, it is observed that the higher the amount of citric acid (2%), the intensities of the peaks decrease, indicating lower crystallinity index of the film as prepared, which collaborates with the calculated values of crystallinity (Table 2). The results indicate that when 1% of citric acid was introduced, the crystallinity index decreased significantly from 74.6% to 41.8%. For this reason, as the concentration of citric acid increases, the biofilms become more flexible.

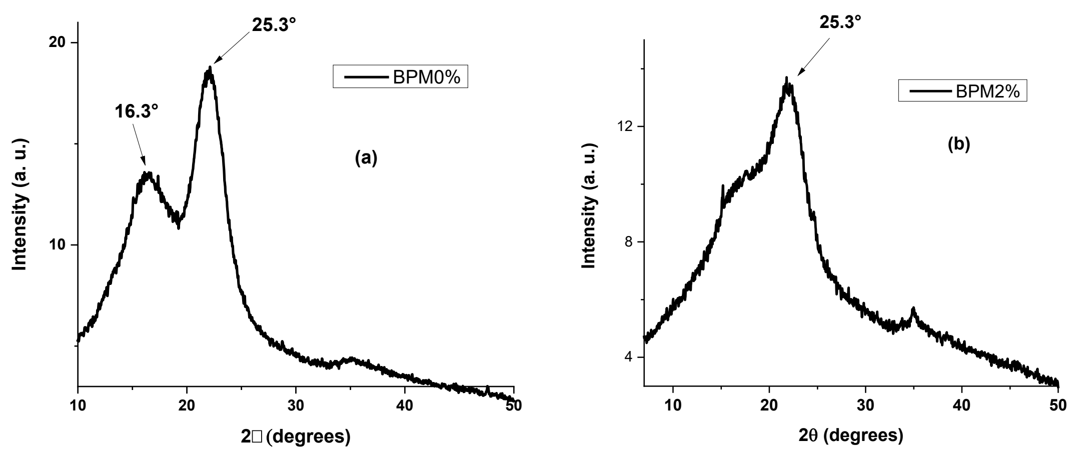


**Figure 4**. Diffractograms of passion fruit based bioplastic (BMP): a) BPM0% and b) BPM2% citric acid.

In gel formation with high methoxyl pectins, it is reported that at pH 3.0 ≈ 90% of the peptidic acid groups are in undissociated form and are therefore able to form hydrogen bonds with acid or hydroxyl groups of adjacent chains. These binding sites can be considered as “crystalline”, whereas the parts of the molecule that do not exhibit cross-linked bonds are in solution (Ferreira, 2007).

**Table 2**. Crystallinity index of passion fruit BMP bioplastic at different citric acid concentrations.

| Citric acid (%) | Cristalinity (%) |
|---|---|
| 0 | 74.6 |
| 1 | 41.8 |
| 2 | 38.4 |
| 3 | 36.5 |

## CONCLUSIONS

Films of a bioplastic (BPM), obtained from the passion fruit mesocarp, have been elaborated with different concentrations of citric acid (up to 3%). SEM analysis revealed that, as the citric acid content increases, the surface becomes more irregular, granular and folded. The crystallinity index of MPA (74.6%) decreased ≈ 2 times with increasing citric acid and BPM3 had 36.5% crystallinity. This change led to a decrease in gelation and the films resulted in more flexibility. Thus, the BPM3 bioplastic resulted with a better consistency, greater flexibility, due to its less crystalline structure. The results obtained are well corroborated by FTIR analysis, where the absence of a pronounced elongation in the esterified carboxylic groups was observed (band 1750 $cm^{-1}$).

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