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Electrical and Mechanical Analysis of a Natural Biopolymer

Análisis Eléctrico y Mecánico de un Biopolímero Natural

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Abstract

This work presents the formulation of a polymer based on biodegradable materials. The polymer formulation consists on the selection of appropriate percentages of the combination of starches of natural origin, plasticizers and waste of fruits, such as pineapple, orange, chilacayote, guava, lemon, mango, apple, pineapple, watermelon and banana. The resulting polymer characteristics are studied in mechanical and electrical analysis. The test probes of the polymer are films, molds and test wires. The conducted experimentation includes the doping and electropolymerizing processes with different compounds and different electrical parameters respectively. The changes in the two processes aim to modify the physical and electrical intrinsic properties of the polymer. The test molds are used accordingly to the ASTM standard that provides the guidelines for mechanical tests. The resistance measurements are performed on the polymer wire to determine its resistivity. The electrical and electronic instrumentation is developed to perform an electropolymerization process by a pulsed power supply that provides variable electrical parameters at the output, namely voltage (1-24V), current (1-3A), frequency (10-1000Hz) and pulse widths (10-100 μs).

Biopolymers, Doped, Characterization

Resumen

En este trabajo se presenta la formulación, análisis mecánico y eléctrico de películas, probetas y alambres de un polímero hecho a base de material biodegradable. La formulación consiste en la selección del porcentaje más adecuado de la combinación de almidones de origen natural, plastificantes y desechos de frutas tales como la piña, naranja, chilacayote, guayaba, limón, mamey, mango, manzana, sandia y el plátano. La experimentación realizada es sometida a un proceso de dopado y electropolimerizado con diferentes compuestos y con diferentes parámetros electricos respectivamente, acciones realizadas para modificar las propiedades intrínsecas (físicas y eléctricas) del polímero. Se utilizan moldes de prueba de acuerdo a la norma ASTM para realizar ensayos mecánicos y para determinar la resistividad se realizan mediciones de resistencia en el alambre del polímero obtenido. Se desarrolla la instrumentación eléctrica y electrónica para realizar el proceso de electropolimerización mediante una fuente pulsada que proporciona a la salida parámetros electricos variables, tales como voltaje (1-24V), corriente (1-3A), frecuencia (10-1000Hz) y ancho de pulso (10-100µs).

Biopolimero, Dopado, Caracterizacion

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Introduction

Before the plastic age, mankind used the directly accesible earth resources as the only source to get tools (Garcia, S., 2009), instruments and everyday use devices (Rodríguez, A. 6, 2008). Recently, the consumption needs of products pushed the industry to create cheaper materials with physical properties like those available in nature (Hottle, T., 2013). Plastic is a petrochemical derivate developed for mass usage. Today plastic has innumerable applications. Relevant plastic applications are emerging for biomedical purposes (Bret, D., 2011). The spread of plastic all over the world is mainly due to its low cost. Nevertheless, thousands of tons of plastic are discarded daily. The huge amount of waste is a problem since plastic is not biodegradable.

Plastic decomposition lasts hundreds of years causing considerable environmental pollution (Vroman, Isabelle, 2009). It is important to find alternatives that largely resolve the pollution derived from plastic waste (Kumar, A., 2011). Research and development of plastic allows the incorporation of biodegradable material reducing the disintegration time (Tanaka, M., 2015). However, it is a big challenge to generate biodegradable plastics with the same characteristics of common polymers, such as Polystyrene (PS), Polyurethane (PU), Polypropylene (PP) or polyvinyl chloride (PVC) among others (Mohanty, AK, 2000). The constraints are the physical, mechanical or electrical requirements of plastic products. It is important to study and develop polymers with a base different from petrochemical (Iwata, T., 2015). The following sections describe a novel polymer formulation with water base, starch and fruit peels. Mechanical and electrical tests are performed on the new material after doping and electropolymerizing processes.

Formulation

There are two main biodegradable plastic types described in the literature, the so-called Hydro-biodegradable (HBP) and Oxo-biodegradable (OBP). These biodegradable plastics are made of at least one of the following: starch, vegetable waste, aliphatic polyesters, orange husks, tree leaves or wool (Patel, Parth N, 2011).

