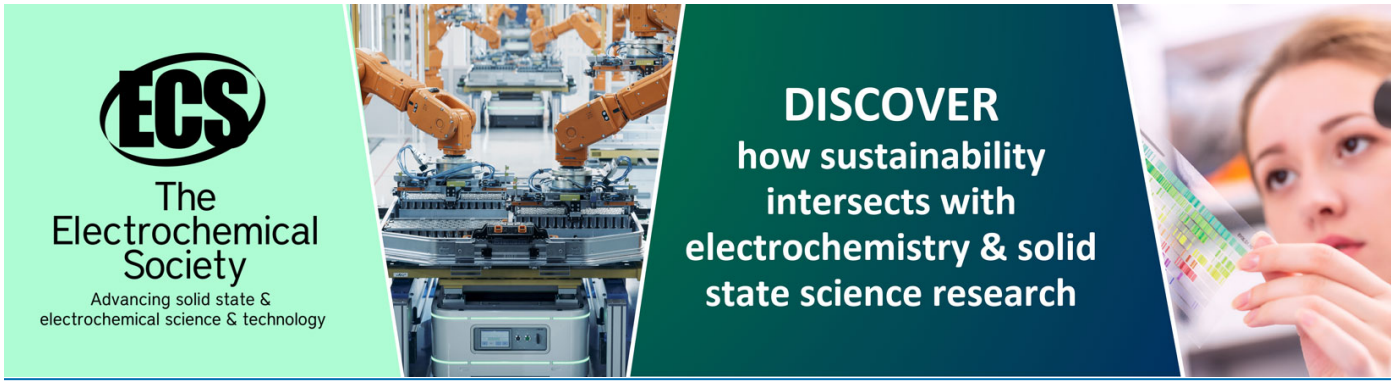
Influence of natural plasticizers derived from forestry biomass on shrimp husk chitosan films



Influence of natural plasticizers derived from forestry biomass on shrimp husk chitosan films

A Gonzaga[1], J Rimaycuna[1], G J F Cruz[1*], N Bravo[3], M M Gómez[2], J L Solis[2] and J Santiago[3]

[1]Department of Forestry Engineering and Environmental Management, Universidad Nacional de Tumbes, Av. Universitaria s/n, Campus Universitario – Pampa Grande, Tumbes, Peru
[2]Faculty of Sciences, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Lima 25, Peru
[3]Faculty of Chemistry and Chemical Engineering, Universidad Nacional Mayor de San Marcos, Calle Germán Amézaga N° 375, Ciudad Universitaria, Lima, Peru

*E-mail: gcruzc@untumbes.edu.pe

Abstract. Three new natural plasticizers (exudates of the *Prosopis pallida* and *Capparis scabrida* trees and gum from the *Cordia lutea* fruit) and polyvinyl alcohol (PVA) in different concentrations were tested to determine their influence on the properties of chitosan films prepared by a casting method. Properties such as thickness, solubility, water vapor permeability, elongation at break, tensile strength, luminosity, and anaerobic biodegradability were evaluated. Chitosan films with exudate of the *Capparis scabrida* tree as plasticizer had better properties than those with the other two natural plasticizers. However, the mechanical properties of the chitosan films prepared with PVA were still better than those with exudate of the *Capparis scabrida* tree. The films that included the three natural plasticizers in their composition were more biodegradable than those made of PVA, with films with exudate of the *Capparis scabrida* tree being the most biodegradable. The exudate of the *Capparis scabrida* tree is a potential biodegradable plasticizer for use in medical or food applications.

