Colegio de Postgraduados

Evaluation of orange peel (*Citrus sinensis*) bioplastic through morphological and thermo-mechanical characteristics

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ABSTRACT

Objective: To evaluate the morphological and thermo-mechanical properties of a bioplastc film obtained from orange peel.

Design/methodology/approach: Pectin, a polysaccharide obtained from orange peel, has the potential to be used as a raw material in the bioplastics industry. The samples obtained were characterized by the Scanning Electron Microscopy (SEM) technique, mechanical tension and by thermogravimetric analysis (TGA).

Results: The elastic modulus was in the range of 7.7 to 29.9 MPa, depending on the plasticizer content. The thermogravimetric analysis showed a thermal decomposition between 134.42 to 153.98 °C depending on the plasticizer content and up to five events were identified.

Limitations of the study/implications: During the process, a pectin yield of 75% of orange peel was obtained.

Findings/conclusions: In developing countries such as Mexico, waste from agricultural and agro-industrial activities represents an important source of natural carbohydrate polymers that can be used to produce bioplastics, intended to replace petroleum-derived materials. In the case of orange peel, it can become a potential raw material to obtain value-added products in sectors of the food industry. These results indicated that our pectin has suitable properties to be used as raw material for the manufacture of bioplastics.

Keywords: bioplastic, mechanical properties, pectin film, thermal properties.

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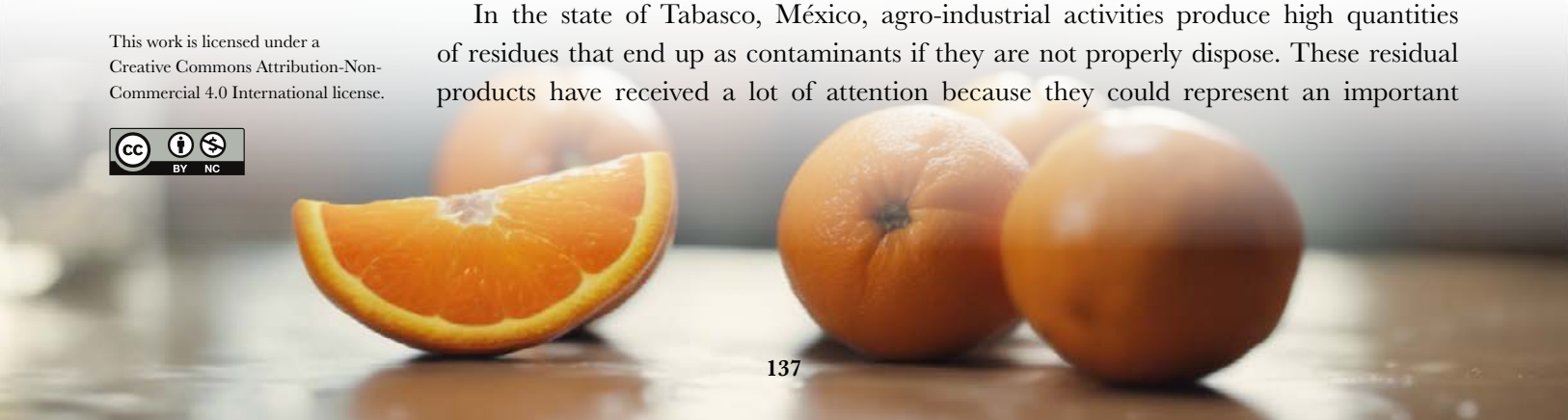
INTRODUCTION