Each of these ingredients gives the polymer a structure that characterizes its final physical form. In this work, the polymer formulation is studied considering the effect of the components in the the bioplastic, 1) the plasticizer: that destroys the secondary and tertiary structures of the macromolecules, 2) the gelatinizer: that causes the molecule crystallinity loss, 3) the additive: that provides mechanical and electrical properties to the final product and, 4) the temperature: that affects the polymer physical texture.

To determine the optimal percentages of the components, the process formulation is designed by trial and error looking for electrically and mechanically stable materials. Figure 1 shows the methodology with the best results in both the formulation and the experimental test phases. The methodology starts with the fruit shell waste selection (1), of which 25 g are used and weighed on a digital scale (2). The selected fruit waste is placed in a crusher (3) and mixed with 100 ml of water (4). The mix is filtered (5) to obtain 75 ml of a concentrate juice (6) to 0.25 g / ml, which has the plasticizer function. Then, 15 g of starch are added to the solution (7) as a polymeric base. The gelatinizer is 5 ml of glycerin (8). Finally, 10 ml of vinegar (9) is used to stabilize the solution pH.

Figure 1 Diagram of the Natural Biopolymer Formulation Methodology
Source: Own Elaboration

The final mixture is considered to be the basis of the formulation tests, and it is classified according to its treatment as natural BP (BPN), doped (BPD) or electropolymerized (BPE). In the BPN, the corn starch molecules, amylose or amylopectin, form the polymer main chain (Guzmán, A. and Gnutek, N, 2011). Figure 2 shows the structure of the BPN main chain.

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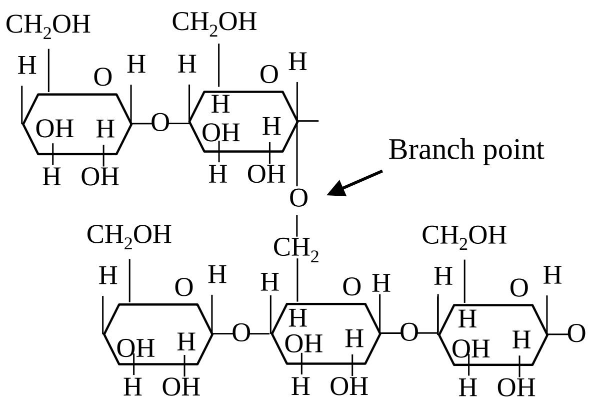

Figure 2 Chemical amylopectin structure.
Source: Own Elaboration

In the natural biopolymer there is no agent that modifies the physical or chemical properties of the bioplastic obtained. The doped biopolymers (BPD) are analog to electric semiconductors. The addition of external elements modifies their properties. Ascorbic acid ($C_6H_8O_6$) and zinc oxide (ZnO) are used in BPD to propitiate the generation of chemical agents in the reaction and therefore to cause the modifications in the BP characteristics (Tassew, A. 2014). Figure 3 shows the chemical structure of the dopants. The doping process is considered as a treatment applied to the final mixture and corresponds to the Point 11 shown in the methodology of Figure 1. Here, 1 g of $C_6H_8O_6$ and ZnO are added to the mixture.

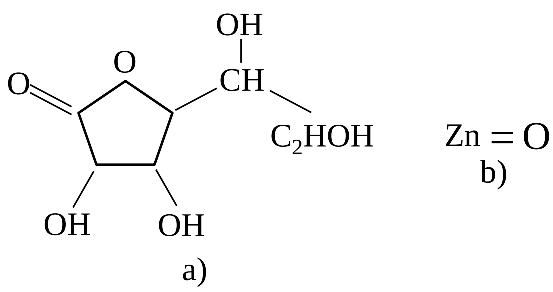

Figure 3 Chemical structure of the usual dopants for the BPD, a) ascorbic acid and b) Zinc oxide.
Source: Own Elaboration

Finally, the BPE undergoes an electrical treatment (Point 10 in Figure 1), in which a pulsed electrical current circulates through the polymer during formation. The method consists in introducing two electrodes (positive and reference ground) to the container with the mixture inside. The electrodes are connected to a pulsed power supply of potential 5 V, current 0.5 A, frequency 1000 Hz and pulse width 100 μs. Figure 4 shows the trigger circuit.

