UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

TÍTULO: Characterization, mechanical properties, and degradation of thermoplastic starch and cellulose blends

Trabajo de titulación presentado como requisito para la obtención del título de Ingeniero (a) en Polímeros

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Urcuquí, julio 2022

Urcuquí, 27 de junio de 2022

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Dedicatoria

Estos años en la Universidad han sido llenos de muchas experiencias y trabajo duro, llegar hasta este punto ha representado un gran esfuerzo en cada semestre. El apoyo de mi familia ha sido fundamental para poder alcanzar esta gran meta, quienes me han apoyado constantemente durante toda mi carrera, en todas las circunstancias en las cuales necesitaba de ellos. Es por esto que el presente trabajo de titulación la dedico a mi amada familia Gabriela (mamá), Xavier (papá) y Daniela (hermana). A mi mamá por siempre brindarme su apoyo, amor incondicional y su compañía en momentos difíciles de salud que atravesé, a mi papá por demostrarme que con trabajo duro y perseverancia se pueden cumplir los sueños, y a mi hermana por contagiarme su pasión hacia las metas propuestas.

Adrián Xavier Yanchapaxi Velasco

Agradecimiento

He aprendido que llegar a un objetivo previamente trazado, involucra el conocer nuevas personas de las cuales vas a aprendiendo en el camino. Además, que el apoyo de mi familia ha representado un gran pilar para cumplir este objetivo. En estos casi 6 años en la Universidad he conocido personas increíbles de las cuales he aprendido mucho. Mis compañeros me han enseñado el trabajo en equipo, la confianza y principalmente el poder mantener amistades duraderas. Mis profesores me han enseñado que tener pasión es un valor muy importante para poder alcanzar cualquier objetivo, además de la paciencia y siempre su predisposición a ayudar a sus estudiantes. Quiero agradecer a mis compañeros y profesores por todo lo que he vivido durante este tiempo en la Universidad. Además, me gustaría hacer un agradecimiento especial a mi tutora de Tesis, Rose Mary Michell, quien me ha apoyado constantemente en esta recta final de mi carrera. Finalmente agradecer siempre a mi familia por todo lo brindado, ya que me considero un reflejo de lo que ellos me han enseñado desde pequeño.

Adrián Xavier Yanchapaxi Velasco

Resumen

Debido a la contaminación causada por el plástico, en los últimos años se han buscado alternativas que lo reemplacen, siendo los más investigados los bioplásticos producidos a base de material orgánico. Uno de los principales materiales orgánicos utilizados es el almidón extraído de la papa y maíz. Sin embargo, existe otro material orgánico que representa un deshecho el cual puede ser aprovechado como fuente de almidón, el cual es la pepa del aguacate. En el presente trabajo se extrae el almidón de la pepa de aguacate con Metabisulfito de Sodio ($Na_2S_2O_5$). Adicionalmente se utiliza Glicerol, Ácido Cítrico y Ácido esteárico para la obtención de Almidón Termoplástico (TPS). Además, se extrae la celulosa de las hojas de agave a través de una desfibriladora para posteriormente ser tratada con NaOH y $NaClO_2$ y obtener Microfibras de Celulosa (CMF), con el fin de que actúen como refuerzo para mejorar las propiedades mecánicas. Posteriormente se realizaron mezclas del TPS con diferentes porcentajes de Microfibras de Celulosa (CMF), las cuales son de 5% (F5), 10% (F10) y 20% (F20), con el objetivo de poder evaluar la interacción entre el almidón termoplástico y la celulosa. La caracterización de las muestras se realiza a través de las técnicas de Espectroscopia infrarroja por transformada de Fourier (FTIR), Termogravimetría (TGA), Calorimetría diferencial de barrido (DSC), Difracción de rayos X, Degradación en Compost y Respirometría. Se realizaron comparaciones de los resultados obtenidos con el almidón nativo y las mezclas de TPS con Microfibras de celulosa.

Palabras Clave: bioplástico; mezclas; almidón termoplástico; microfibras de celulosa; celulosa.

Abstract

Due to the pollution caused by plastic, in recent years alternatives have been sought to replace it, the most investigated are bioplastics produced from organic material. One of the main organic materials used is starch extracted from potatoes and corn. However, there is another organic material that represents a waste which can be used as a source of starch, which is the avocado seed. In the present work, starch is extracted from avocado seed with Sodium Metabisulfite ($Na_2S_2O_5$). Additionally, Glycerol, Citric Acid and Stearic Acid are used to obtain Thermoplastic Starch (TPS). In addition, the cellulose is extracted from the agave leaves through a defibrillator to later be treated with NaOH and $NaClO_2$ to obtain Cellulose Microfibers (CMF), in order to act as reinforcement to improve mechanical properties. Subsequently, TPS mixtures were made with different percentages of Cellulose Microfibers (CMF), which are 5% (F5), 10% (F10) and 20% (F20), with the aim of being able to evaluate the interaction between thermoplastic starch and cellulose blends. The characterization of the samples is carried out through the techniques of Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC), X-ray Diffraction, Compost Degradation and Respirometry. Comparisons of the results obtained with the native starch and the blends of TPS with cellulose microfibers were made.

Key Words: bioplastic; mixtures; thermoplastic starch; cellulose microfibers; cellulose.

INDEX

CHAPTER 1. INTRODUCTION

1.1.General Introduction

The starch represents the principal reserve of food that plants have, also it is a macro-constituent in many foods that can be industrially obtained from some tubers, like potato, rice and avocado seed, and a big variety of grains [1]. In fact, starch is principally used in the food industry as a raw material and a primary ingredient to produce much more food products [2].

In the last decade starch has become a very important renewable biopolymer, that is employed in the food and non-food industries. Currently, the latest investigations have contributed to a better understanding of its structure and functionality, in order to develop properties required to create and manufacture products [3].

It can have unique and different properties that depends on its natural origin. However, in despite of the variety of morphology and size that the granules can present, the internal structure shows almost the same characteristics, these are the blocklets, growth rings, amorphous and crystalline lamellae. On the other hand, the main components of starch are two polysaccharides, that are amylose and amylopectin [4].

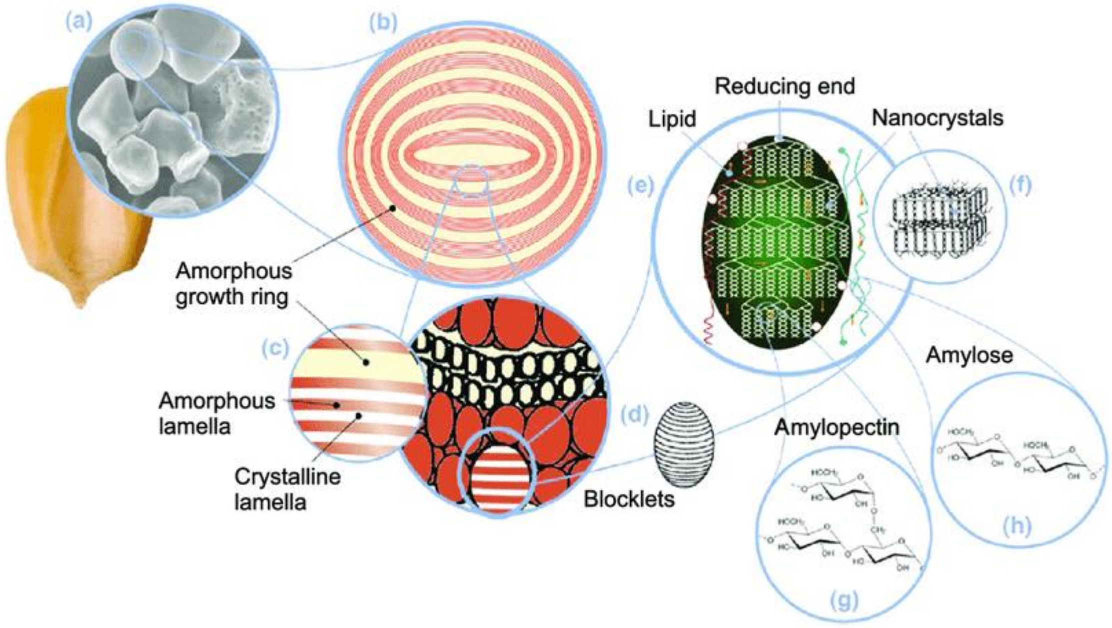

Figure 1. Starch multiscale structure. (a) Starch granules from normal maize (30 μm); (b) amorphous and semicrystalline growth rings (120-500 nm); (c) amorphous and crystalline lamellae (9 nm), magnified details of the semicrystalline growth ring; (d) blocklets (20-50 nm) constituting a unit of the growth rings; (e) amylopectin double helices forming the crystalline lamellae of the blocklets; (f) nanocrystals: other representation of the crystalline lamellae called starch nanocrystals when separated by acid hydrolysis; (g) amylopectin molecular structure; and (h) amylose molecular structure (0.1-1 nm). Recovered from [5]

Both polymers, amylose and amylopectin, only have a α-D-glucose that is connected by an (1, 4)-linkages. Amylose structure is based on few long chains, and its content is around 20% to 30% in starches. Otherwise, amylopectin has a lot of shorter chains bounded by (1, 6)-linkage at the end side, that makes it a very extensive branched polymer, hence represent the major component in starch [6].

1.1.1. Starch in Avocado Seed

Starch can be found in various natural resources, like seeds, and much of them are not used for any other production, hence represents just agro-industrial waste, it is the case of Avocado Seed. This seed represents the 25% w/w of the avocado fruit [7]. The content of starch in Avocado Seed represent an alternative source of obtaining starch and at the same time this seed, which was only considered a waste, can be useful through circular economy [8].

Starch is a natural biodegradable polymer that can replace some synthetic polymers, therefore there are several potential applications for this starch including its use as a vehicle in some pharmaceutical systems, a gelling and thickening agent in food and as an important component in biodegradable polymers for eco-packaging [9]. The percentage of starch present in the avocado seed is around 30%, whereby it is a potential source of starch [8].

1.1.2. Cellulose as reinforcement

Cellulose is a natural polymer, a renewable material, and the most abundant of its kind in the world, besides it is a polysaccharide with a β (1, 4)-linkage D-glucose units [10]. The main sources of cellulose are cotton and wood, and it is used in several applications as a construction material, source of heat, in the production of some commodities in the paper and textile industry, etc [11]. In the last years a great interest in the research of nanocellulose due to its physical and chemical properties has been grown. Two types of nanocellulose stand out, which are cellulose nanocrystals or CNC, and cellulose nanofibrils or CNF, which are obtained through acid treatment and mechanical disintegration, respectively [10].

