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Research Article

Influence of pH in Mechanical Properties of Conductive Polymers Synthesized from Cassava Starch

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Abstract: This study presents experimental investigation on synthesis of conducting polymer films made from cassava starch with the purpose of evaluating the influence of pH on some mechanical and physicochemical properties. Starch increases the mechanical integrity in biodegradable conductor polymers used like sensors, but there are some others potential factors influencing mechanical properties like plasticizers, additives and process conditions. No previous works report the quantitative effect of pH on mechanical properties of cassava starch's film. Glycerol, glutaraldehyde and polyethylenglycol were used as plasticizers. To obtain acid and basic films, pH was modified by HCl and NaOH. Seven different pH levels were reached, in order to evaluate tensile strength, ductility and elastic module. Tensile tests were developed according to the ASTM D638 norm. Clear influence of pH in these mechanical properties was found; which is shown through a regression that relates ductility with a pH input. This research concludes that is possible to modify the mechanical strength or flexibility of the films by changing pH, which is in general terms a practical process. Acid films have a higher elastic module (50-70 MPa) than polymers with basic pH (15-25 MPa). Basic films' deformation shows higher values than acid films; the first ones reach 0.95 mm/mm of deformation and the second ones have average values of 0.3 mm/mm.

Keywords: Cassava starch, ductility, elastic module, pH, tensile strength

INTRODUCTION

Although the petrochemical sources have greatly favored the technological and industrial development of modern society, their use implies strong environmental impact. In this sense, researching efforts during the last decades have been aimed to the improvement of the so-called clean energies (Singh and Gu, 2010; Tsai *et al.*, 2016). One of the challenges of materials engineering is to develop new materials that answer to the requirements of functionality of the market, mitigating the environmental impact associated with the life cycle. The recent development of so-called biodegradable polymers obtained primarily from renewable resources is intended to mitigate the negative mark on the environment caused by not recyclable polymers (Pircher *et al.*, 2014; Arrieta *et al.*, 2011; De Aquino *et al.*, 2015). Favorable results have been obtained in mechanical and electrical properties of biopolymers used as conductors and semiconductors materials (Arrieta *et al.*, 2010; Deep *et al.*, 2012; Venugopal *et al.*, 2014).

This study reports the development and physicochemical evaluation of biofilms made of cassava starch, which is a natural and biodegradable polymer, it is a material easy to get and inexpensive. Some concentrations reported for the synthesis of films (Arrieta and Jaramillo, 2014; Almario *et al.*, 2015) were used to guarantee the conductivities achieved with this type of biopolymers. Plasticizers used in the synthesis were glutaraldehyde, glycerol and polyethylene glycol in addition to the lithium trifluroide salt methanesulfonate. The purpose of this research is to establish the influence of different pH, acid and basic, in some physicochemical properties of films made from cassava starch.

MATERIALS AND METHODS

Previous work (Arrieta and Jaramillo, 2014; Almario *et al.*, 2015) guarantee the polymerization of cassava starch with plasticizers like glycerol, glutaraldehyde, polyethylenglycol and a salt of Lithium

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Fig. 1: Tension test specimen of biopolymers films of cassava starch

trifluoro-methanesulfonate. The starch was obtained of cassava from Córdoba, a Caribbean department of Colombia. The first step is to peel cassava, to get the starch of the interior of the root and not from bark. After that, cassava is cut into small pieces; the smaller the better the final performance. Water is applied to the particles of cassava to extract the starch. After vacuum filtration, the starch is macerated to get a small particles size; in this research starch was filtered on a sieve allowing passage of particles of 300 μm of diameter.

All the additives were acquired in Sigma-Aldrich. pH was adjusted in a volume of ultra pure water of mili-Q milipore quality. Seven pH levels were used during the experimentation: three acid levels, three basic levels and another one close to neutral value; HCl 0,1 M and NaOH 0,1 M were used to get different pH levels. The purpose of changing pH is to evaluate its influence on mechanical properties because in previous tests, significant differences in the physical integrity of the material were observed when the pH was modified. Cassava starch was dissolved in water with additions of GLY, GLU, PEG and TL at constant stirring speed while temperature was 25°C. All solutions were heated at a controlled temperature of 75±1.0°C for 15 min; then they were poured into a flat tray and finally they were dried in an oven for 48 h at 70°C. Figure 1 shows the biopolymers films.