In the state of Tabasco, México, agro-industrial activities produce high quantities of residues that end up as contaminants if they are not properly dispose. These residual products have received a lot of attention because they could represent an important



source of highly valuable materials such as bioplastics used in food packaging, biomedical applications, and drug delivery (Lara-Espinoza *et al.*, 2018). Banana, orange, cocoa, pineapple, coffee, sugar cane and mango are some agricultural products that generate organic waste which can provide mainly fibrous materials as cellulose and nanocellulose, and others like lignin and pectin. The orange is one of the main citrus fruits with the largest number of hectares planted in our country, mainly in the states of Veracruz and Tamaulipas. The production forecast for the 2020/22 campaign was 4.85 million metric tons (SAGARPA, 2022). Within the waste generated from within the juice industry is the orange peel, obtaining up to 60%, which, due to its characteristics, cause various environmental problems such as soil contamination, since it has a degradation time of approximately 6 months. To reduce this problem, various investigations have been carried out to give added value to this agro-industrial residue. Pectin is found in the primary wall of mesenchymal and in the parenchymal tissue of fruits and vegetables, and pectin acts as an intercellular adhesive (Nwanekezi, Alawuba and Mkpolulu, 1994; Tandon, Kaira and Neelima, 1996). It has different properties according to its esterification degree and can be classified as high methoxylated pectin (HMP) for high esterification degree, and low methoxylated pectin (LMP) for a low content of ester groups. Commercial HMP can be obtained from citric peels and apple pulps. Orange peel has been reported to contain pectin up to 25% calculated on dry weight basis (Müller-Maatsch *et al.*, 2016). HMP is a potential raw material to produce bioplastic. This bioplastic has physical-mechanical characteristics that can be transformed in dishes, bags, or other containers for packing biodegradable goods (Mellinas *et al.*, 2020). In this work, morphologic, mechanical, and thermal characteristics of a bioplastic film obtained from pectin extracted from orange peel are reported.

MATERIALS AND METHODS

Orange peel waste was collected in city of Cárdenas, Tabasco, Mexico, citric acid anhydrous and glycerol were purchased from Meyer.

Preparation of Bioplastic Film

The used procedure was previously described by Ramos-Alvarado (Ramos-Alvarado *et al.*, 2020). In brief, orange peel was washed with abundant water to remove impurity and then rinsed with distilled water. Orange peel is cut into pieces and placed in 0.1% citric acid at 90 °C for 90 min. Subsequently, a homogeneous mass was obtained using a blender, and it was filtered with a 250 μm sieve to obtain pectin. Glycerol was added at 3% (PG3) and 5% (PG5) in two different containers mixing vigorously in order to evaluate its plasticizer effect Next, the mixtures were placed on aluminum foil and spread as thin films. Finally, the films were dried in an oven at 45 °C for 24 h (Figure 1).

Scanning Electron Microscopy (SEM)

A morphological analysis was performed using a JEOL JSM-7500P scanning electron microscope. The samples PG3 and PG5 were previously dried in a desiccator and then covered with a thin layer of gold. Images were collected using 5,000x magnification.

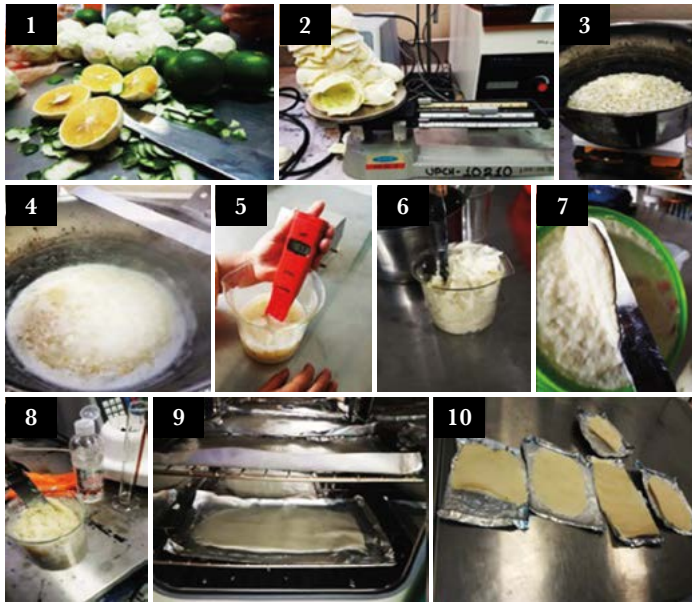


Figure 1. Extraction of Bioplastic from orange peel waste (*C. sinensis*). 1) Orange peels; 2) Weighing of shells (mesocarp); 3-4) Hydrolysis; 5) pH measurement; 6) Pectin mass obtained; 7) Pectin sieving; 8) Mixture of pectin with glycerol: 9) Drying of biofilms in a conventional oven; 10) Orange biofilms obtained.