Recently, among the previous mentioned applications of cellulose, it has been implemented as a filler reinforcement in polymers, where cellulose has demonstrated to be a promising material [12] that favors characteristics such as excellent mechanical properties, high crystallinity, and low molecular weight [13]. Hence by implementing cellulose, as a filler reinforcement, with starch, it can provide a higher value biopolymer with improved properties [12].

1.1.3. Glycerol as plasticizer

It is a viscous liquid, polyol compound, that is odorless, colorless, and its boiling point is high. The most used application is as plasticizer in the film production, that helps soften the materials. During the production of plastic and bioplastic it is necessary to improve some needed properties, hence the use of plasticizer fulfil some of them, such as the flexibility. Glycerol implemented as a plasticizer helps to improve and increase the intermolecular distance, because it decreases the hydrogen bonds [14]. In 2018, Lubis et al. [14] reported that by increasing the addition of glycerol it promotes the increasing on the percentage of elongation, therefore the bioplastic becomes even more elastic. In addition, glycerol as a plasticizer decreases the film brittleness and improve the workability [15].

1.1.4. Blends of starch, cellulose and glycerol

The production and manufacture of bioplastics entails the mixture of necessary components that can bring ideal properties to the bioplastic. Hence several investigations have been carried out regarding the interactions between these components, since starch is the main component as a biopolymer, cellulose represents a necessary reinforcement that provides better properties in the starch matrix, and finally glycerol, which is used as a plasticizer that also implements attractive properties [16].

In 2011, Shinoj et al. [17] detailed that a good interaction between the starch matrix and cellulose can promote better mechanical properties of the bioplastic. In the other hand, glycerol enhances the processibility and flexibility of the starch [18]. Miranda et al. [19] reported that the mixing of starch, cellulose and glycerol increase the maximum stress and elastic modulus, besides the barrier and thermal properties. Furthermore, according to the investigation of Lubis et al. [20] reported that the addition of cellulose decreases the elongation at break but increase the tensile strength, and the adding of glycerol increase the elongation at break but decrease the tensile strength.

Then Balakrishman et al. [21] in 2017, obtained that some properties as water sorption, moisture sorption and water vapour permeability had a significant increase which is due to a correct adhesion and dispersion of the nanofibers in the matrix of the starch, because of a very similar structure of polysaccharide. Additionally, when performing a thermal analysis, there can be an increase in the film stability, due to the mixture with cellulose, making the film friendly to the environment and being able to be used in various packaging options [22]. Finally in the investigation done by Serra et al. [23] concludes that a bioplastic derived from the starch with cellulose and glycerol represent a viable alternative of synthetic packaging. Additionally, it mentions that this film has antioxidant and antimicrobial properties, and that the aggregation of cellulose increases the mechanical strength and reduces the water vapor permeability, moisture and water activity, which are essential properties for food packaging [20].

1.2.Problem Statement

In recent years, the plastic packaging production industry has produced enormous amounts of waste, 67 million tones, which caused several problems in the environment. For this reason, in search for an alternative solution, several scientists have carried out research in this field of biodegradable polymers, as a substitute for synthetic polymers derived from petrochemicals [24]. These biopolymers or bioplastics demonstrate environmentally friendly properties compared to a conventional polymer or plastic [25]. However, there is a problem in the development and production of bioplastics, which is the high cost of their production, hence in order to reduce these costs, there are several proposals to use natural waste to obtain essential raw material for this production [26]. Therefore, the utilization of starch from avocado seed, represents a good alternative, however bioplastics that are based on starch still shows many disadvantages principally their poor mechanical properties [12]. In consequence it is necessary to analyze the mixture of starch, cellulose and glycerol in order to accomplish suitable mechanical properties, in order to offer an alternative for plastic packaging.

1.3.General and specific objectives

1.3.1. General objective

To characterize and analyze the blends between thermoplastic starch and cellulose microfibers (CMF), in order to find a material that achieves the requirements of mechanical properties for bioplastic and replace the common synthetic plastic.

1.3.2. Specific objectives

- To characterize and analyze through mechanical properties of the blends (starch, cellulose and glycerol)
- To characterize the blends trough infrared spectroscopy, X-ray diffraction, scanning electron microscopy and differential scanning calorimetry.
- To analyze the mechanical properties of the blends.
- To study the degradation in compost.

CHAPTER 2. EXPERIMENTAL SECTION

2.1.Materials

- Avocado seeds, from UYAFARMS company
- Agave Leaves, from UYAFARMS Company
- Sodium metabisulfite ($Na_2S_2O_5$)
- Citric Acid ($C_6H_8O_7$)
- Stearic Acid
- Sulfuric Acid (H_2SO_4)
- Sodium Hydroxide (NaOH)
- Hydrochloric Acid (HCl)
- Potassium hydroxide (KOH)
- Glycerol
- Distilled water

2.2.Extraction of starch from avocado seed

1. Drying and manual pulping of the seed.
2. Grind the seed in a blender with a metabisulfite solution in 0,1% in weight. Ratio between the solution and the seeds is 1 liter of solution for every 300g of seeds.
3. Liquefy for 5 minutes (Figure 2) and leave in the refrigerator for 24 hours.

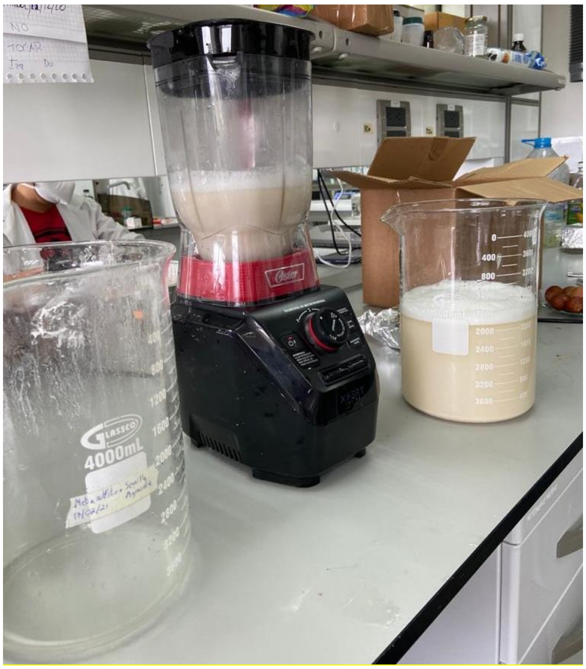

Figure 2. Blending Process

4. Then liquefy for 3 minutes and filter it twice. Covered it with aluminum and left undisturbed in the refrigerator for 24 hours. The residue of the filter is placed with sodium metabisulfite and distilled water, covered it with aluminum and leave in the refrigerator, in order to perform a second filtering after 24 hours (Figure 3).

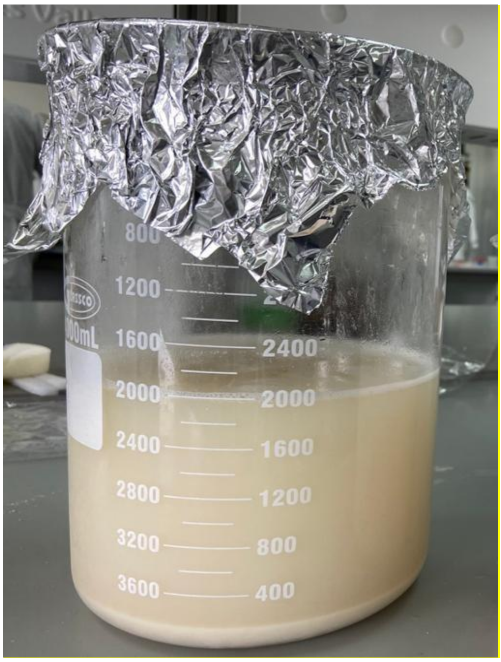

Figure 3. Suspension obtained after the first filtering

5. The sedimentation of the starch can be observed in Figure 4, and it is placed in a centrifuge vial.

Figure 4. Suspension after 24 hours, the arrow indicates the starch deposited at the bottom of the beaker

6. Centrifuge for 6 minutes at 3000 revolutions per minute (rpm) (Figure 5).

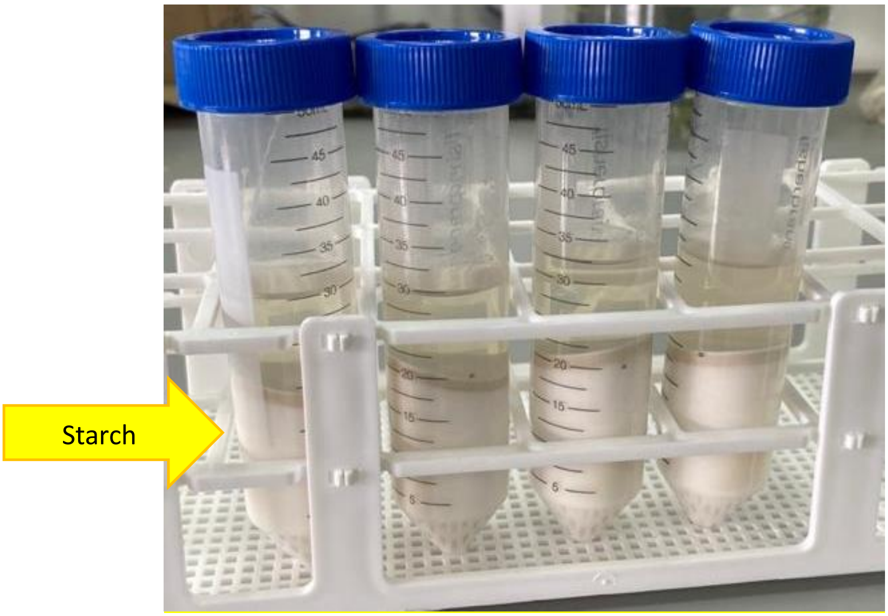

Figure 5. Vials after the centrifugation process, the arrow points to the starch.

7. The excess solution is decanted and the dark layer on top is removed, then the starch is washed and the centrifugation process is repeated.
8. The starch is placed in the oven for 24 hours to dry it, see Figure 6.

Figure 6. Dry starch obtained using 0.1% metabisulfite solution.

9. Finally, the starch from the avocado seed is obtained, which is weighed and stored in a closed plastic container.

2.3.Production of Thermoplastic Starch (TPS)

1. From the starch previously obtained, mixtures in batches of 35g are made with glycerol, anhydrous citric acid 2% and stearic acid 1.5%. Then formulations are made by varying the percentage of starch in 80, 70 and 65%. Additionally, a 70% starch test is carried out with higher content of anhydrous citric acid 3%, see Figure 7.