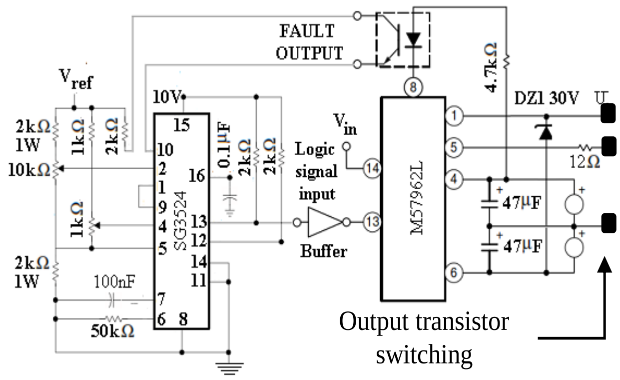

Figure 4 Electric diagram of the pulsed power supply trigger circuit
Source: Own Elaboration

Table 1 shows temperatures and the transition times during the reaction of the BP in the three forming processes, as well as for each of the fruit waste used in the formulation.

Process (N,D y E)	**Forming temperature [ºC]**			**Forming time [min]**		
Fruit	N	D	E	N	D	E
Chilacayote	70	71	71	5	5	4.5
Guava	72	71	72	4.3	4.2	3.8
Lemon	73	73	72	4.5	4.4	4
Mamey	72	72	71	5.1	5.1	4.5
Mango	72	73	72	4.9	4.8	4.1
Orange	70	72	70	5.5	5.5	4.9
Apple	72	73	72	5.1	5	4.4
Banana	72	73	71	5.4	5.4	5
Pineapple	72	72	70	5.1	5.2	4.6
Watermelon	71	70	70	5.5	5.3	4.7

Table 1 Typical temperatures and times of biopolymer formation under natural (N), doped (D) and electropolymerized (E) conditions
Source: Own Elaboration

The transition temperatures shown in Table 1 for the natural processes (N), doped (D), and electropolymerized (E), are between 70-73 ºC, however the reaction time for BPE it is a little lower, since electrical processes imply thermic addition to the forming temperature.

The physical forms of test tubes and films obtained during experimentation (see Figure 5) change their morphology according to the process. The BPN is more flexible and sensitive to touch. On the other hand, the doped material is more solid, more uniform and more elastic. BPD are less sensitive to ruptures and the density loss during the process is lower than the natural ones.

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BPE are apparently resistant to mechanical traction, some are elastic and others are fragile and rigid, but with smooth texture. Each one of the BP obtained in the experiments has different physical characteristics that depend on 1) the formulation, 2) the doping percentage and 3) the power pulsed supply electrical parameters. It was noted that the density loss (ρ) depends directly on the specimen thickness. For the test tubes the physical tests results were favorable, however after a few days their density decreased by 40%. This effect was less dramatic with film specimens, in which the density only decreased 10%.

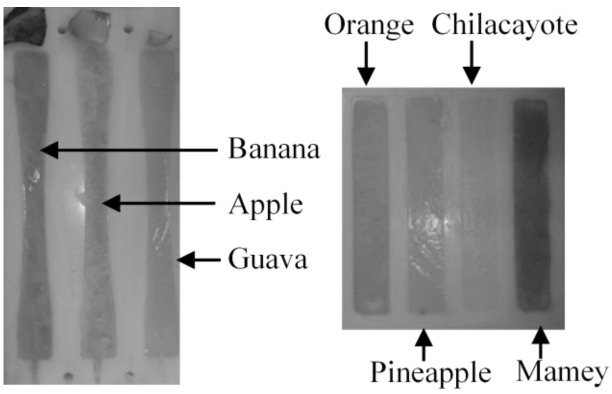


Figure 5 Films and test tubes under norm ASTM D882-12 and D638-02a respectively
Source: Own Elaboration

Electrical Testing

During the doping (D) and electropolymerized (E) processes, some bonds of the polymeric base of the starch break apart, generating free radicals (OH) and some free electrons (Fernández, T, 2003). The BP electrical resistivity changes depending on the amount of free charge carriers. To measure the resistivity we take electrical resistance measurements on the obtained material films with thicknesses less than 1 mm. The method used to determine the resistivity of the films is called four-point method or the Kelvin method (Severin, J., 1971). The measurement method is illustrated in Figure 6.