1. Introduction

The dry forest in northwest Peru is a vast area with moderate biodiversity. Inside this area, many communities perform different economic activities related to the forest, such as bee product elaboration and goat breeding for meat and milk production. However, the population in this area is still qualified as poor or extremely poor. In the dry forest, it is possible to develop different sustainable activities related to the forest that could help the population to increase their incomes sustainably. One of those activities is the utilization of potential nonwood products such as essential oils, gums, exudates, and fruits. *Prosopis pallida*, *Capparis scabrida*, and *Cordia lutea* are three tree species from the dry forest with potential nonwood products to be used. *Prosopis pallida* and *Capparis scabrida* commonly produce exudates when they are mechanically damaged to accelerate the cicatrization process. *Cordia lutea* produces a fruit with a gum that is used for local people as improvised glue [1]. Gums and exudates are mixtures of polysaccharides that are hydrophilic in nature and contain simple sugars; they can also

be composed of some proteins, Ca and Mg [2]. Gums from various plant sources have been used recently, mainly in pharmaceutical applications and in the food industry [3-7]. Most plant-derived gums and mucilage are hydrophilic and gel-forming in nature [8] and have the potential to be used as plasticizers.

Chitosan is a polymer derived from chitin, the structural polysaccharide of crustaceans and insects. This polymer is widely used in the production of packaging materials and medical applications. To improve the mechanical and physicochemical properties of chitosan, different plasticizers, such as glycerol, polyvinyl alcohol, and starches, have been used. The current tendency is to use natural plasticizers instead of synthetic ones.

In this framework, the present work aimed to determine the influence of three natural, new plasticizers derived from forestry biomass on the properties of chitosan films.

2. Materials and Methods

2.1. Production of films with different plasticizers

An experiment was conducted to evaluate the effect of the type and concentration (0.6, 1.0 and 1.5 %) of three natural plasticizers in solution (exudates of *Prosopis pallida* and *Capparis scabrida* and gum from the *Cordia lutea* fruit) on chitosan film properties. Chitosan was derived from *Litopenaus vannamei* (shrimp) with a deacetylation degree of 81%. Polyvinyl alcohol (PVA) was used as the blank to be compared with the natural plasticizers. For the preparation of the films, solutions of 1% chitosan (p/v in 1% acetic acid solution) were mixed individually (20 min at 1200 RPM) with solutions of every plasticizer in the three initial concentrations. Table 1 depicts the list of the prepared samples and their respective code.

Table 1. Code and description of the prepared films used in the first experiments

Code	Description
QS	Chitosan + *Capparis scabrida* tree exudate (0.6, 1.0 and 1.5 %)
QA	Chitosan + *Prosopis pallida* tree exudate (0.6, 1.0 and 1.5 %)
QM	Chitosan + *Cordia lutea* fruit gum (0.6, 1.0 and 1.5 %)
QP	Chitosan + PVA (0.6, 1.0 and 1.5 %)

2.2 Characterization of prepared films

The characterization of the prepared films included thickness (mm), water solubility (%), vapor water permeability ($g \cdot mm \cdot hPa^{-1} \cdot m^{-2}$), mechanical properties such as elongation (%) and tensile strength ($N \cdot mm^{-2}$), luminosity (%) and anaerobic biodegradation. The thickness of the films was measured using a digital micrometer (Mitutoyo IP 65 Coolant Proof, Japan) with 0.001 mm accuracy. For water solubility, 2 cm × 3 cm sections of the film samples were cut and weighed using an analytical balance (Sartorius Quintix, Germany). Every section was placed into a 100 mL flask, and 80 mL of distilled water was added. The samples were stirred for 1 h at room temperature, taking care that the film fraction was still submerged in the water. Every sample was filtered and dried at 105 °C until a constant weight was reached. Water solubility (%) was calculated from the difference between the initial and final weights divided by the initial weight and multiplied by 100.

The water vapor permeability ($g \cdot mm \cdot hPa^{-1} \cdot m^{-2}$) of the films was determined by the desiccant method according to standard test method ASTM E96M/E96-05.