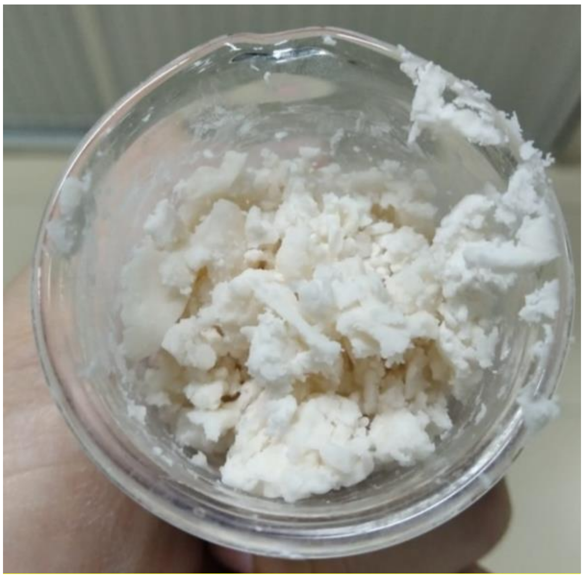

Figure 7. Homogeneous mixture prior the process for obtaining the TPS

2. The gelatinization (67°C) and thermoplasticization (170°C) of the starch are carried out at 70 rpm, in a Brabender brand torque rheometer (Figure 8). The temperature and screw speed are varied in order to see the effects on the plasticizing time of the TPS (70% of starch).

Figure 8. Brabender Plastograph EC Plus Torque Rheometer

3. The obtained TPS is manually pelletized (Figure 9) and store in a laboratory desiccator for a subsequent thermopressing.

Figure 9. TPS: 70% Starch, 3% Citric Acid

2.4.Extraction of cellulose from Agave Leaves

1. The spines from the agave leaves are removed with a stylet and a defibrillator machine, see Figure 10.

Figure 10. a) Agave Leaves and b) Defibrillator machine

2. The obtained fibers are washed and dry in an oven at 40°C (Figure 11).

Figure 11. a) Wet agave fibers and b) Dry agave fibers

3. The agave fibers are cut (1mm) and dry, for then been placed in a 4% NaOH solution in a weight-volume ratio of 1g:20ml at a temperature between 70-80°C and under magnetic stirring for 2 hours (Figure 12a).
4. The fibers are washed in order to obtain a neutral pH.
5. The fibers are treated with $NaClO_2$ with a concentration of 1.7% at a temperature of 70-80°C for 4 hours (Figure 12b). Then the fibers are washed until reach a neutral pH.
6. Finally, the fibers are dried in the oven at 40°C and are grinded again (Figure 12c).

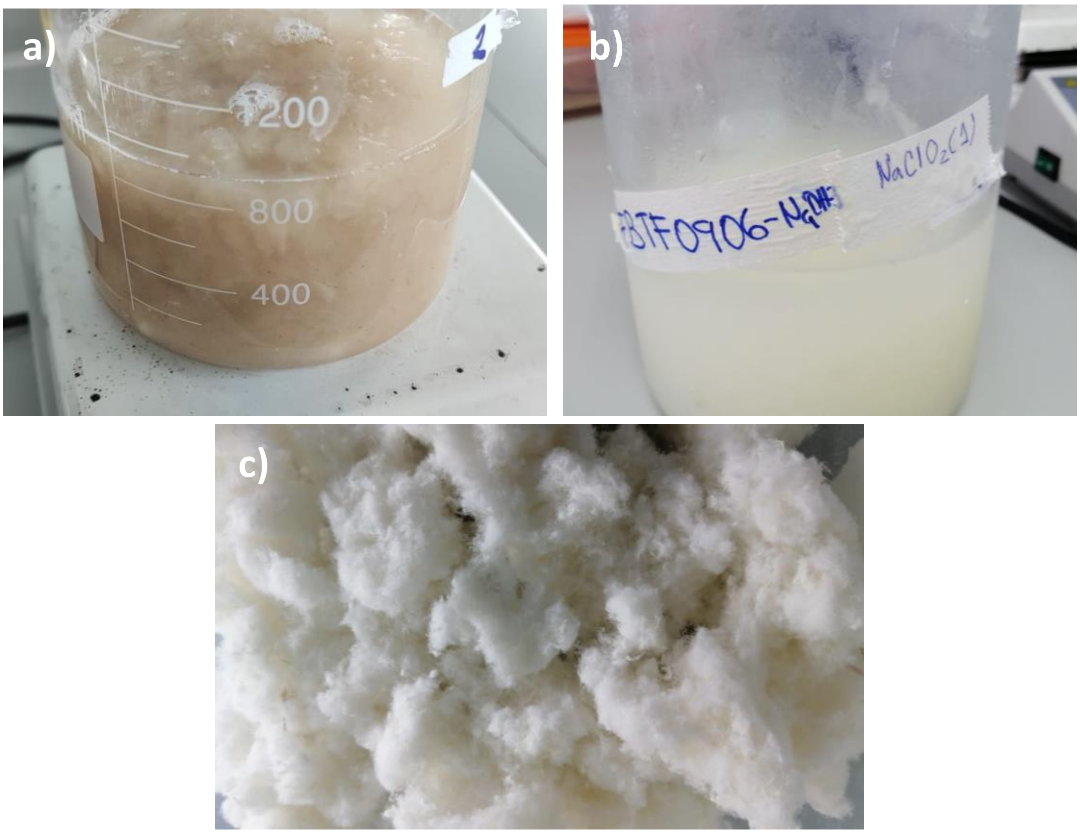

Figure 12. Treatment with a) NaOH and b) $NaClO_2$; c) Cellulose fibers obtained

2.5.TPS blend and blending conditions

The samples are carried out by Professor Andres Rigail research group, at the Escuela Superior Politécnica del Litoral, ESPOL, Mechanical Engineering and Production Sciences Faculty.

1. To obtain the TPS reinforced with cellulose microfibers (CMF), the homogenization of glycerol together with the CMF and citric acid is first attempted. For this procedure it is used a three-shaft mixer FlackTek, SpeedMixer^{TM} Model, for 5 minutes at 2000rpm, see Figure 13.

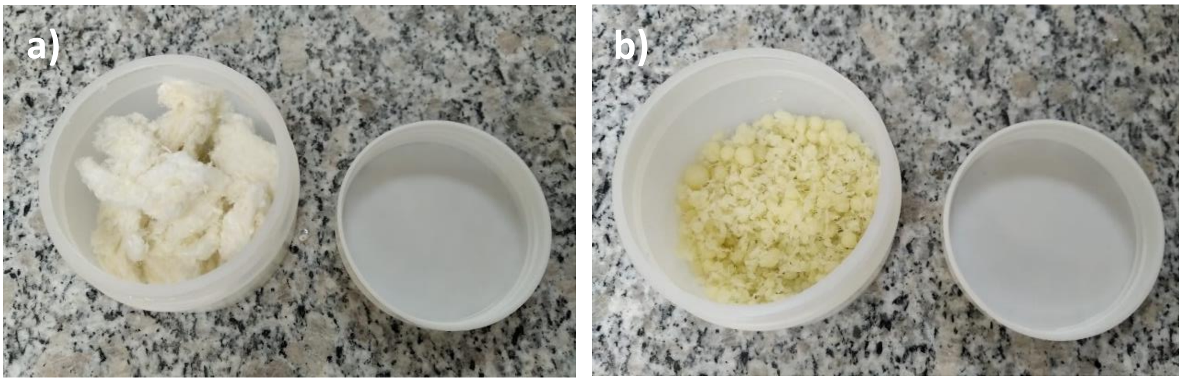

Figure 13. Glycerol and fiber homogenization a) Prior to mixing and b) After mixing

2. Once mixed the glycerol with the fiber, the starch and stearic acid are incorporated with a hand blender for 5 minutes, to ensure homogenization.
3. Then a torque rheometer is used at 70rpm, for 5 minutes of gelatinization at 67°C and 15 minutes for destructuring at 170°C, in order to obtain the TPS.
4. Then, for the preparation of the films, a pneumatic thermal press is used at 170°C (±5°C) and 1200psi (±100 psi) for 3 minutes. For the films to be used to obtain the tensile test pieces, 8 to 9g of sample are pressed with a 0.5mm (±0.1mm) thick steel frame (Figure 14). For the films intended for permeability tests, a mass between 1 and 2g of the biocomposite is set. These films were cut to standardize the diameter at 7cm (Figure 15).

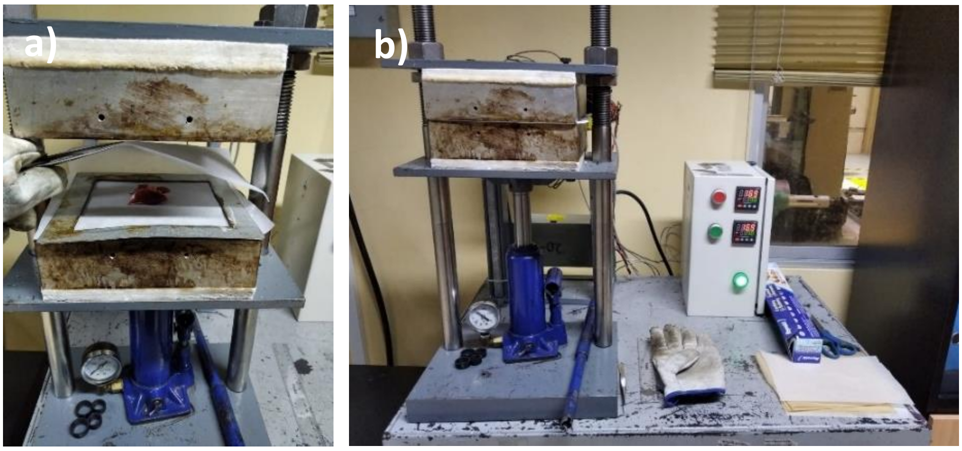

Figure 14. Film pressing a) sample preparation and b) pressing

Figure 15. Film obtained

The set of prepared formulations (Table 1) is made according to the previously detailed methodology. All the fibers are worked under the same conditions (process temperature, rpm, pressure, time) for the purposes of a comparative study.

Table 1. Formulations (%) of TPS reinforced with extracted Cellulose Microfibers (CMF).

	TPS	F5	F10	F20
Starch	70	70	70	70
Glycerol	30	30	30	30
Citric Acid	3	3	3	3
Stearic Acid	1.5	1.5	1.5	1.5
Cellulose Microfiber	-	5	10	20

2.6.Characterization Techniques

2.6.1. Fourier transform infrared spectroscopy (FTIR)

An Agilent model 630 Cary equipment was used, in attenuated total reflectance mode, a sweep was made from 4000 to 400cm^{-1}.

2.6.2. Thermogravimetry (TGA)

A Mettler Toledo TGA model TGA / DSC 1HT, was used. The heating scans were made using 20mg of sample at a rate of 10°C/min, in an N_2 atmosphere, from 25°C to 700°C.