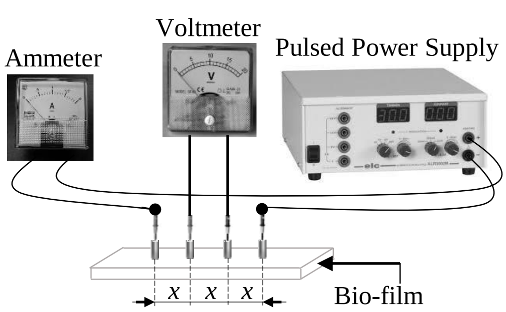
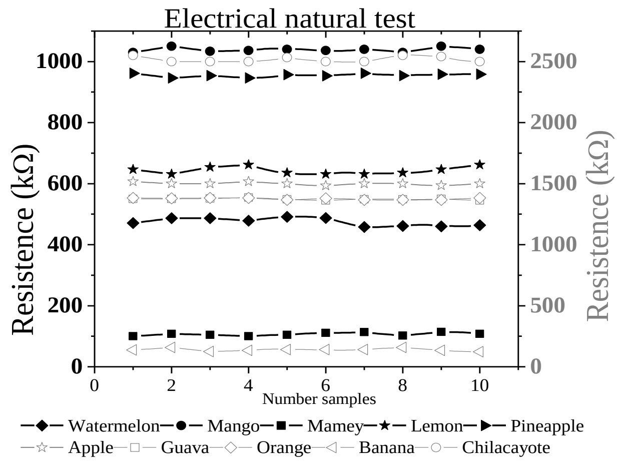
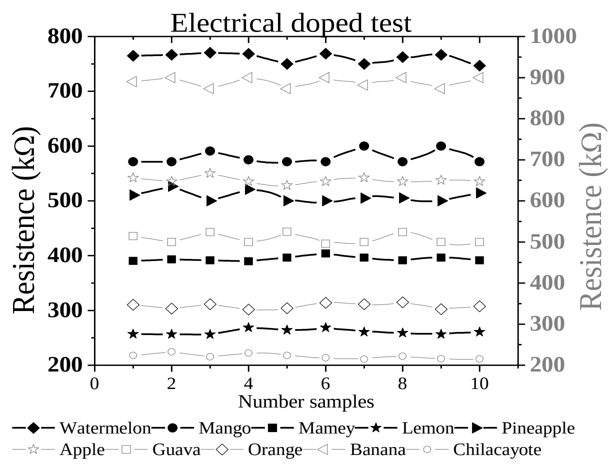


Figure 6 The four-point resistance measurement method
Source: Own Elaboration

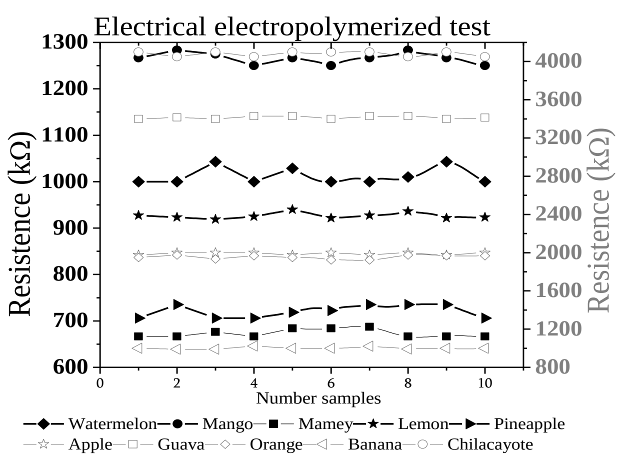
With this method, the characteristic electrical values of bio-films are obtained. The instrumentation consist of digital multimeter UNI-T UT139C, with micro measurements scales. The following graphs show the concentration of the average ohmic values for the natural, doped and electropolymerized process respectively.