Through a tension test is evaluated the material response to external forces in function of resistance and deformation and the relation between these two properties. Because of the geometric characteristics of the film, the appropriated norm to make the test is the ASTM D638. The thickness of the films doesn't exceed 14 mm (Quiroga and Díaz, 2011) whereby the dimensions of test specimen suggested by the norm were used. Figure 1 shows the molds made for the tests.

Tension test was made in an universal mechanical testing machine Instron, model 5582 at 27.5°C with a relative humidity of 53.2%. Test specimen were put in pneumatic grips, with a previous electronic autocalibration of the load cell of 50 N. This load cell was calibrated by a national certification institute. The universal machine was parameterized considering the race frame; tests were conducted at a constant speed of 5 mm/min. An increasing load to failure the specimen by breakage was applied for each pH conditions.

RESULTS AND DISCUSSION

Mechanical properties: Polymerization process used in this research let the gelatinization of all films made. Particles size of starch of 300 μm of diameter let a homogeneous mixture. Additives were added one by one and not at the same time to ensure a better mix. Stirring rate was maintained constant in the process in order to avoid the precipitation of any of the components. Films had a uniform thickness, measured with a digital Vernier Mitutoyo model CD-6A CSX-B; there weren't air bubbles or lumps in the films which is important to guarantee the reliability of the mechanical properties measured. The lowest pH level tested was 3, because at lower values the polymerization did not occur, resulting in a thin layer of a very dark color.

For the mechanical characterization of the films three replicates were performed for each pH evaluated. Yield resistance, tensile strength and deformation values were obtained from the test; the average values are shown in Table 1.

According to the results in Table 1, Yield of the films decreases when the pH increases. There is a notable difference between extreme values of the pH; the films with the most acid pH have values of approximately 150 kPa of Yield and the most basic films have values of 100 kPa. Results show that variations in pH do not affect significantly the samples' tensile strength; the average value is 192.55 kPa. In order to quantify the rigidity of the films, the modulus of elasticity is calculated through the relation: $E = \text{yield} * \text{strain}^{-1}$. After a variance analysis a p-value smaller than 0,05 was found, which leads to the conclusion that there is a statistically significant difference between the mean of the modulus of elasticity between one pH level and another with 5% significance level.

In this sense it is possible to find a regression that allows to know the modulus of elasticity as a function of pH as shown in Eq. (1). pH acids generate more rigid films than basic pH. Ductility of the films is directly related to the pH; the strain represents the lenght that the material can deform for each unit of length before the fracture. Films made at acid pH can be deformed less than those whose pH is basic; in the acid pH range, deformation does not show a significant change since it oscillates approximately between 0,2 and 0,3 mm/mm, whereas for basic pH the change is more noticeable, ranging from 0,28 to 0,95 mm/mm. The results also show that the ductility of films increases with the increase of the pH in the basic range.

$$y = -2.1045x2+26.049x-7.775 \tag{1}$$

In Fig. 2, the rigidity of the synthesized biofilms changes with the pH. The flexible behavior is attributed to the addition of plasticizer (glycerol), because it reduces the hydrogen bonds between the starch glucose

Table 1: Mechanical results of the tensile test

pH	Yield resistance (kPa)	Strain (mm/mm)	Tensile strength (kPa)
3	149	0.277	157
4	211,2	0.303	225,4
5	138	0.286	206
8	186	0.186	228
10	58,75	0.508	105
11	123,75	0.534	205,75
12	109,25	0.952	220,75