2.6.3. Differential Scanning Calorimetry (DSC)

A Perkin Elmer model 8000 calorimeter was used, calibrated with Indium and tin, hermetic aluminum capsule. It was left to equilibrate for 30min and a heating scan was carried out at 10°C/min. To determine the Tg of the starches, the starch (3% starch in water) was gelled for 30min at boiling. The gel was placed in Petri dishes and allowed to dry for 1 week. The obtained film was evaluated at 150°C/min from 0°C to 120°C. In the case of thermoplastic starch and its blends, heating scans were carried out at 150°C/min from 0 to 120°C at 2.5mg of sample.

2.6.4. X-ray diffraction

A Rigaku model Miniflex600 40kV and 15mA diffractometer was used, using CuKα radiation source with a wavelength of 1.54Å.

2.6.5. Degradation in Compost

The samples were cut into 150 x 150mm squares, dried and weighed. They were placed between 1 and 3cm from the surface in earthworm humus, points were extracted in triplicate at 5, 7, 9, 11, 13, 15 and 17 days. The extracted samples were carefully cleaned to remove soil residues, dried and weighed.

2.6.6. Respirometry

350g of earthworm humus were placed at the base of the desiccators where the sample was evenly spread. Desiccators were used to maintain a closed atmosphere, a beaker with 50ml of water and 20ml of a 0.3868 M KOH solution was placed, see Figure 16. Triplicate assays were performed for: a. Blank (no sample), b. Positive (commercial cassava starch), c. TPS, d. TPS/MF at 5% by weight. The 0.3868M KOH was removed and the air inside the desiccators was renewed every 3 or 4 days. The extracted KOH was titrated with 0.06498M HCl solution.

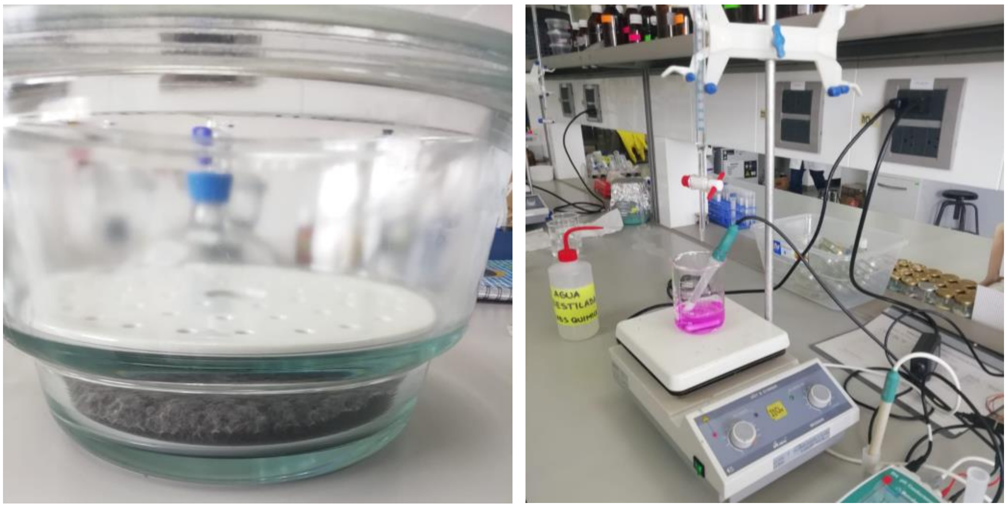

Figure 16. Respirometry experiment

CHAPTER 3. RESULTS AND DISCUSSION

3.1.Starch from avocado seed

3.1.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was used in order to determine the presence of important and characteristic bands.

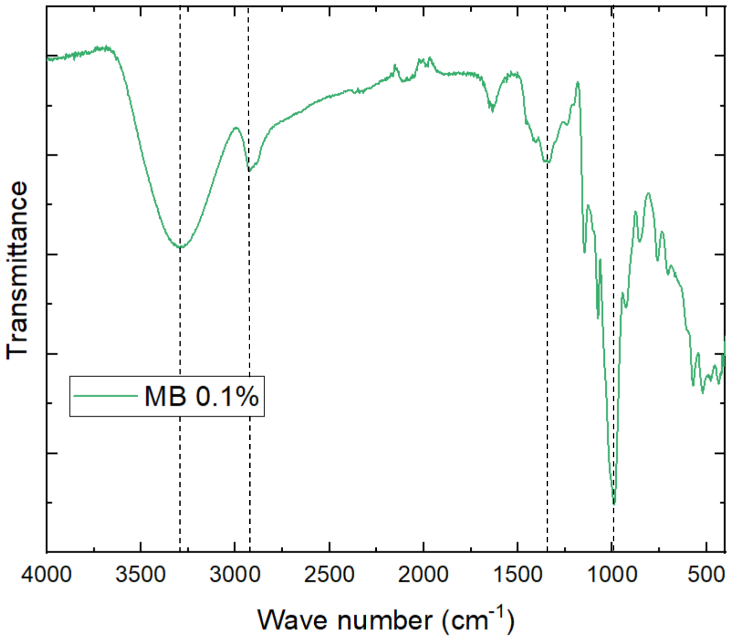

Figure 17. FTIR of native starch extracted from avocado seed

In Figure 17 the characteristic bands of starch are shown, such as the peak at 757 cm^{-1} that indicates the presence of the glucose pyranose ring, the presence of OH, through the signals at 3176, 1252 and 1078 cm^{-1}, the presence of the group glucose ring ester at 982 and 930 cm^{-1}, as well as the presence of CH at 2923 and 1461 cm^{-1}. Additionally, there is an important peak at 3391 cm^{-1}, that means the presence of a hydroxyl group OH [27]. These bands confirm that the product of the extraction was, majority, starch.

3.1.2. Thermogravimetry (TGA)

In this test, the percentage of weight loss of the starch and its derivative is measured. Then, it was possible to check the purity of the starch obtained using a solution of sodium metabisulfite, through TGA. Two weight loss processes were exclusively found, one around 90°C and the other at 300°C, see Figure 18. The first one is attributed to moisture content while the other one is typical of starch processing. The obtained results have been compared with the temperatures reported for potato starch and cassava starch, which are 320°C and 290°C, respectively [28] [29]. The result obtained of temperature is below potato starch and above cassava starch. The presence of only two processes, confirm the findings of FTIR, indicating that the starch is the main component, also no other substances are in significative amounts.

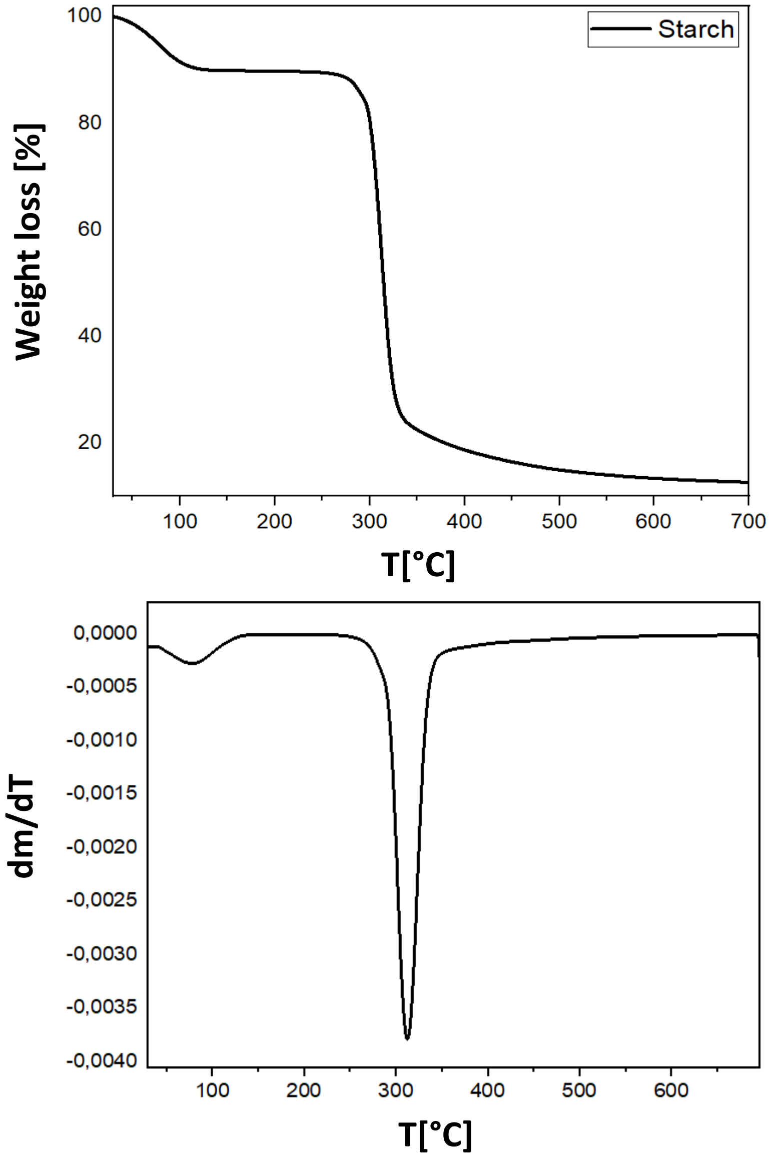

Figure 18. Thermogram and derivative obtained for starch extracted

3.1.3. Differential Scanning Calorimetry (DSC)

Using the DSC technique, the gelatinization temperature value obtained was 67.42°C, see Figure 19. This value is similar to that reported for other starches such as potato (64°C), corn (67°C) and sorghum (62°C) [30].

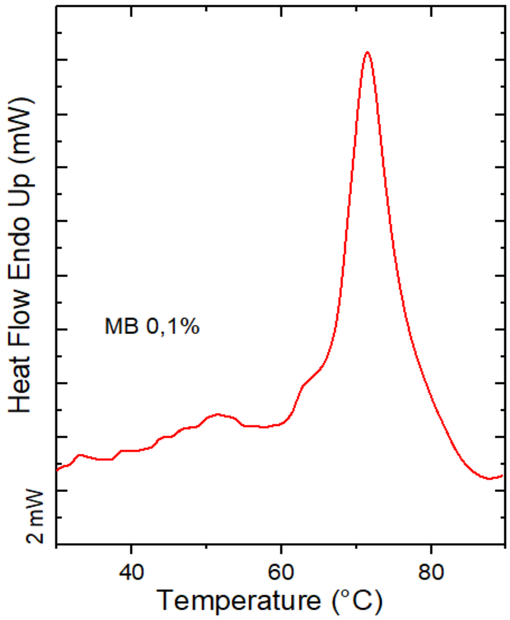

Figure 19. Heating sweep at 20°C/min for avocado seed starch in a 50:50 water: starch mixture (DSC)

On the other hand, the glass transition temperature of gelled starches shows a complex behavior, showing a very wide transition where overlapping transitions are distinguished, possibly attributed to the amylose and amylopectin present in the starch, obtaining a Tg of 53°C (Figure 20), and by comparing this result with the literature, where is reported a Tg of 47°C [31], it can be seen that the obtained result is a slightly higher. This difference may be due to the process used for the extraction of the starch.