Tensile strength ($N \cdot mm^{-2}$) and elongation at break (%) were calculated using the standard test method according to ASTM D882-01[9]. The measurements were performed with a universal texturometer (Brookfield CT3, Canada) with an activation charge of 0.05 N. Samples of 10 cm × 2.5 cm (length × width) were cut, placed into a desiccator with a saturated NaCl solution for 24 h, and then loaded into

the fixing accessory of the texturometer. The crosshead speed was set at 0.5 mm·s^{-1} until break. Tensile strength was calculated by dividing the maximum force on the film during the fracture between the cross-sectional area (width × thickness). Elongation at break (%) was calculated by dividing the maximum extension of the film samples by the length of the samples.

To determine the luminosity factor of the films, a colorimeter (Konica Minolta CR400, Japan) was used with white color as the reference.

A gravimetric method based on the underground microbial decomposition of the films was applied to determine the anaerobic biodegradability of the different prepared films. A period of 15 days was considered the total exposure time for this measurement. The weight of the samples was measured four times within the experimental time using an analytical balance (Sartorius Quintix, Germany). A 2.5 cm × 2.5 cm portion of each film sample was taken for the experiments. The samples were buried 30 cm deep in agricultural soil. The data for the first 2 days of the test were eliminated to avoid the influence of the water content (moisture) in the films. The q vs. t data were fitted to the zero- and first-order models [10]:

$$q = q_0 - k_0 t \quad (1)$$

$$\ln(q) = \ln(q_0) - k_1 t \quad (2)$$

where q (g) is the measured remaining weight of the films after time t (days), and k_0 and k_1 are the rate constants of the zero-order and first-order models, respectively. Values of the determination coefficient (R^2) and Chi-square (X^2) were calculated to determine the model that best fits the data.

Additionally, every plasticizer and its respective films mixed with chitosan were characterized using an FTIR spectrophotometer (Shimadzu IRPrestige-21, Japan).

3. Results and discussion

3.1 Influence of type and concentration of natural plasticizers

Table 2 depicts the peaks of the FTIR spectra of the different natural plasticizers, PVA and chitosan. In all the spectra, there is a very wide peak centered at approximately 3300 – 3330 cm^{-1}, which corresponds to the OH stretching mode. Samples of exudates of the *Capparis scabrida* tree (S) and gum of the *Cordea lutea* fruit (M) show peaks at 2922 and 2928 cm^{-1}, respectively, which correspond to C-H or CH_2 stretching. A similar peak is shown by PVA (P) and chitosan (Q). The three natural plasticizers present a peak between 1547 and 1597 cm^{-1}, which corresponds to –CO asymmetric stretching. Typical peaks at 1643 and 1587 cm^{-1} are visible for the chitosan sample, corresponding to C=O (amide I) stretching and N-H (primary amide) bending. As shown in table 2, natural plasticizers, PVA and chitosan depicted peaks that correspond to CH_2 bending, CH-OH, C-O stretching and C-O-C. According to different authors [11, 12], the peak in the range of 1500 to 500 cm^{-1} represents the carbohydrate fingerprint, confirming the nature of the natural plasticizers.

In the case of sample M, most of the peaks coincide with those in a previous work reported by Troncoso, Zamora and Torres [1] for the same sample.

Figure 1 shows the FTIR spectra of the film prepared with chitosan and of those prepared with a combination of chitosan and plasticizers. One of the most important parameters to be analyzed is the peak centered at 3260 cm^{-1} for the pure chitosan sample, which corresponds to OH stretching, shifted slightly in the case of the samples in which the plasticizers were added. Even the intensity of the peak reduced in the case of the films in which plasticizers were added. Another important parameter is the behavior of the peak at approximately 1543 cm^{-1}, which similarly corresponds to the N-H bending of the primary amide. When the chitosan film is combined with the plasticizers, the peak is shifted to a slightly higher wavenumber. According to a different author [13], these facts demonstrate the interaction between chitosan and plasticizers.

Table 2. Peaks (cm^{-1}) of FTIR spectra of the different natural plasticizers, PVA and chitosan used in the study.