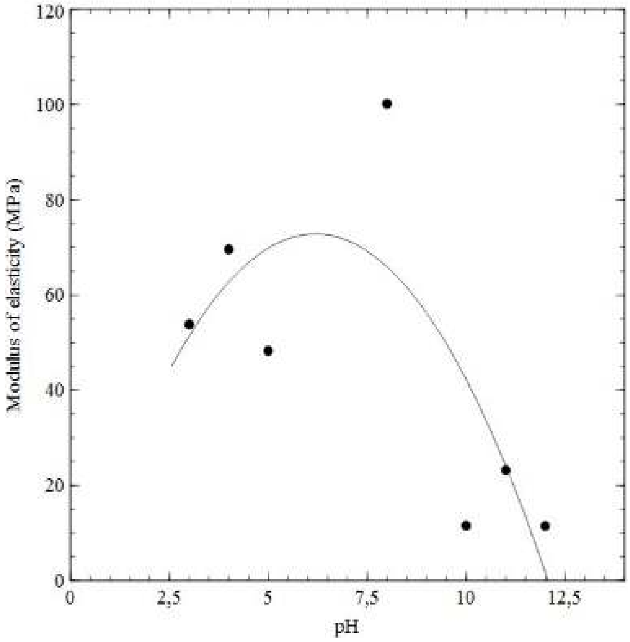

Fig. 2: Modulus of elasticity to different pH

chains and it increases the space between the molecules; the more rigid behavior presented at low pH could be attributed to the fact that in acidic environments, reaction mechanisms directed to the formation of organic salts could be generated by the interaction of hydrochloric acid with glycerol and in this way the flexibility of the material is reduced.

In a previous work (Arrieta and Jaramillo, 2014) films were made at pH of 9 with good physical homogeneity and flexibility. These results are support in this research, Table 1 shows a ductility value of 50% for a pH close to 9 (10) and values greater than 50% for all the basic pH; so it is showed in this study that a good homogeneity and flexibility can be achieved in all the basic range.

ATR-IR analysis of cassava starch films: Study of FTIR spectra of starches biofilms in four main regions is useful for the successive interpretation and characterization of key bands. These regions were as follows: Below 800 cm^{-1}, 800-1500 cm^{-1} (the fingerprint region), the region between 2800 and 3000 cm^{-1} (C-H stretch region) and finally the region between 3000 and 3600 cm^{-1} (O-H stretch region). Infrared spectra of starches biofilms exhibited complex vibrational modes at low wave numbers (below 800 cm^{-1}) due to the skeletal mode vibrations of the glucose pyranose ring.

The vibrations originated from C-O-C of R-1,4 glycosidic linkages were observed as the infrared absorption band at 930 cm^{-1}; this behavior is attributed to the glycosidic linkages in starches.

Adsorbed Water, in the amorphous region of starches, could be identified as a broad infrared band with a peak at 1651, 07 cm^{-1} (Table 2).

As the crystallinity of starch polymer increases, this band becomes weaker in the infrared spectra and for the most crystalline amylose, the band at 1651, 07 cm^{-1} was barely observed. This finding supports the hypothesis that the 1651, 07 cm^{-1} band is a result of the vibrations of water molecules adsorbed in the non-crystalline region of starch polymer. The band observed at 1651,07 cm^{-1} (Fig. 3) was attributed to the adsorbed water in the amorphous region of biofilm. As this band is related to the crystallinity of starch polymer, variations in the crystallinity of different biofilms have the potential to affect this band. It was observed in this study that biofilms in different conditions of pH offered sharper bands around 1651, 07 cm^{-1} than those other biofilms, because of the similarities in the amorphous

Table 2: Peak table of spectrum IR of starch biofilms

No.	Peak	Comment
1	640,37	skeletal modes of pyranose ring
2	763,81	C-C stretching
3	810,1	C(1)-H, CH2 deformation
4	941,26	skeletal mode vibrations of α−1,4 glycosidic linkage, (C-O-C)
5	1026,13	C(1)-H bending
6	1149,57	C-O, C-C stretching
7	1249,87	CH2OH (side chain) related mode
8	1411,89	C-O-H bending, CH2 twisting
9	1458,18	CH2 bending, C-O-O stretch
10	1651,07	water adsorbed in the amorphous regions of starch
11	2931,8	CH2 deformation
12	3410,15	O-H stretching