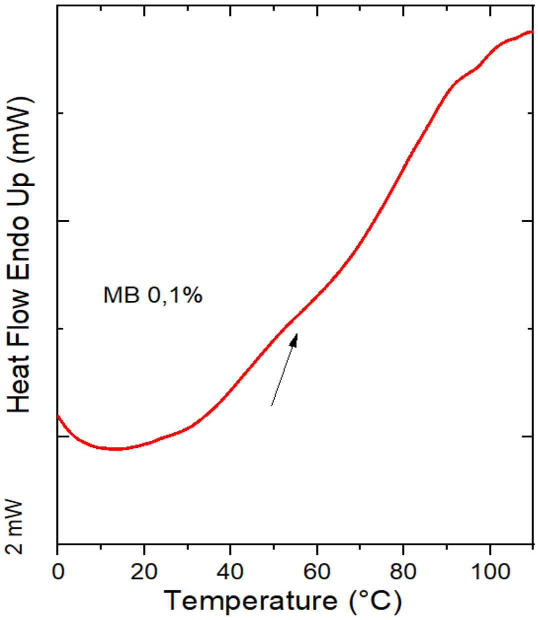

Figure 20. Heating sweep at 150°C for the film of gelled starches from a 3% solution of starch in water (DSC)

3.1.4. X-ray diffraction

Starch has a semi-crystalline structure, where the amorphous region is composed of amylose and long amylopectin chains, while the crystalline region is composed of small amylopectin chains. In this crystalline structure that starch presents, three polymorphisms can be found, which are type A, B and C. The type A presents an orthogonally packed helices with an inclusion of structural water. Type B is formed by double helices in an orthogonal packing with approximately 36 water molecules per unit cell. Type C presents the polymorphism of A and B [32], see Figure 21.

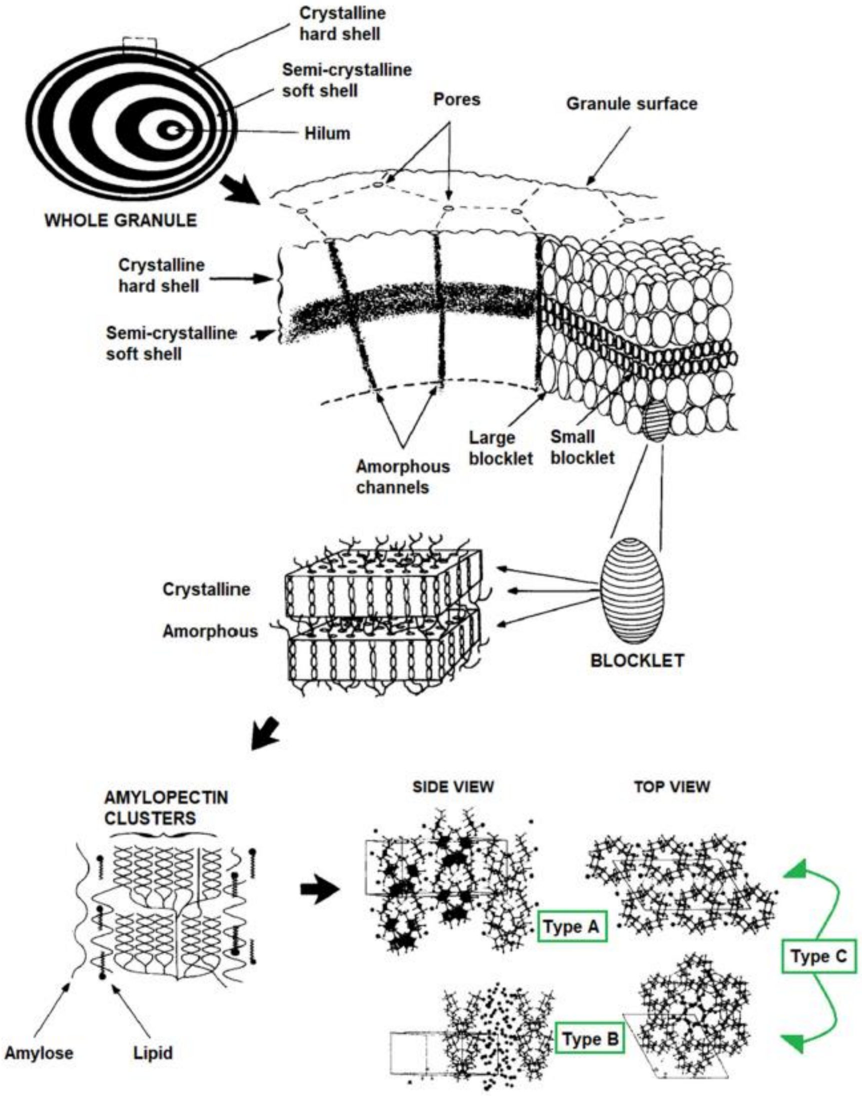

Figure 21. Crystallographic description of the native starch granule. Recovered from [32].

The characteristic peaks of the crystallographic planes of starch can be observed in Figure 22. The peaks presented are those characteristics of starch that forms type B crystals. Like potato starch, the starch obtained from the avocado seed presents a peak at °2ϴ = 5.76 and another at

22.14, which correspond to the planes (001) and (113), both characteristic of type B crystals. Additionally, it presents peaks at 11.3; 14.97; 17.16; 19.86; 22.14; 24.27 corresponding to planes (111), (140), (131), (103), (132) respectively. These peaks are present in all starches [33].

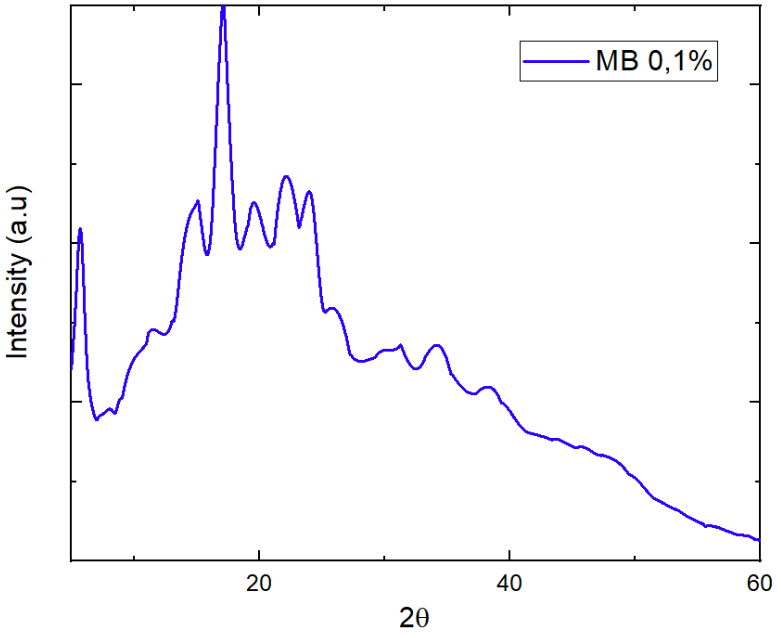

Figure 22. X-ray diffractograms of avocado seed starch

3.2.Cellulose

The crude cellulose fibers, Figure 23a, were extracted through an automated process, using a homemade defibrillator normally used to extract fibers from the cabuya. In this case, the agave leaves were passed through the machine with the help of a motor that removes the pulp, thus obtaining only the fibers.

3.2.1. Scanning Electron Microscopy (SEM)

Cellulose fibers are composed of several layers, which constitute lignin, hemicellulose and cellulose, reaching a diameter of approximately 198 µm. In Figure 23b the cellulose fibers are observed once the lignin and hemicellulose are removed, with an ovoid cross-section, and with a diameter of approximately 24.37 ± 6.20 µm, so these fibers can be considered as cellulose microfibers (CMF) [34].

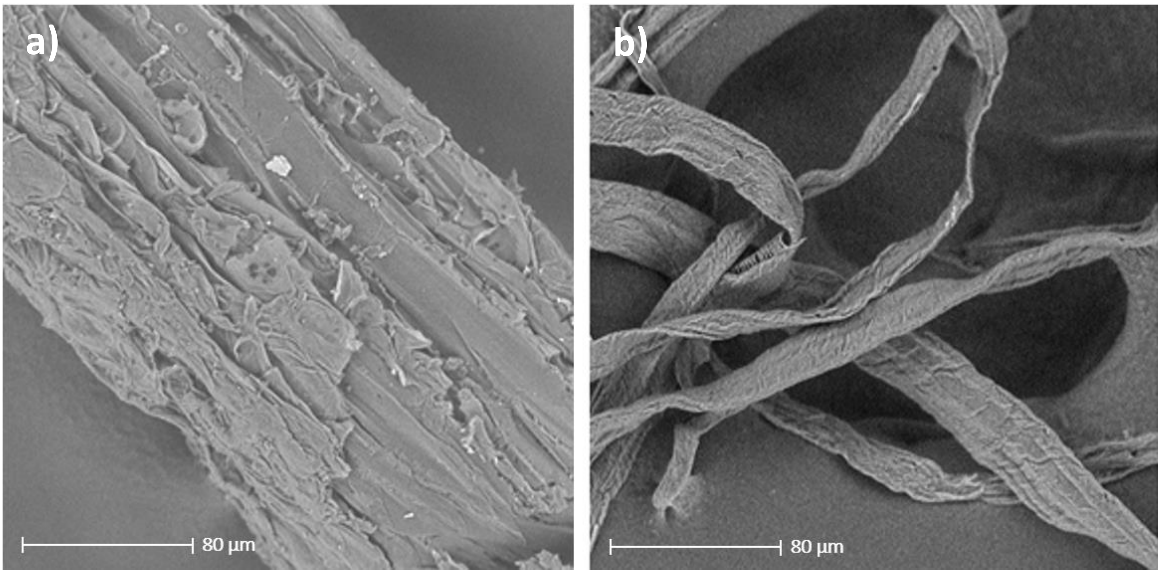

Figure 23. Images from SEM of cellulose obtained, a) crude cellulose fibers and b) cellulose microfibers (CMF)

3.2.2. Fourier transform infrared spectroscopy (FTIR)

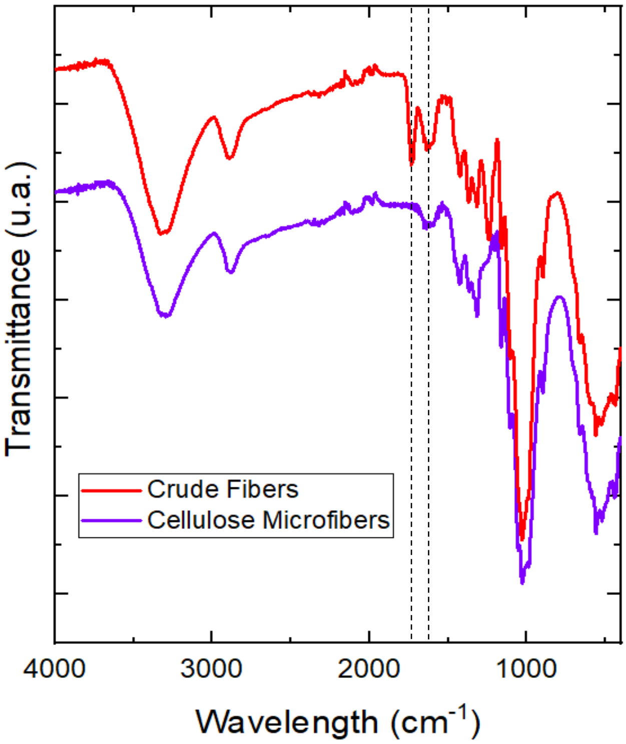

Figure 24. FTIR of cellulose obtained from agave leaves

After treatment with NaOH and $NaClO_2$, it can be seen that both lignin and hemicellulose were eliminated, this can be seen by a decrease of the peaks at 1592 cm^{-1} and 1654 cm^{-1}, which are characteristic of lignin [35] (Figure 24).