Exudate of *Capparis scabrida* tree **(S)**	**Exudate of** *Prosopis pallida* tree **(A)**	**Gum of** *Cordia lutea* fruit **(M)**	**PVA (P)**	**Chitosan (Q)**	**Modes**
3306	3316	3357	3329	3335	OH stretching [11, 14, 15]
2922	2928		2940-2911	2882	CH_2 stretching [11, 14]
			1732, 1712		C-O stretching of COOH [16]
				1643	C=O stretching – amide I [17]
				1587	N-H bending – primary amide [17]
1597	1599	1547, 1501			-CO asymmetric stretching [14]
1412	1411	1388	1435, 1375, 1323, 1246	1426	CH_2 bending CH-OH
1018	1011	1033	1090, 1026	1058, 1153, 1020	C-O stretching [15] C-O-C [1]
660, 601	902, 837, 667, 603	828, 667	841, 950, 652, 598	897, 874, 660	C-H bonds [11]

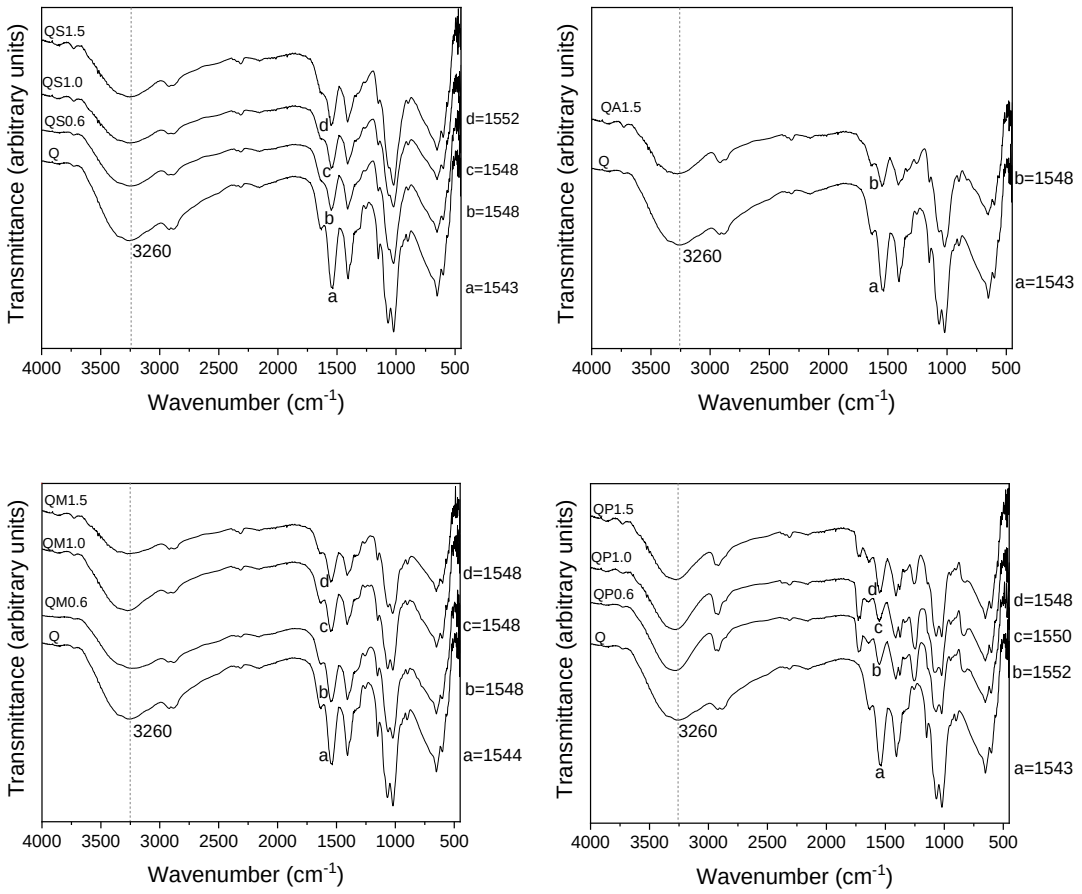


Figure 1. FTIR analyses of the films with different types and concentrations of natural plasticizers.