Graph 1 BPN Ohmic values
Source: Own Elaboration



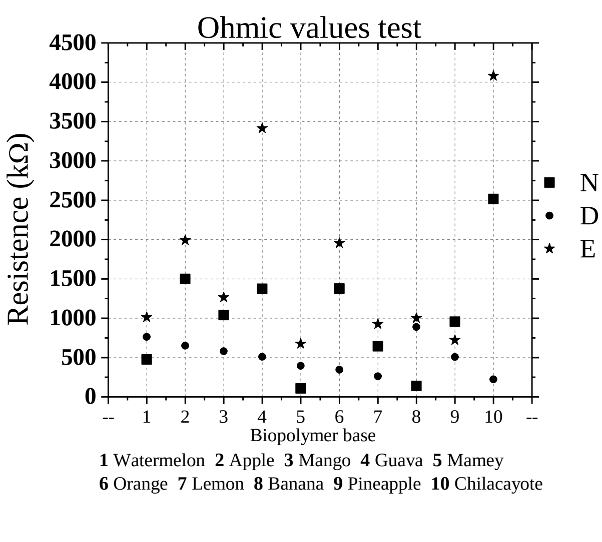
Graph 2 BPD Ohmic values.
Source: Own Elaboration



Graph 3 BPE Ohmic values.
Source: Own Elaboration

In Graph 1 it is observed that the lower ohmic values are characteristic for the mamey and the banana. The maximum resistive values are present in the chilacayote and the apple. On the contrary, in Graph 2 we can see that the banana and the chilacayote have reversed roles, now the BP made with chilacayote has the least resistance value and the banana shows one of the highest values. In these tests, an important aspect to comment is the resistance value range because is less to 1 MΩ. We can note that while some compositions increase their ohmic values, others decrease it until reaching the mentioned interval. The doping elements influence the BP conductivity, so now this depends largely on the percentage of zinc oxide and ascorbic acid added to the formulation and at a lower rate to the fruit waste intrinsic characteristics.

In Graph 3 we notice that the ohmic values have increased notoriously. Nevertheless, the mamey and the chilacayote maintain properties of low and high resistance in comparison with the others test within the same experiment, which indicates that probably the current action in the process directly magnifies the fruits conductive properties. The conductivity increment is observed because there is no dopant. Therefore, according to the electrical parameters of the pulse applied the ohmic values vary. Graph 4 shows a comparison of the resistive values measured in the BP subjected to the three different processes.



Graph 4 Comparison of ohmic values between the natural (N), doped (D) and electropolymerized (E) tests
Source: Own Elaboration

In Graph 4 it is observed that except for the watermelon, mamey and banana, a pattern is followed in which the resistance increases in the order of the test D, N and E. It is also observed in the test that the resistance value most significant change is present in the polymer with residues of chilacayote and guava. On the other hand, the less representative variations are found in those of watermelon, mamey and pineapple. We conclude that the type of fruit waste used in the formulation essentially provides the final electrical resistance of the bioplastic.

It is verified that the final conditions during doping depend directly and almost exclusively on the aggregate material percentages (the resistance decreasing in almost all cases). In the electropolymerized process, the pulsed electric current acting during the formation of the bioplastic strengthens the polymer bonds making it less conductive.

Mechanical Tests

Mechanical tensile tests are performed for the BPN, BPD and BPE films on the Universal Instron machine (see Figure 7) using the Bluehill software. The main objective is to characterize the BP according to the analysis of its stress-strain characteristic curve (Ward I., 2013). The results obtained define whether the material is fragile or not. In the same way, the interpretation of the graph results specifies if the BP is suitable for elastic or plastic applications and shows how deformed the material can be (Mendoza, R. 2011).