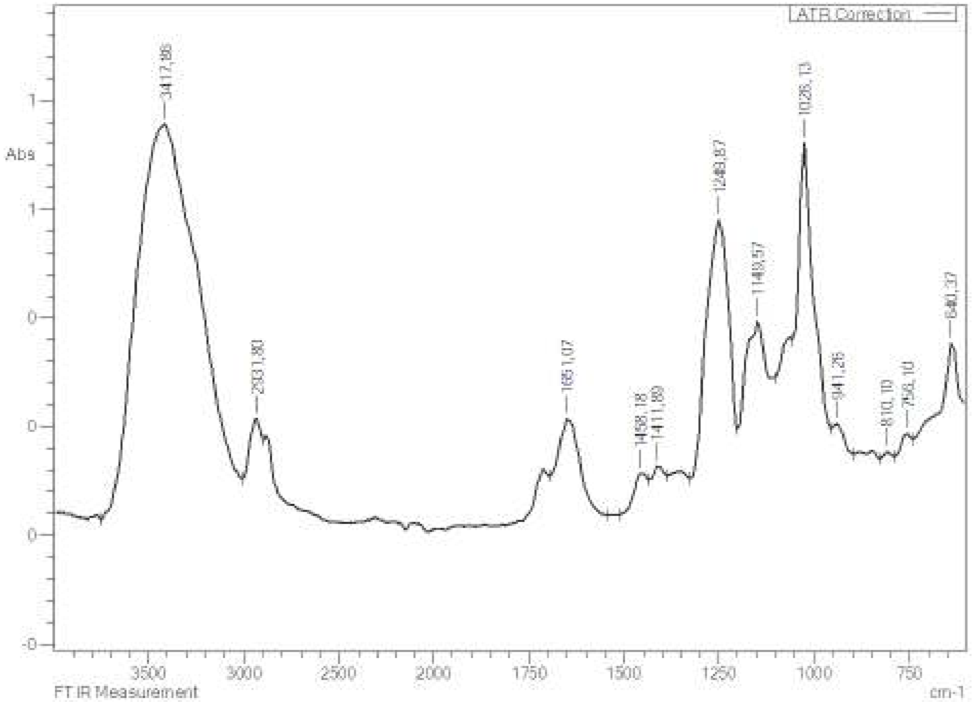

Fig. 3: ATR-IR spectroscopy of cassava starch film to pH 3

structure of the material. Characterization of C-H and O-H stretch could be readily accomplished by spectral analysis. FTIR spectra of biofilms showed C-H stretching modes in the 2800-3000 cm^{-1} region. Intensity changes, in this range, could be attributed to the variations of pH conditions, perhaps through the influence of plasticizers additives in the opened and accommodated polymeric chain. The O-H stretching mode of starches observed was in the region of 3000-3600 cm^{-1} in the FTIR spectra.

EIE analysis of cassava starch films: Bode diagram (Fig. 4) shows the different graphics of pH 3, 4, 11 and 12, excluding other pH because they exhibit similar comportment to the observed images, so that the curves tend to overlap. Bode diagram represents frequencies in Hertz on the abscissa and the magnitude of the impedance in ohms on the ordinate; it is important to highlight the values of resistance to acidic pH which were more stable and constant to be represented in the same order of magnitude from 1 to 1×101 ohms, whereas, in the responses of resistance to basic pH present less stability as they can do to be appreciated by one order of larger magnitude, 1 to 1×102 ohms.

Moreover, when performing analysis EIE to films prepared at different pHs, there were observed higher values of conductivity and resistance where those in which the pH was acid or moderately basic, which vary in the range of 1.76×10-1 Scm-1 to 2.74×10-1 Scm^{-1} and 17.14 to 26.14 ohms respectively (Table 3).