When the concentration of the films is higher, the thickness increases when the natural plasticizer concentration is increased (see figure 2a). Ayoubi Najafabadi, Askari, Mousavi and Emamdjomeh [18] explained this fact because when the amount of gum in a film formulation is increased, the resistance to rearrangement during casting and drying because of the increase in solid content is higher, favoring the formation of intermolecular spaces and loose structures. Thickness is variable according to the type of plasticizer. QS samples are thicker than the other natural films made of the other natural plasticizers (QA and QM) and even thicker than the films made of PVA.

Films prepared with 0.6% plasticizers exhibited the same level of water vapor permeability (WVP) (figure 2b). However, the behavior of this parameter is different according to the increase of the plasticizer content. When the concentration of plasticizer was increased to 1%, the WVP remained at the same level; however, when the concentration was increased to 1.5%, the WVP increased. In the case of the QA samples, the level of WVP remained constant independently of the plasticizer content. For the QM samples, when the concentration of plasticizer was increased to 1%, the WVP remained at the same level; however, when the concentration was increased to 1.5%, the WVP decreased. Finally, for the samples prepared with the commercial plasticizer (QP), WVP reduced at the same level when the plasticizer content was increased to 1 or 1.5%.

In general, solubility decreases when the concentration of plasticizer is increased in the films (figure 2c). The QS sample presents the highest levels of solubility for the different concentrations of plasticizers, even higher than samples with PVA (QP). This could be explained by the fact that the

addition of plasticizer reduced the molecular attraction because of the solvation of the polar group of the polymeric chains.