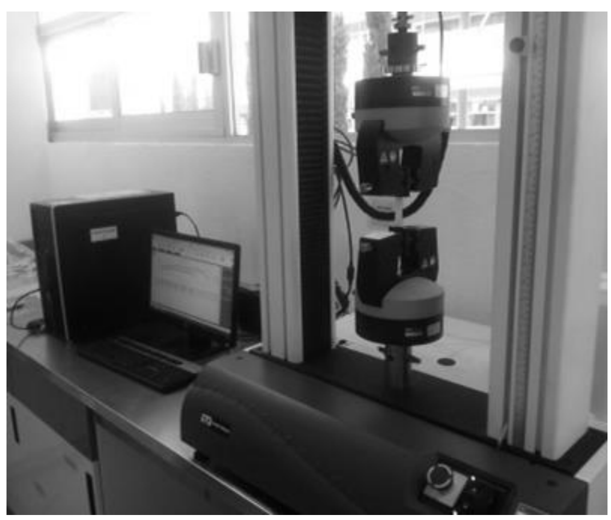


Figure 7 Tensile test in the biopolymers.
Source: Own Elaboration

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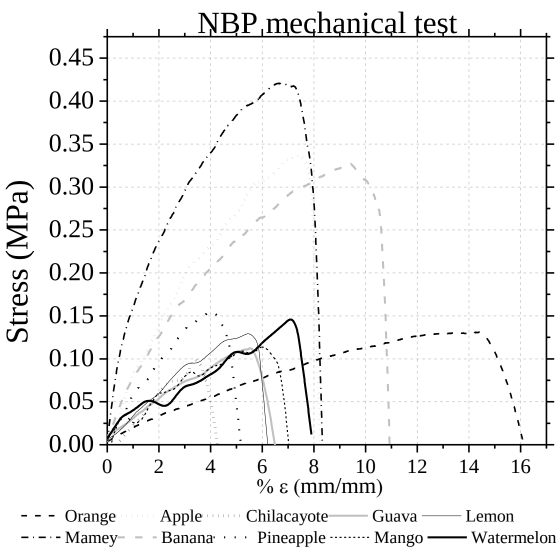
Tensile test	
Column 1	Young module
Column 2	Creep load
Column 3	Breaking load
Column 4	Traction stress
Sampling	100 ms
Width	17.2 mm
Lenght	91 mm
Thickness	0.56 mm
Geometry	Rectangular

Table 2 Tensile test characteristics
Source: Own Elaboration

The sample geometry and the most important parameters for the bio-polymer characterization considered in the stress test, are shown in Table 2 and taken from the ASTM D882 standard for thin films (tensile properties of thin plastic sheeting).

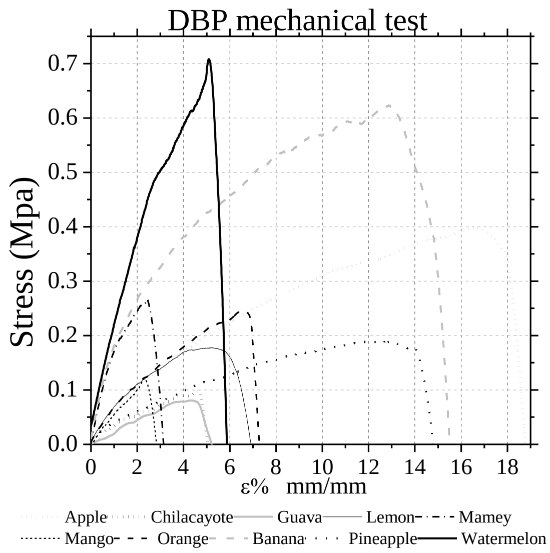


Graph 5 Natural bio-polymers stress test results
Source: Own Elaboration

Graph 5 shows the NBP formulation stress test results. The material that has a larger deformation (~ 16 mm/mm) is the formulation based on orange peel. Here the break is not abrupt, that means the material is not very fragile. The break occurs when the final elongation corresponds to ~ 8 mm, with a strain around ~ 130 kPa.

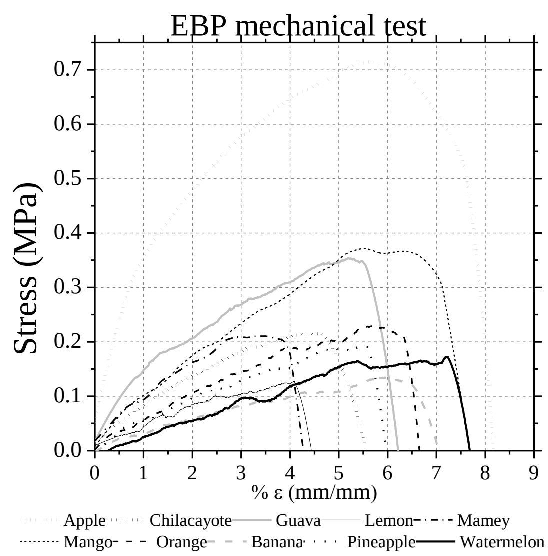
The material based on mamey presents the bigger value of the Young's modulus (inclination slope). This material is capable of supporting more effort (~ 420kPa). The elastic zone slope is almost directly proportional for values deformation less than 2mm, this mean that it supports large loads at the beginning of the traction compared to the others, however it is not very elastic.