Tension Mechanical Test

A mechanical test was conducted in an Instron model 1120 universal machine in accordance with the ISO 527-3 standard. Six samples were prepared from each film with a thickness of ~0.3 mm by cutting with a die in a hydraulic press. A strain rate of 10 mm/min was used, at atmosphere temperature, with a relative humidity of 50%.

Thermogravimetric Analysis

A thermic analysis was carried out in a TA Instruments model TGA Q5000 equipment. Samples from 4.8 to 10.87 mg were used. The heating range was from 34 to 600 °C with a ramp of 10 °C/min. Nitrogen was used as an inert atmosphere.

Statistical Analysis

The data from the mechanical properties of the bioplastic film were evaluated using Student's t-test, with a $p \leq 0.05$ indicating statistical significance.

RESULTS AND DISCUSSION

Bioplastic and its Morphological Characteristics

The yield of pectin extracted was 75% with respect to the dry mass. The films were flexible, with a smooth texture, a pleasant smell, and an opaque yellow color. The color tone visibly decreases with increasing glycerol content, as previously reported (Ramos-Alvarado *et al.*, 2020). The obtained thickness was ~0.3 mm. The films did not present cracks and were homogeneous in their conformation, which indicates that the drying temperature was optimal. The mechanical integrity of the films allowed to easily detach

them from the aluminum foil. The surfaces of the bioplastic films (Figure 2) in samples PG3 and PG5 have a heterogeneous surface, with agglomerates and striations that may be caused by fibrous material. It is evident that the PG3 sample has a greater number of striations, and it presents agglomerates above 2 μm. On the contrary, the PG5 sample is seen to be smoother and more uniform. It is possible that the proportion of 3% of plasticizer in the PG3 sample was not enough to completely disintegrate the pectin domains, creating agglomerates that could be caused by its interaction with the residual fibrous content generated during the extraction process. It is known that pectin films are characterized by the absence of a homogeneous structure, which is apparently due to the formation of packed pectin agglomerates (Giancone *et al.*, 2011).

Bioplastic films based on pectin with a high content of methoxy groups have a high degree of esterification, which gives them the ability to form networks with a high degree of gelation at room temperature. This type of film had high values of tensile strength ~21 MPa, which made it rigid and with little deformation capacity (~1-3.6%), making it feasible to produce films for food packaging (Giancone *et al.*, 2011; Bátori *et al.*, 2019). To improve the performance of these films, the use of a plasticizer is required. Glycerol is one of the most widely used plasticizers in the food and pharmaceutical industries. Due to its low molecular weight (92.09 g/mol), glycerol can permeate the intermolecular spaces of the pectin main chains, hindering the formation of hydrogen bonds and reducing polymer-polymer interactions, promoting an increase in the mobility of the polysaccharide chains.

Mechanical Analysis

The mechanical behavior of the bioplastic films was evaluated by the stress-strain curve. Elastic modulus, tensile strength, and strain at break were obtained. The curve of the tensile test of both PG3 and PG5 samples (Figure 3) showed that they possess a characteristic behavior of a plastic material, since no change in the slope of the curve of each sample is observed.

The proportion of plasticizer modified the mechanical properties of the bioplastic film (Figure 4). The elastic modulus was reduced by 67.86% when going from 23.976±3.993 MPa, to 7.705±0.470 MPa, for PG3 and PG5, respectively. Regarding the tensile strength, the PG5 sample presented a reduction of 57.41%, when changing from 4.560±2.588