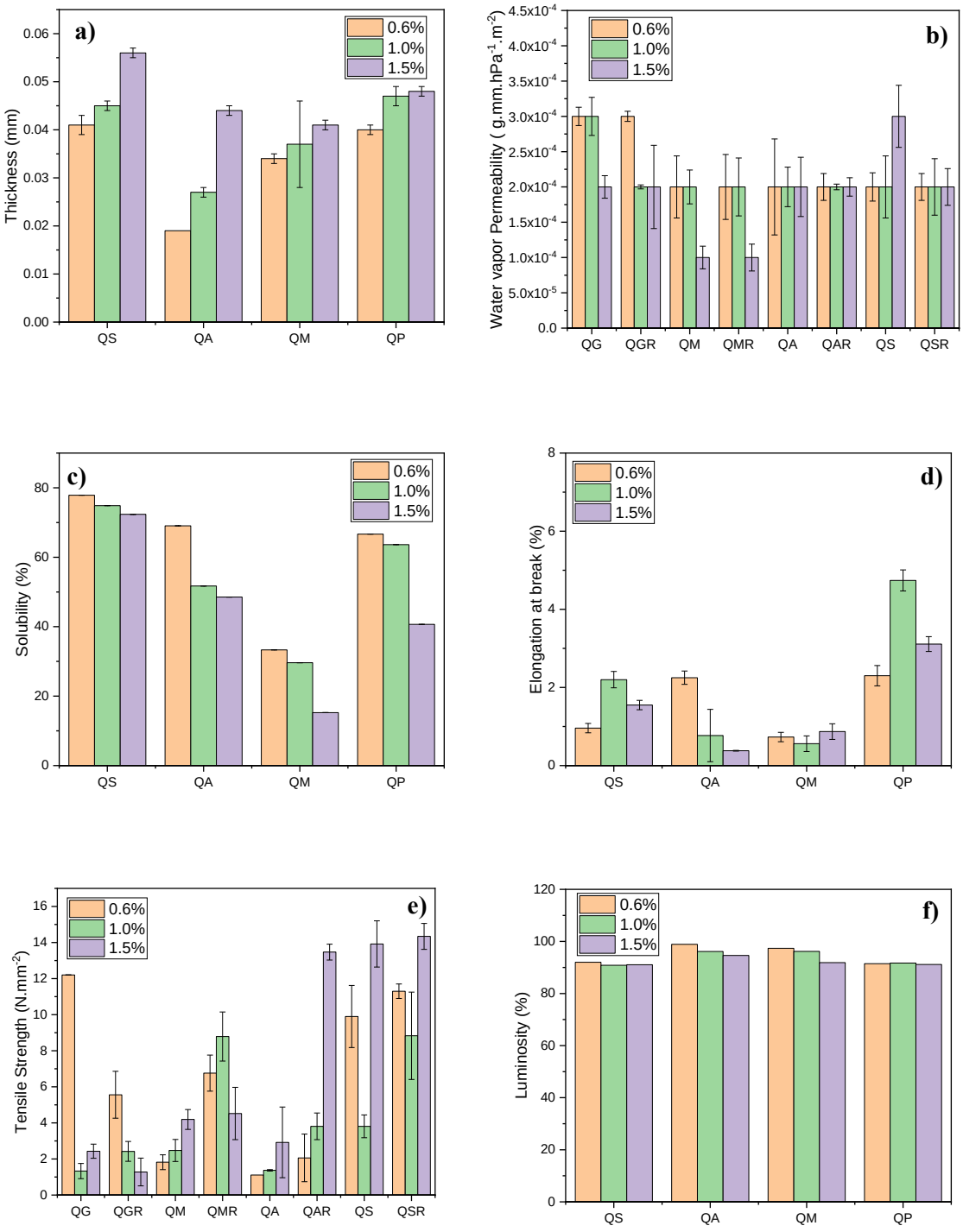


Figure 2. Properties (a) thickness, (b) water permeability, (c) solubility, (d) elongation at break, (e) tensile strength and (f) luminosity of prepared chitosan films with different types and concentrations of natural plasticizers and PVA.

In the case of mechanical properties, films with natural plasticizers in different concentrations showed lower levels of elongation at break (EB) and tensile strength (TS) (figures 2d and 2e respectively) than the films prepared with PVA. However, a comparison of the films with natural plasticizers reveals that the QS sample has higher levels of both mechanical properties than the rest of the films with natural plasticizers. The behavior of the mechanical properties is similar when the concentration of plasticizer is increased in the chitosan films for samples QS and QP; i.e., EB increases and then decreases when the plasticizer concentration is 1 and 1.5%, respectively, and TS decreases and then increases when the plasticizer concentration is 1 and 1.5%, respectively.

Luminosity reduces slightly when the concentrations of natural plasticizers P and M are increased (figure 2f). However, in the case of chitosan films made of S and PVA, luminosity was almost constant when the concentration of plasticizers was increased. It seems that plasticizers P and M in the compounds could be oxidized during the drying process of film preparation.

The biodegradability of chitosan films made of natural plasticizers (1%) was higher than that of films made of PVA (1%). Figure 3 depicts the remaining weight of the samples during the experimental time (15 days).

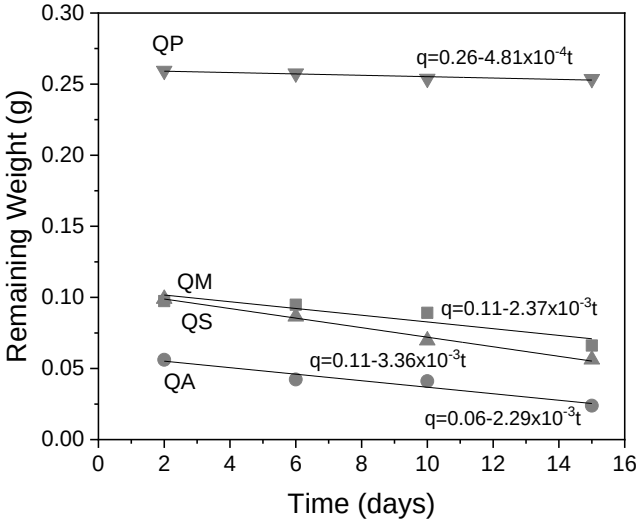


Figure 3. Biodegradability in anaerobic conditions of films prepared with natural plasticizers and PVA (1%).