In the test there are two other formulations with similar behaviors that are those of apple and banana base, noting that the latter has greater elongation capacity. For the other BPN, the behavior between them is very similar, due to the fact that they support loads of the order of 120kPa and deform ~ 3mm.



Graph 6 DBP tension tests
Source: Own Elaboration

The BPD traction test results are shown in Graph 6. The watermelon formulation is fragile when reaching a stress close to 700kPa. Note that the apple-based material is the most elastic with an elongation around ~ 9.5 mm when supporting a strain of ~ 400 kPa.



Graph 7 EBP tension tests
Source: Own Elaboration

Graph 7 shows the mechanical tests results of the formulation subject to pulsed electrical discharges. Here the apple film has the highest deformation percentage which corresponds to approximately 4 mm, generated when reaching a maximum stress of ~ 700 kPa. There are two other similar behavior cases, that of guava and mango, in these the stress is near to 350 kPa with deformations of 3 and 4 mm respectively. For the rest of the tests with the other fruits not mentioned, the behavior is similar between them, a maximum stress is ~ 200 kPa with a deformation of between 2 and 4 mm.

Optical Microscopy

A simple analysis is carried out using an AxioCam ERc 5s digital optical microscope (Zeiss), shown in figure 8. 200x lenses and immersion oil are used to maintain the refractive index of the uniform light (which does not change angle), which generates more light reaching the object. A sample of natural, doped and electropolymerized orange film is analyzed as shown in the following figure.

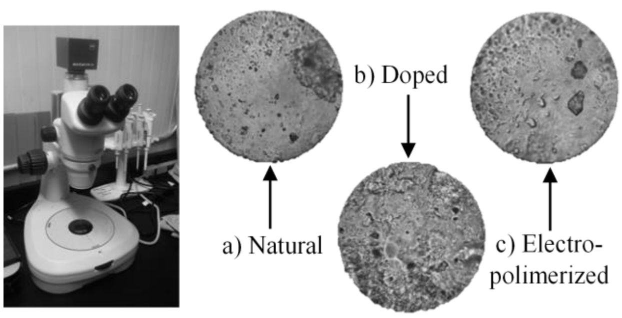


Figure 8 Optical microscopy test
Source: Own Elaboration

In figure 8 it is noted that the biopolymer surface structure changes form of a) natural formulation to b) doped, where it is notable that the structure is less uniform, this is due to the action of the oxides present in the process. On the other hand, for the electrically treated sample, we observed that there is not a very significant change with respect to the EBP.

Conclusions

It is important to consider new material options to replace the petroleum-based plastics. We introduced new formulations to make hydro-biodegradable films and tubes test.

In the new materials, the starch provides the polymer characteristics base and the residues of fruit peels add particular characteristics that are modified in posterior doping and electro polymerization processes. It was observed that the electrical characteristics of the doped biopolymers are apparently uniform, within a defined interval, but their mechanical characteristics are not uniform. The mechanical properties of electropolymerized biopolymers are more stable with respect to the two posterior processes, since the properties only change slightly irregardless of the type of fruit used.

We conclude that to obtain a more conductive BP, it is necessary to use the doped formulation, and for mechanically resistant materials, the electrical process is the option. A combination of doping with electrical treatment will most likely obtain a BP with suitable mechanical and electrical characteristics, as electrical conductor as specified according to the dopant and so mechanically resistant according to the pulsating source electrical parameters. A remarkable observation is that the EBP electrical resistance is higher than for a plastic straw, with a similar texture (significant example the banana EBP). Also, the DBP are more flexible and have a latex-like behavior that adheres to the container and takes its shape.

For future works, it is proposed to combine simultaneously the doping and electropolymerized processes. It will be necessary to conduct a study using an electron scanning microscope to get insight into the internal structure of the obtained BP. Another property to be measured is the flow index (MFI) with a plastometer, to determine if the BP is suitable for extrusion or for injection. Further experiments varying the electrical parameters such as voltage, current, frequency, and pulse width of the applied electrical signal, will fully characterize the electrical and mechanical effects in the BP. Further work is to find the most appropriate application options for each obtained material.

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