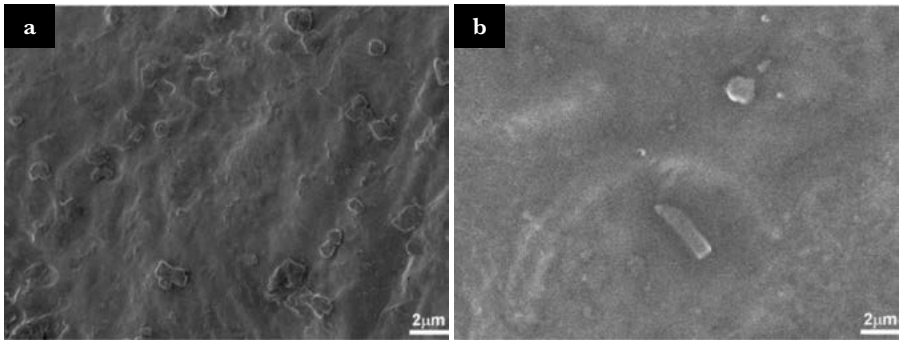


Figure 2. Scanning electron microscopy, PG3 (a), PG5 (b); 5000x resolution.

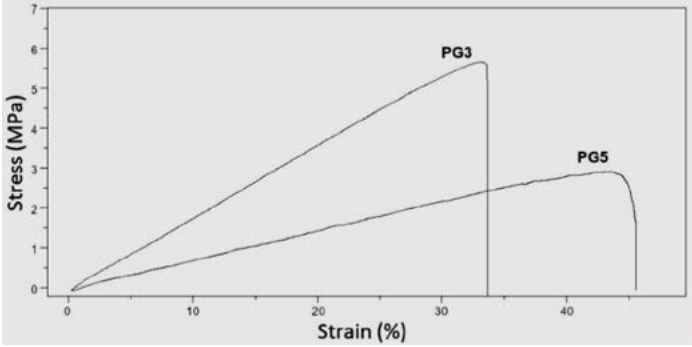


Figure 3. Stress-strain curve of bioplastic films.

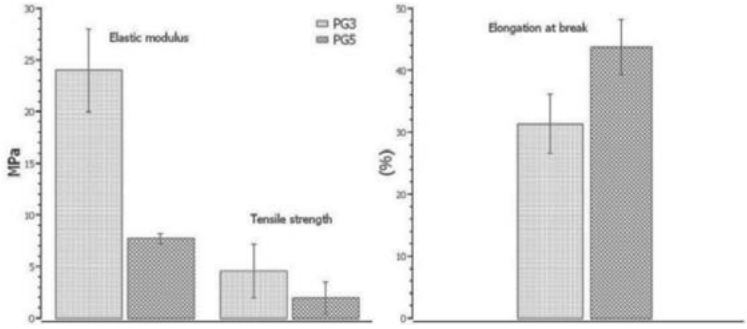


Figure 4. Mechanical properties of bioplastic film. The bars indicate the standard deviation. In all parameters, the proportion of glycerol produced changes with statistical significance $p<0.05$.

MPa, to 1.942±1.550 MPa. Finally, the strain at break was improved with an increase in plasticizer, since the PG5 sample presented a value of 43.716±4.435%, against 31.370±4.765% of PG3.

Thermogravimetric Analysis (TGA)

Thermal decomposition appears in 134.42 °C and 153.98 °C for PG5 and PG3, respectively. Five events of thermal decomposition were observed in the TGA curve of the bioplastic films (Figure 5). This behavior depended on the proportion of glycerol

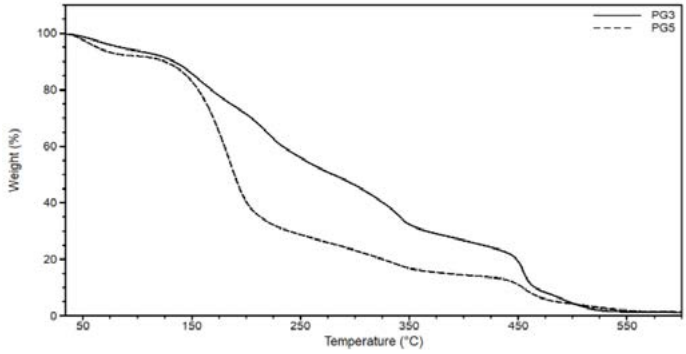


Figure 5. TGA curve of orange peel bioplastic films.

in the film. The first two events corresponded to the evaporation of water and thermal degradation of pectin, respectively. There was a clear difference in PG3 and PG5, which corresponds to the plasticizing effect of glycerol. The greater proportion of water in PG5 originated from the fact that a greater number of glycerol molecules which favored the formation of more intermolecular spaces to admit water.