The remaining weight data were fitted to zero-order and first-order models, fitting the best to the zero-order model in the case of films made of natural plasticizers (R^2=0.854 – 0.993 and X^2=3.89x10^{-6} – 4.43x10^{-5}) (table 3). Although the data for films with PVA as plasticizer fit best to the first-order model, the parameters R^2 and X^2 of the zero-order model are almost similar.

The value of k_0 for the QP sample is lower than that of the chitosan films made of natural plasticizers; therefore, the rate of biodegradation of the films made of natural plasticizers is higher than that of films made of PVA. Comparing the natural plasticizers shows that the QS sample has the highest biodegradation rate. The reduction in weight during the soil burial test was significantly higher for films made in this work compared with that for biodegradable plastics used as packaging materials found in the markets and tested by Gutierrez, Daupan, Fabian and Miclat [19].

Table 3. Parameters of the zero-order and first-order models fitted to the anaerobic biodegradation data of the films with natural plasticizers.

Model	Parameters	QS	QA	QM	QP
Zero-order	R^2	0.993	0.933	0.854	0.885
	X^2	$3.89x10^{-6}$	$1.75x10^{-5}$	$4.43x10^{-5}$	$1.39x10^{-6}$
	k_0	$3.36x10^{-3}$	$2.29x10^{-3}$	$2.24x10^{-3}$	$4.81x10^{-4}$
First-order	R^2	0.992	0.915	0.816	0.887
	X^2	$4.24x10^{-6}$	$2.21x10^{-5}$	$5.59x10^{-5}$	$1.38x10^{-6}$
	k_1	$4.37x10^{-2}$	$5.61x10^{-2}$	$2.63x10^{-2}$	$1.89x10^{-3}$

4. Conclusions

Three new natural plasticizers (exudates of the *Prosopis pallida* and *Capparis scabrida* trees and gum from the *Cordia lutea* fruit) and polyvinyl alcohol (PVA) in different concentrations were tested to determine their influence on the properties of chitosan films. Chitosan films with exudate of the *Capparis scabrida* tree as plasticizer had better properties than those with the other two natural plasticizers. However, the mechanical properties of the chitosan films prepared with PVA are still better than those with exudate of the *Capparis scabrida* tree. The films that included the three natural plasticizers in their composition were more biodegradable than those made of PVA, with films with exudate of the *Capparis scabrida* tree being the most biodegradable. The exudate of the *Capparis scabrida* tree is a potential biodegradable plasticizer for use in medical or food applications.

Acknowledgments

The National Program of Innovation for Competitiveness and Productivity (INNOVATE-Peru) Project PIAP-2-P-490-14 is acknowledged for financial support. MMG and JLS thank Vice-President for Research of the National University of Engineering (VRI-UNI) for the researcher grants.