According to the results obtained by SEM and FTIR, it can be concluded that cellulose microfibers were successfully extracted with the method used.

3.2.3. X-ray diffraction

The characteristic peaks of cellulose can be observed at 15 and 22, however the peaks of CMF at 18, 32, 34 and 36 are not from cellulose, these can be impurities during the extraction of native cellulose, see Figure 25. During the CMF extraction and modification processes, the amorphous zones, hemicellulose and lignin are removed, obtaining a more defined crystalline structure. Peaks that are narrower and higher imply a higher crystallinity in the structure, which is expected to be obtained by removing the other non-crystalline components.

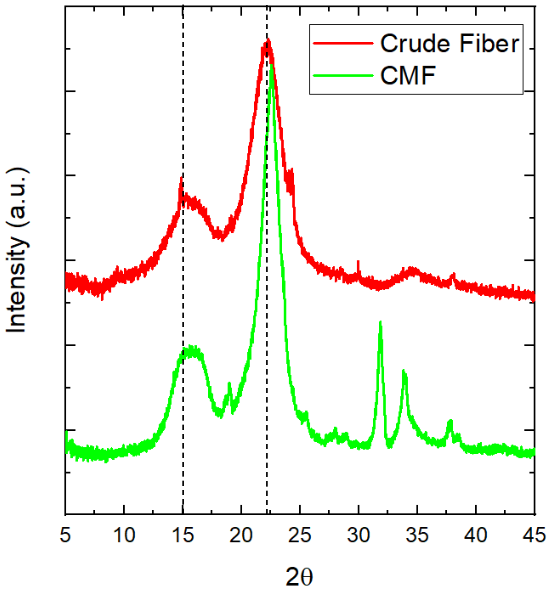

Figure 25. X-ray diffraction of cellulose

3.2.4. Thermogravimetry (TGA)

The thermal stability of the obtained cellulose was analyzed by TGA. In Figure 26, two processes of water loss can be evidenced, one at low temperatures at 50°C corresponding to water, and the other at high temperatures at 320°C corresponding to cellulose. Comparing this result with the literature, that reported a temperature of water loss at 315°C [36], hence it is possible to confirm the presence of cellulose.

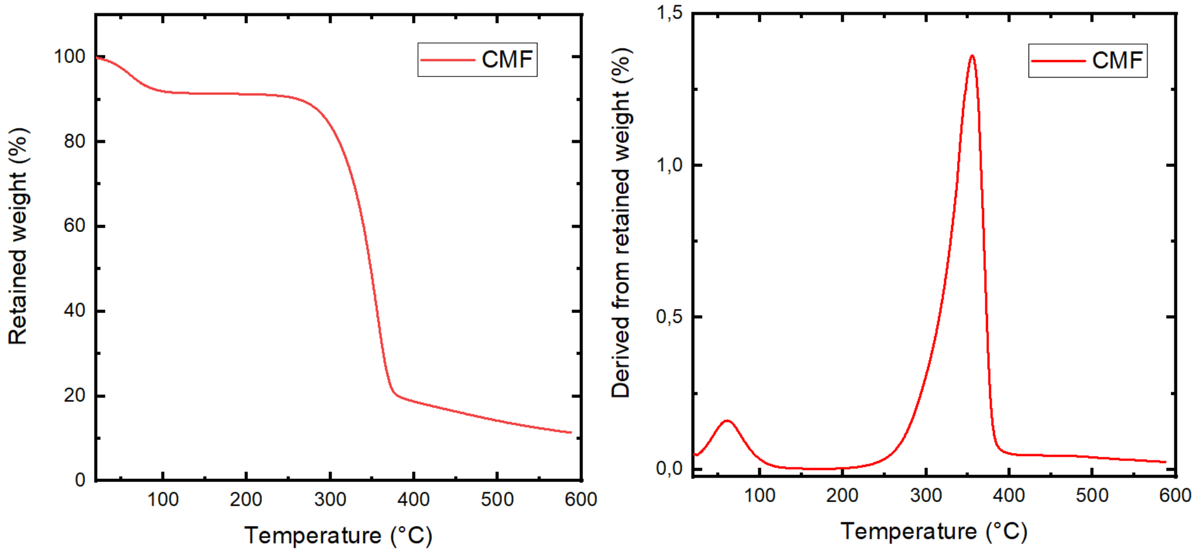

Figure 26. Retained weight of CMF (Cellulose Microfibers) and its derivative

3.3.Blends TPS, F5, F10 and F20

The mixtures obtained were analyzed by DSC, XRD and IR. The obtained results were compared with the starting materials, starch and the corresponding cellulose.

3.3.1. Differential Scanning Calorimetry (DSC)

For all cases it is possible to observe changes in the thermograms indicative of Tg, glass transition temperature, presenting in most cases complex behaviors such as multiple Tg, that are processes due to residual plastification. In general, in Figure 27, no trend is observed relative to the size or content of the celluloses present. It is important to note that starch is composed of amylose and amylopectin, which can have different Tg values. The Tg obtained for TPS, F5, F10 and F20 are: 21°C, 20°C, 17°C and 18°C, respectively. These are results below of the Tg obtained for the avocado starch, which has a Tg of 53°C, which is due to the process that the native starch went through. The native starch is semicrystalline, while thermoplastic starch is mostly amorphous. The plasticization process, it breaks with the crystalline structure and also glycerol not only breaks with the crystalline structure but also increases molecular mobility, consequently, the Tg decreases.

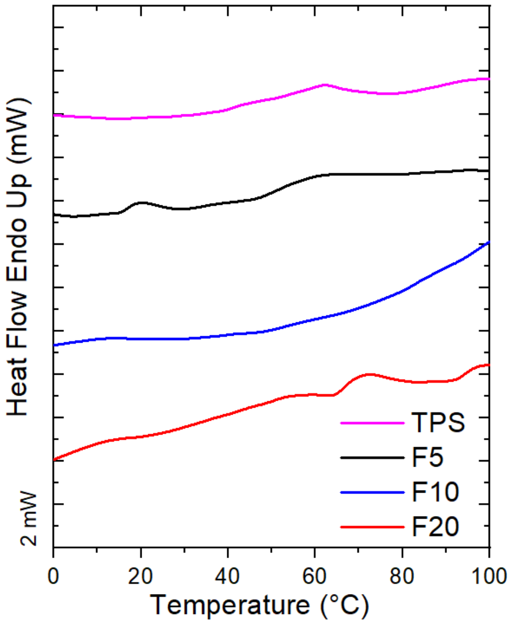

Figure 27. Heating sweep at 150 °C/min of the indicated mixtures (DSC)

3.3.2. X-ray diffraction

Figure 28 shows the diffractograms obtained for the blends of thermoplastic starch and the corresponding cellulose. The most relevant is that in all cases the curves show a less defined structure from the crystallographic point of view than the starting starch (See Figure 22 X-ray diffractograms of avocado seed starch), this is what is expected, because during the plasticization process the granule disruption occurs and partial loss of crystallinity. In this case, an increase in the intensity of peaks 15 and 22° corresponding to the cellulose microfibers is observed in Figure 28. Blends of starch and cellulose are presented, where the TPS is considered amorphous, since its granules were destroyed, however traces of crystallinity are observed. During the plasticizing process, the blends were homogenized in order to be able to transform them into different films, where the granules were destroyed with the help of the temperature used and the screw speed.

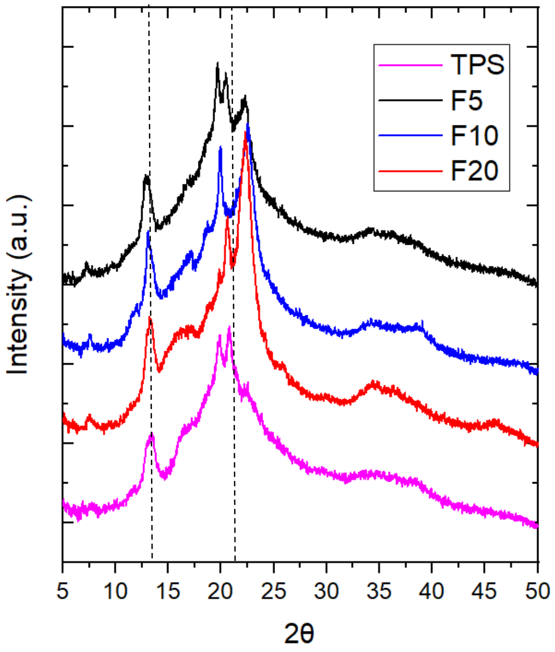

Figure 28. X-ray Diffraction of Mixtures

3.3.3. Fourier transform infrared spectroscopy (FTIR)

The results shown in Figure 29 shows the characteristic peaks for both cellulose and starch. No chemical changes are observed in the FTIR, so it can be concluded that both starch and cellulose did not undergo significant changes during the process.