Through the calculation conductivity was found that synthesized biopolymers from cassava starch have high values of electrical conductivity, therefore, cassava starch can be classified as conductive material. The calculations were performed on the model of equation, where conductivity is in function of the thickness of the biofilm, resistance and area (Table 3).

Table 3: Resistance and conductivity values of the biofilms to different pH

pH	Resistance (ohms)	Conductivity (S*cm-1)	Conductivity/resistance
3	17,14	2,40E-01	1,40E-02
4	23,54	2,35E-01	9,98E-03
5	20,71	1,76E-01	8,50E-03
8	26,14	2,74E-01	1,05E-02
10	6,723	7,40E-02	1,10E-02
11	7,924	6,74E-02	8,51E-03
12	4,801	3,84E-02	8,00E-03

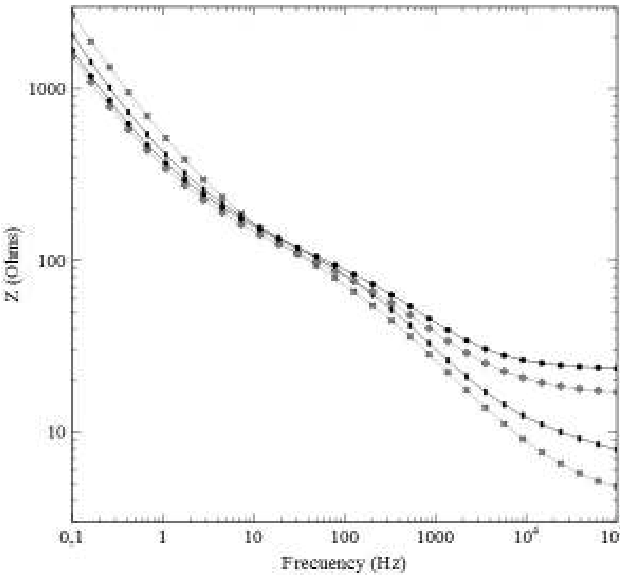

Fig. 4: Bode plot for different levels of pH; ♦ = pH3, ● = pH4, ■ = pH 11, x = pH 12

One of the characteristics of electric conductive materials is that they have a good relationship of conductivity-resistance, hence one of the sought objectives is that the material possesses the highest possiblility to conduct and the lowest resistance to be obtained; in that sense, the values that gave the ratios on the relationship, were in the range of 8×10-3 to 1.4×10-2. At acid pH, resistance values represented in the range of 17.14 to 23.54 ohms and the conductivity values of 1.76×10-1 to 2.40×10-1 S * cm^{-1} (Table 3).

At basic pH, resistance values were represented in the range of 4.801 to 26,14 ohms and the conductivity values represented 3.84×10-2 to 2.74×10-1 S* cm-1 (Table 3).

Two ranges of conductivity-resistance were also seen, which had good relations between the ratios relationship. The first ranged from 9.98×10-3 to 1.4×10-2 in acidic pH and the second in the range of 1.1×10-2 to 1.05×10-2 in basic pH, thus it can be said that a change in the conditions of synthesis of the material, oriented acidic or basic environments, can improve the electrical properties of the biopolymer.

In the Fig. 5 Resistance Vs Conductivity, it is shown a lineal comportment with R2= 0.8965, where it can be seen an increment ascent with positive slope of conductivity in regard to Resistance.

It is worth to mention that the aim, in this case, is that the conductivity values were high and the resistance values were low. The higher conductivity and lower resistance value were 2.74E-01 S*cm-1 and 4.801 ohms respectively. As the Resistance range as conductivity range were (4.801 to 26.14) ohms and (3.84E-02 to 2.74E-01) S*cm^{-1} respectively.

CONCLUSION

It was demonstrated, based in statistical proofs, that pH of the biopolymers made of cassava has a significant effect in the mechanical strength and deformation of the films. For acid pH between 3 and 5, the modulus of elasticity oscillate between 50 and 70 MPa, whereas that basic pH between 10 and 12 the modulus oscillate between 15 and 25 MPa which represents half of those reported in acid pH. The ductility of the films is smaller in acid pH than basic pH.