References

[1] Troncoso O P, Zamora B and Torres F G 2018 Thermal and Rheological Properties of the Mucilage from the Fruit of Cordia lutea *Polymers from Renewable Resources* **8** 79-90
[2] Mirhosseini H and Amid B T 2012 A review study on chemical composition and molecular structure of newly plant gum exudates and seed gums *Food Research International* **46** 387 98
[3] Basu S, Prasad M N V, Suthari S and Kiran B R 2017 Prosopis juliflora (mesquite) gum exudate as a potential excipient *The EuroBiotech Journal* **1** 76-81
[4] Hasnain M S, Rishishwar P, Rishishwar S, Ali S and Nayak A K 2018 Extraction and characterization of cashew tree (Anacardium occidentale) gum; use in aceclofenac dental pastes *Int J Biol Macromol* **116** 1074-81
[5] Mohd Azam N A N and Amin K A M 2017 The Physical and Mechanical Properties of Gellan Gum Films Incorporated Manuka Honey as Wound Dressing Materials *IOP Conference Series: Materials Science and Engineering* **209** 012027
[6] Singh B, Sharma S and Dhiman A 2017 Acacia gum polysaccharide based hydrogel wound dressings: Synthesis, characterization, drug delivery and biomedical properties *Carbohydrate Polymers* **165** 294-303
[7] Saha A, Tyagi S, Gupta R K and Tyagi Y K 2017 Natural gums of plant origin as edible coatings for food industry applications *Crit Rev Biotechnol* **37** 959-73
[8] Avachat A M, Dash R R and Shrotriya S N 2011 Recent investigations of plant based natural gums, mucilages and resins in novel drug delivery systems *Ind J Pharm Edu Res* **45** 86-99
[9] Damas M S P, Pereira Junior V A, Nishihora R K and Quadri M G N 2017 Edible films from mucilage of Cereus hildmannianus fruits: Development and characterization *Journal of Applied Polymer Science* **134** 45223

[10] Reddy M B, Belkacemi K, Corcuff R, Castaigne F and Arul J 2000 Effect of pre-harvest chitosan sprays on post-harvest infection by Botrytis cinerea and quality of strawberry fruit *Postharvest Biology and Technology* **20** 39-51
[11] Dabestani M, Kadkhodaee R, Phillips G O and Abbasi S 2018 Persian gum: A comprehensive review on its physicochemical and functional properties *Food Hydrocolloids* **78** 92-9
[12] Hashemi Gahruie H, Ziaee E, Eskandari M H and Hosseini S M H 2017 Characterization of basil seed gum-based edible films incorporated with Zataria multiflora essential oil nanoemulsion *Carbohydrate Polymers* **166** 93-103
[13] Ren L, Yan X, Zhou J, Tong J and Su X 2017 Influence of chitosan concentration on mechanical and barrier properties of corn starch/chitosan films *Int J Biol Macromol* **105** 1636-43
[14] Ali A, Ganie S A and Mazumdar N 2018 A new study of iodine complexes of oxidized gum arabic: An interaction between iodine monochloride and aldehyde groups *Carbohydr Polym* **180** 337-47
[15] Anicuta S-G, Dobre L, Stroescu M and Jipa I 2010 Fourier transform infrared (FTIR) spectroscopy for characterization of antimicrobial films containing chitosan *Analele Universită Ńii din Oradea Fascicula: Ecotoxicologie, Zootehnie şi Tehnologii de Industrie Alimentară* **2010** 1234-40
[16] Saruchi, Kumar V, Rehani V and Kalra G S 2018 Synthesis and characterization of Gum tragacanth, acrylic acid–methacrylic acid based interpenetrating polymer network: its application for controlled release of agrochemicals *Journal of the Chinese Advanced Materials Society* **6** 222-33
[17] Fernandes Queiroz M, Melo K R, Sabry D A, Sassaki G L and Rocha H A 2014 Does the use of chitosan contribute to oxalate kidney stone formation? *Mar Drugs* **13** 141-58
[18] Ayoubi Najafabadi A, Askari G, Mousavi M and Emamdjomeh Z 2016 Novel Biodegradable Cast Film from Cherry Tree Gum, Development, Modification and Characterization *Journal of Polymers and the Environment* **25** 241-9
[19] Gutierrez R M, Daupan S, Fabian A V and Miclat C C 2015 Microbiological Investigation on Some Biodegradable Plastics used as Packaging Materials *Asian Journal of Applied Sciences* **3** 75-81