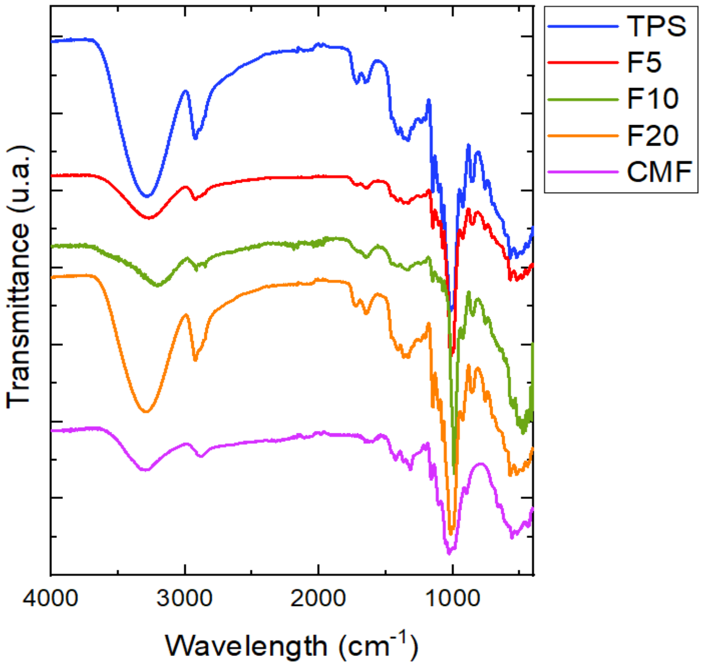

Figure 29. FTIR of Blends

3.3.4. Thermogravimetry (TGA)

To determine the thermal stability of the TPS with the different percentages of cellulose applied, thermogravimetric tests were carried out. The weight loss process for mixtures is a complex process that involves, in most cases, 4 steps. The lowest temperature attributed to the loss of water, followed by the decomposition of glycerol, and then at a similar temperature the decomposition of starch and cellulose (Figure 30). Comparing the results obtained with native starch, see Figure 18, it can be seen that the temperature at which native starch begins to degrade, 300°C, is higher than all these blends, which start around 250°C. Additionally, the degradation residue obtained for native starch, see Figure 18, is lower compared to those obtained for these blends, where TPS has the lowest degradation residue, and while more CMF% is added it has higher values, as it can be seen for F20. Finally, the mass loss of the blends ends mostly around 600°C, except for TPS which ends at 400°C, while for starch it ends at 700°C.

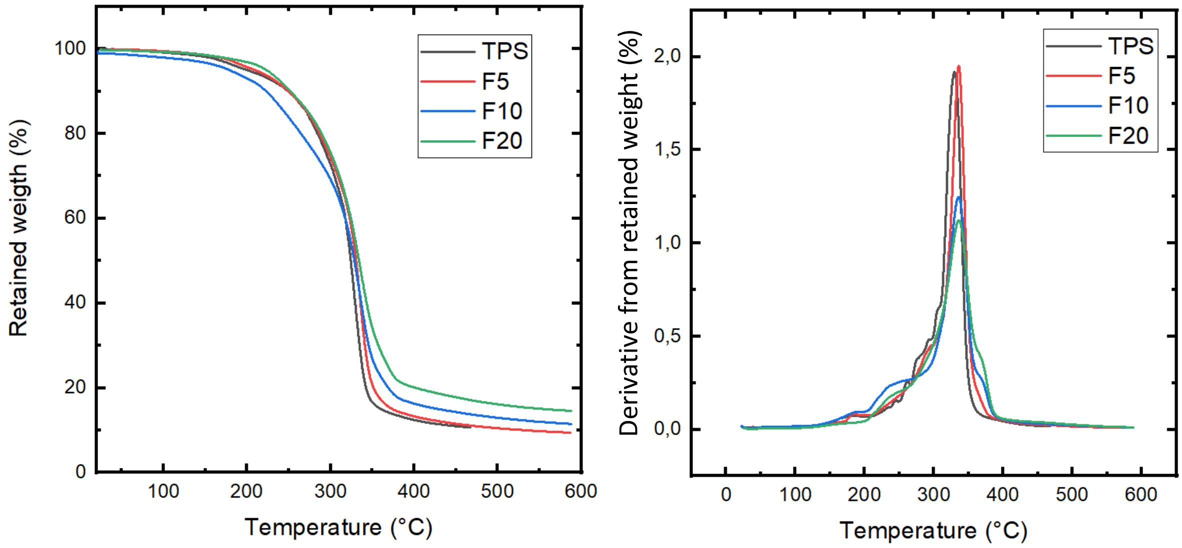

Figure 30. Retained weight and its derivative of Blends

3.3.5. Scanning Electron Microscopy (SEM)

The following Figure 31 presents the images obtained from the bio composites, fractured with liquid nitrogen, by scanning electron microscopy.

Figure 31a shows the morphology of thermoplastic starch. In the image, it can be seen a slightly rough surface. Defects such as cavities and ungelatinized starch could be found throughout the matrix. Additionally, there are rounded structures that can be considered as starch granules swollen by glycerol that after gelatinization did not lose their form.

As well it can be seen the images of the bio composites of TPS reinforced with cellulose fiber (F5, F10 and F20), where the fibers are covered by the TPS which indicates an excellent interaction between the fiber and the matrix, see Figure 31. Although the adherence of the filaments in the TPS matrix can be observed, however it is not complete. With the increase in the percentage of fiber in the biopolymer (Figure 31d), it is easier to find fibers that are not completely embedded in the interface. Additionally, the surface of the TPS is completely rough.

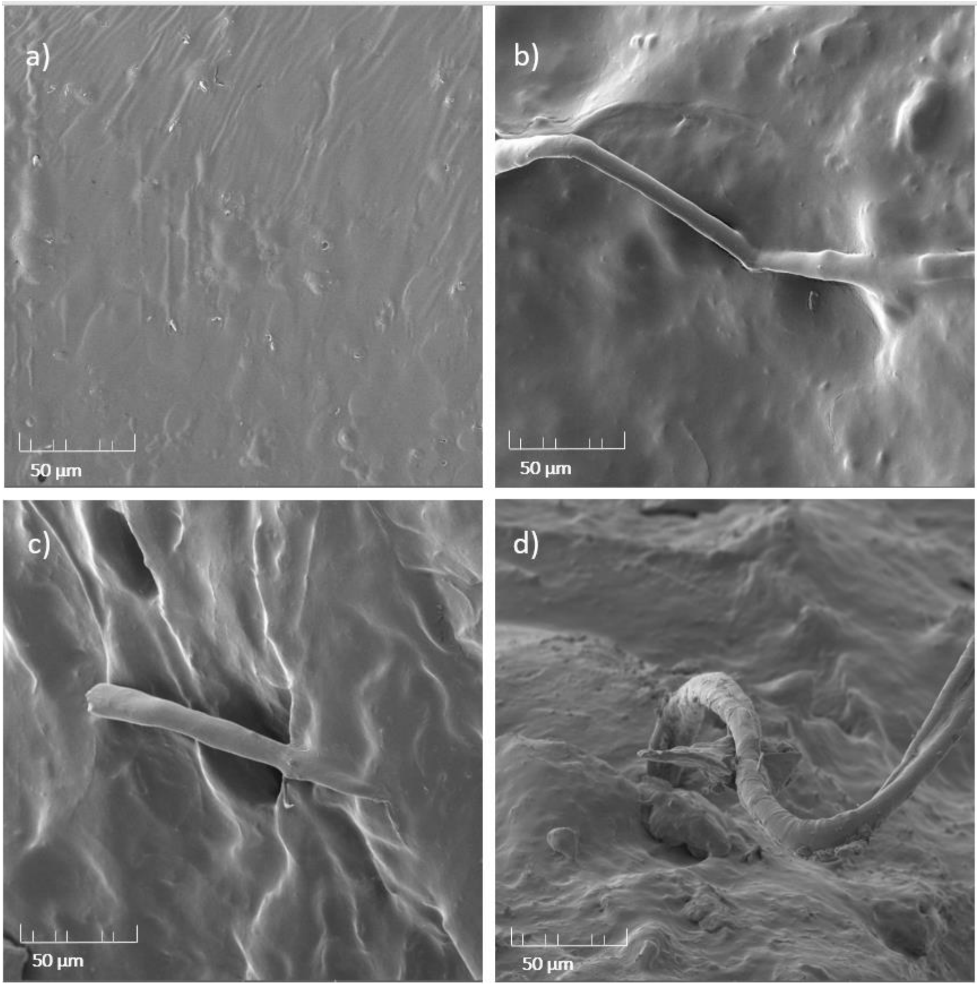

Figure 31. Micrography of blends a) TPS, b) F5 (TPS + Fiber 5%), c) F10 (TPS + Fiber 10%) and d) F20 (TPS + Fiber 20%)

3.3.6. Mechanical Properties

The typical stress-strain curves of the Blends of TPS with cellulose are shown in Figure 32. A rubbery-like shape with very low stress values can be observed. When adding the fibers, an increase in the stress values can be seen, and a curve shape that shows the semi-ductile materials. The value of the stress at rupture is low, especially given the shape of the curve, which passes through a maximum corresponding to creep and falls, but without stabilizing the neck (See Figure 32).

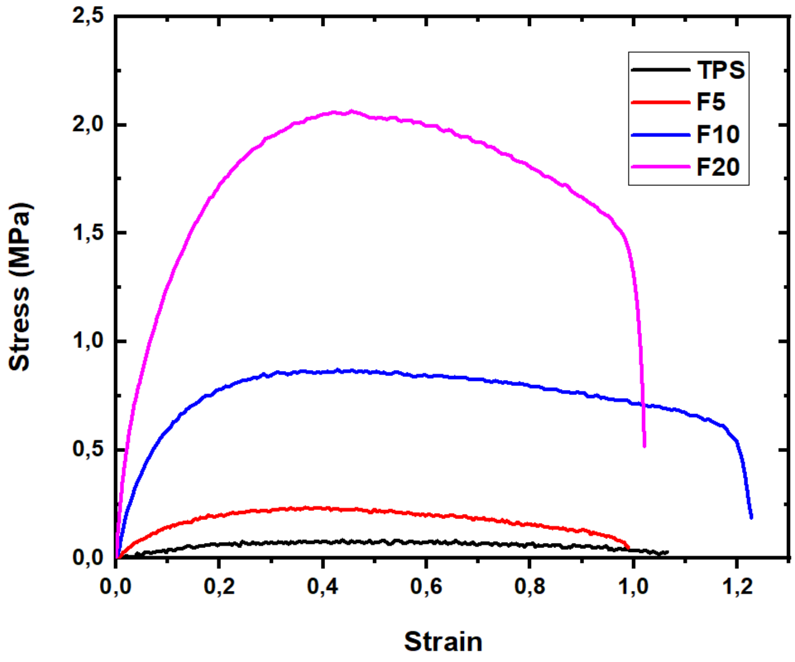

Figure 32. Typical stress-strain curves of the indicated TPS/Cellulose blends

On the other hand, in Figure 33a, it can be seen how the presence of the CMF considerably increases the tensile strength, increasing this value by almost 300%. The tensile strength increases in relation to the increase in the amount of CMF in the TPS, so it can be seen that the TPS has the lowest tensile strength, while the F20 has the highest value. On the other hand, with respect to breaking stress, it can be seen that there is an increase, but not very significant in relation to the values obtained for TPS, F5 and F10, but for F20 there is a relevant change.