The DTG curve (Figure 6) represents the kinetics of thermal degradation. Pectin in PG3 decomposed in two events, the first one with a peak at 156.8 °C and the second one at 220.1 °C. The first presented a shift to the left, while the second was within the common interval of decomposition. This degradation behavior may be due to structural differences within the polymeric matrix, caused by the heterogeneous distribution of the hydrogen bonds of the pectin-pectin interactions, which may benefit from the heterogeneous dispersion of the glycerol molecules, possibly caused by the high fibrous content of the sample (Darni *et al.*, 2017; Costanza *et al.*, 2019). This fiber content may also be related to the better thermal stability of PG3. The insoluble fiber content in orange peel is between 42.7 and 48.3%, mainly composed of cellulose and lignin (Rincón *et al.*, 2005; Garcia-amezquita *et al.*, 2019). Finally, the last event corresponds to the gasification of carbonaceous residues. The results of the quantitative analysis of the thermal decomposition are shown in Table 1.

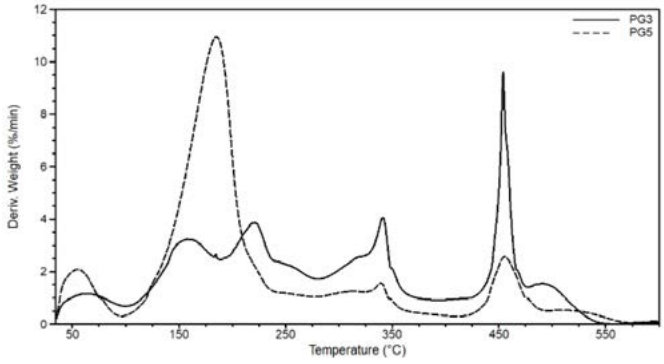


Figure 6. TGA curve of orange peel bioplastic films.

Table 1. Thermal events of the orange peel bioplastic in PG3 and PG5 samples.

PG3				PG5				Events
T_{On} (°C)	T_P (°C)	T_{Off} (°C)	Δm (%)	T_{On} (°C)	T_P (°C)	T_{Off} (°C)	Δm (%)	
33	63.9	98.5	7.55	33	55.3	96.1	8.13	Water evaporation
117.4	-	280.2	53.03	101.9	184.6	277.5	72.33	Pectin decomposition
328.1	340.6	392.0	15.25	329.2	338.8	409.2	5.68	Glycerol decomposition
425.8	454.9	475.5	15.96	418.6	455.7	489.5	9.09	Cellulose-lignin breakdown
476.0	-	559.3	6.71	490	-	565	3.1	Carbonaceous gasification
1.25 %				1.43 %				Ashes

T_{On} Onset Temperature, T_{Off} Offset Temperature, T_P Peak Temperature, Δm mass loss during TGA.

In our bioplastic films, the proportion of evaporated water from the sample corresponds to the proportion of glycerol (Figure 7), since a higher content of plasticizer molecules increases the admission of water.

The difference in free water content (Table 2) is an indicator of the type of pectin structural arrangements in the film matrix and could also be an indicator that at a greater amount of free water, a greater amount of energy is required to convert the water molecules to the gaseous state.

The plasticizing effect of glycerol can be explained in two ways; the first is that the hydroxyl groups of glycerol can interact with the OH and COOH groups of pectin, to form covalent ester bonds of the hydroxyl-hydroxyl or hydroxyl-carbonyl type, through condensation reactions. The second way of glycerol-pectin interaction is through the solvation of the polar sites in polysaccharide main chain, which causes a masking of the hydrophilic sites. This produces a reduction in pectin-pectin interactions, increasing the mobility of the chains to produce films with a lower elastic modulus and tensile strength, but with greater deformation capacity (Darni *et al.*, 2017; Costanza *et al.*, 2019). The thermogravimetric analysis showed that the water content in the bioplastic films increased with the glycerol content. It is possible that this mechanism explains the difference observed in the surface of the films, in which a higher proportion of plasticizer in PG5 served to promote a better distribution of the pectin domains, obtaining a smoother surface, since in the dehydrated state and without glycerol, the hydrophilic regions of the pectin can form aggregates causing an increment of hydrogen bonds and reducing the amount of water admitted. One way to infer the level of pectin-