Figure 33b shows how the strain at break increases when 5% of CMF (F5) is placed and then decreases, which corresponds to the increase in stiffness. The values obtained, if it is taking into account the error bars, are practically the same and there are no important changes in the deformations. This is due to a very good interaction between the matrix and the disperse phase, hence in this case the deformity is not affected, because there is continuity in the stresses. Finally, as observed in SEM (Figure 31), the CMF fibers were covered by the TPS, this causes that the stresses are transmitted throughout the material without causing interruptions in the interface.

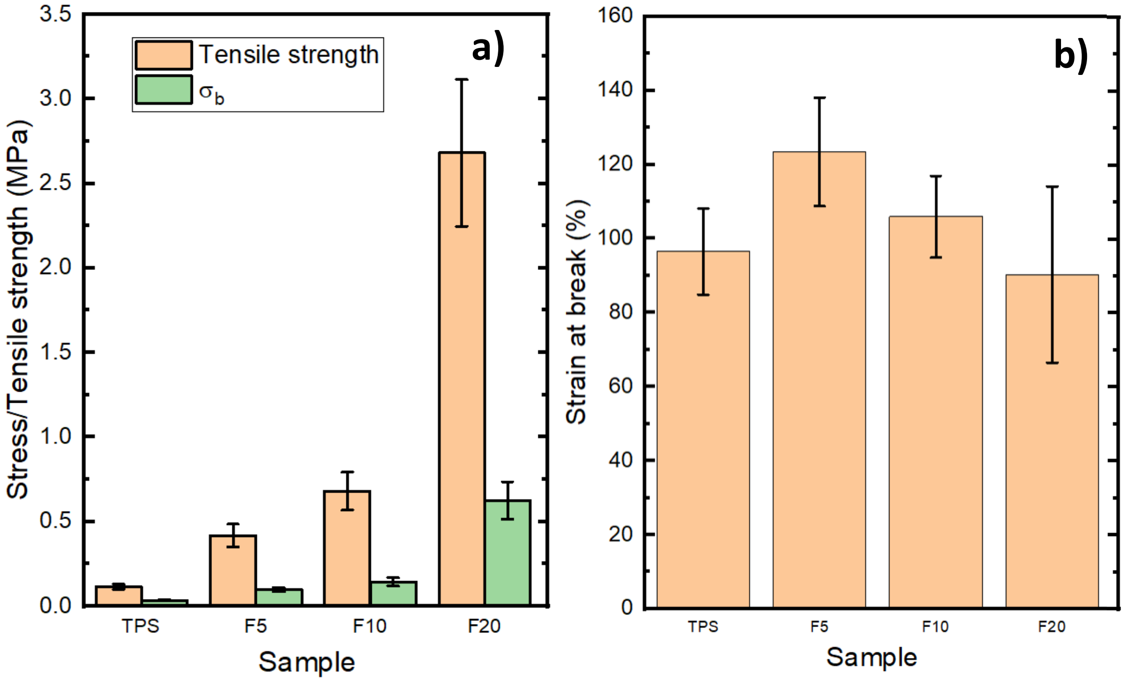

Figure 33. a) Tensile strength and breaking stress, and b) Variation of breaking strain versus CMF content

3.3.7. Compost Degradation Test

The study of the effect of the content and size of the cellulose is studied through the biodegradability of the blends by degradation in compost. For this, the samples are placed in contact with earthworm humus, the weight loss and the amount of carbon that has been released in relation to the theoretical carbon content of the samples are measured. The partial results that have been obtained up to date are shown in Figure 34.

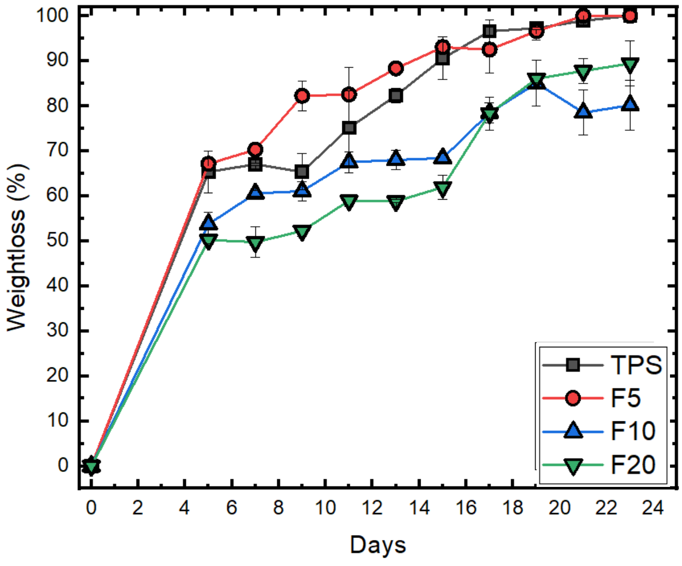

Figure 34. Weightloss of Blends in Compost Degradation Tests

In Figure 34, it is also possible to observe how the samples with only 5 days lose between 40 and 70% of their original weight. This can be caused by a rapid migration of glycerol, which is reflected by a decrease in the flexibility of the samples once they were dry. After 5 days, the loss has been progressive, and in 24 days it reaches values of approximately 97% loss for the TPS and the TPS with 5% CMF (F5), and 80% and 90% for the samples with 10 and 20% of fibers (F10 and F20), respectively. Especially for the case of higher fiber contents, it can be seen that the degradation is slightly slower, possibly caused by a higher content of crystalline structures in the system. Additionally, according to the ASTM D6400 norms, which represent international standards that help validate the compostability of a plastic material, hence it defines that a material is considered compostable in three important aspects [37]:

1. The material was able to disintegrate by 90% and its residues are smaller than 2 x 2 mm, within a period of 12 weeks (Disintegration).
2. If within a period of 180 days it had 90% of degradation (Inherent biodegradation).
3. If it does not have any damage towards the growth and development of plants (Ecotoxicity).

Therefore, the samples meet with the second requirement of this regulation, which indicates that it is complying with the characteristics of a compostable material. Subsequently, more and different tests are expected to help verify requirements 1 and 3 according to the ASTM standard.

3.3.8. Respirometry

Respirometry results for the TPS and for the F5 (5% of CMF) sample are shown in Figure 35.

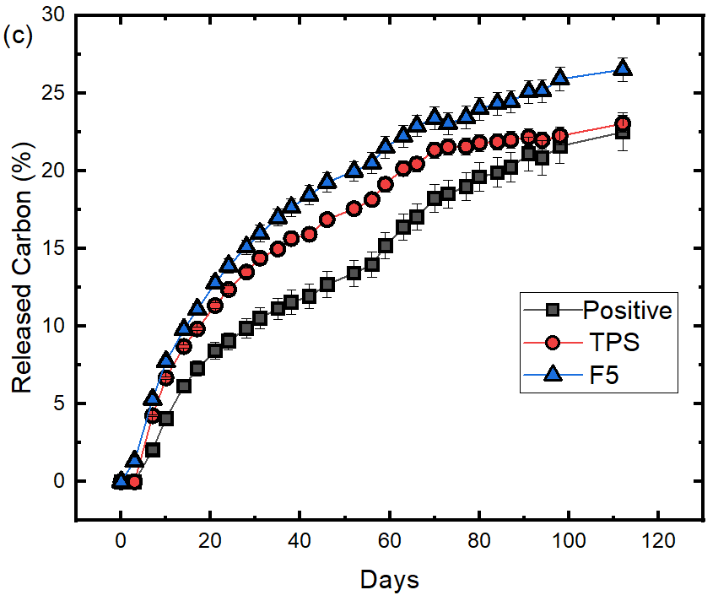

Figure 35. Respirometry, amount of C released for the mixtures of TPS with CMF.

It can be seen how the F5 sample is slightly faster than the TPS in the decomposition process, in this case it is possible that the incorporation of interfaces and a greater capacity to absorb water tend to accelerate the degradation, hence TPS and F5 can be consider that are biodegradable. Something interesting is that the rate of degradation is higher for TPS and for F5 compared to the positive sample, that is cassava starch. In this case, the fundamental difference is the decrease in the amount of crystalline structures and the presence of the plasticizer, which, for being a low molecular weight substance, is more susceptible to degradation. For the three samples it is observed that at 100 days the stabilization of the curve has been reached. Finally, the carbon percentages are low due to the used technique, where, because of the constant manipulation during the respirometry experiment, a quantity of CO_2 could have been released, since the desiccators had to be moved and opened in order to carry out the experiment.

CONCLUSIONS

The extraction of native starch from the avocado seed is possible from the process used with metabisulfite in 0.1% in weight, which represents a viable method for this extraction. Subsequently, from the native starch, thermoplastic starch (TPS) was obtained through the implementation of glycerol, anhydrous citric acid and stearic acid. On the other hand, obtaining cellulose microfibers (CMF), could be achieved by treatment with NaOH and $NaClO_2$. In order to characterize different samples, TPS mixtures were made with different percentages of cellulose microfibers, 5% (F5), 10% (F10) and 20% (F20), from which 7cm circular films were obtained diameter.

Through the FTIR and TGA tests, it was possible to determine the purity of the native starch obtained, in addition, with the DSC technique it was confirmed that the gelatinization temperature obtained is very similar to that found for potato, corn and sorghum starch. On the other hand, through X-ray diffraction, it is possible to observe the characteristic peaks of starch that form type B crystals, and characteristic peaks of all starches.

The extraction of the cellulose microfibers (CMF) from the agave leaves was carried out with the help of a defibrillator, which removes the pulp. With the application of SEM, it was possible to observe the removal of lignin and hemicellulose, obtaining a diameter of 24.37 ± 6.20 µm, finally considering the obtaining of microfibers. The FTIR test confirmed the elimination of these two compounds and ratified the extraction of cellulose microfibers (CMF) through the process used. Through X-ray diffraction, it was observed that the cellulose microfibers demonstrate a more defined crystalline structure, compared to the raw fibers. The TGA showed two important processes of water loss, in which one of them corresponds to cellulose at high temperatures.

For the TPS blends, F5, F10 and F20, they showed similar behaviors in the DSC, X-ray diffraction and TGA tests. Likewise, in the FTIR, no significant changes were observed during the process, showing the same characteristic peaks of cellulose and starch. The mechanical properties performed on the TPS, F5, F10 and F20, showed that it is possible to reinforce the TPS with Cellulose Microfibers, where the highest reinforcement resulted when adding 20% microfibers. Finally, the samples showed a great capacity to be degraded under home compost conditions, with degradation rates higher than those shown by cassava starch, and the one that showed the highest rate of degradation was sample F5 (TPS+5%MCF). Besides the material meets one of the three points indicated by the ASTM D6400 standards, to be consider as a compostable material.

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