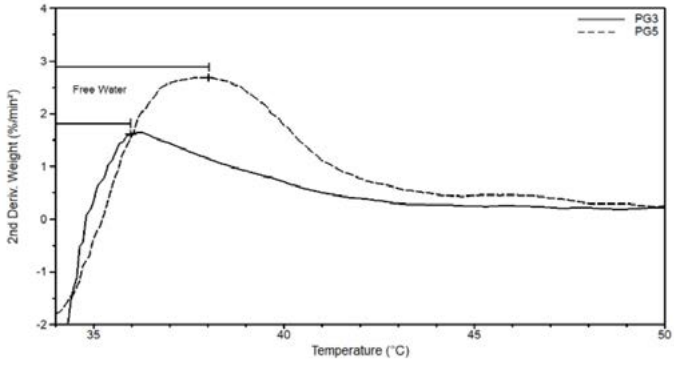


Figure 7. 2ndDTG curve (second derivative of thermal degradation) corresponding to water loss in PG3 AND PG5 samples.

Table 2. Quantification of the free water contained in the PG3 AND PG5 bioplastic film samples.

Parameter	PG3	PG5
T_P (°C)	35.98	38.15
Mass loss (%)	0.18	0.40
Free water ratio (%)	2.38	4.92

TP Peak temperature indicates the change in kinetics.

glycerol interaction in the film is by monitoring the peaks at 925 cm^{-1} and 850 cm^{-1} of the FTIR spectrum, corresponding to the vibration of the C-C bonds. On this orange peel bioplastic, this behavior is observable since these peaks reduce their intensity by changing the proportion of glycerol from 3 to 5%, as reported in a previous FTIR analysis (Ramos-Alvarado *et al.*, 2020). Pectin films can thermally decompose in an interval from 150 to 580 °C, with a maximum decomposition peak between 201 and 260 °C. The thermal degradation of pectin begins with the depolymerization and degradation of the galacturonic acid chains, followed by secondary decompositions related to the breaking of bonds and functional groups, which gives rise to a gas phase. Subsequently, chemical reactions of the gaseous phase and oxidation of volatile organic compounds take place to form CO, CO_2 and H_2O, even under inert atmosphere conditions (Giancone *et al.*, 2011; Espitia *et al.*, 2014; Aburto *et al.*, 2015; Al-Amoudi *et al.*, 2019).

CONCLUSIONS

The water in the polymeric matrix of pectin exists as free water and as bound water. The bound water consists of all the water molecules that are joined by hydrogen bonds to the different components of the polymeric matrix, while the free water is admitted within the free volume caused by the plasticizer, without forming hydrogen bonds. This phenomenon can be observed in the curve of the second derivative of the mass loss (2ndDTG). During the water evaporation process, a peak appears in the 2ndDTG indicating the change in the kinetics of mass loss, which means that the free water finishes its evaporation process to allow the evaporation of bound water. The matching of maximum of that peak with the TGA curve indicates the mass of evaporated free water. The occurrence of this peak depends on factors such as the rate of heating and the velocity of the gas flow during the TGA. It has been observed that the peak of this event appears shifted to the left with the increase in the heating rate (Aburto *et al.*, 2015; Wang *et al.*, 2018; Costanza *et al.*, 2019). The pectin obtained has properties of potential use for the food product packaging industry. By surface analysis, the films have good integrity. Mechanical tests showed a direct effect of plasticizer content, obtaining a reduction of elastic modulus about 68% but an increasing of deformation at break around 28 % when changing from 3 to 5% the plasticizer content. Thermogravimetric analysis indicate that the bioplastic obtained from orange peel waste has fiber content. Both results indicate that our film provide suitable properties to make it a potential material for production of packaging for food products.

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