The best values of electric conductivity and lowest values of electric resistance were found in acid conditions. Through the electroquimic study of the biofilms in different pH, was demonstrated that is possible improve electric properties by changing pH conditions; in acid environments the best results were in pH 3 to 4, while in basic conditions the best values were in pH 8 to 10.

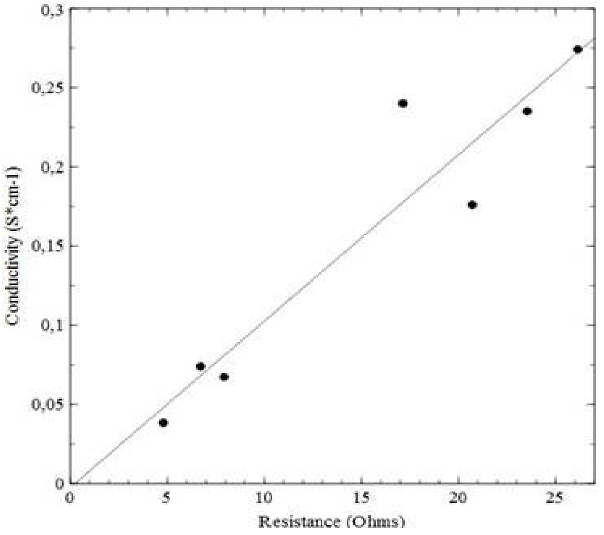

Fig. 5: Resistance vs conductivity in biofilms of cassava

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REFERENCES

Almario, Á.A., A.J. Muñoz and M.P. Luna, 2015. Películas conductoras de almidón de yuca (cassava) como material para un acumulador electroquímico de carga (batería). Rev. Soc. Quím. Perú, 81(4): 328-338.

Arrieta, A. and A. Jaramillo, 2014. Bioplásticos eléctricamente conductores de almidón de yuca. Rev. Colomb. Mater., 5: 42-49.

Arrieta, Á.A., M.L. Rodríguez-Méndez and J.A. De Saja, 2010. Aplicación de una lengua electrónica voltamétrica para la clasificación de vinos y estudio de correlación con la caracterización química y sensorial. Quim. Nova, 33(4): 787-793.

Arrieta, A.A., P.F. Gañan, S.E. Márquez and R. Zuluaga, 2011. Electrically conductive bioplastics from cassava starch. J. Braz. Chem. Soc., 22(6): 1170-1176.

De Aquino, A.B., A.F. Blank and L.C.L.D.A. Santana, 2015. Impact of edible chitosan–cassava starch coatings enriched with Lippia gracilis Schauer genotype mixtures on the shelf life of guavas (*Psidium guajava* L.) during storage at room temperature. Food Chem., 171: 108-116.

Deep, A., A.L. Sharma, P. Kumar and L.M. Bharadwaj, 2012. Nanostructured polyaniline-silicon substrate for protein biosensing. Sensor. Actuat. B-Chem., 171-172: 210-215.

Pircher, N., S. Veigel, N. Aigner, J.M. Nedelec, T. Rosenau and F. Liebner, 2014. Reinforcement of bacterial cellulose aerogels with biocompatible polymers. Carbohyd. Polym., 111: 505-513.

Quiroga, R.M. and W.V. Díaz, 2011. Metodología para la caracterización termo-mecánica de películas plásticas biodegradables. Prospect, 9(1): 46-51.

Singh, J. and S. Gu, 2010. Commercialization potential of microalgae for biofuels production. Renew. Sust. Energ. Rev., 14(9): 2596-2610.

Tsai, B.H., C.J. Chang and C.H. Chang, 2016. Elucidating the consumption and co2 emissions of fossil fuels and low-carbon energy in the united states using lotka–volterra models. Energy, 100: 416-424.

Venugopal, V., H. Zhang, R. Northcutt and V.B. Sundaresan, 2014. A thermodynamic chemomechanical constitutive model for conducting polymers. Sensor. Actuat. B-Chem., 201: 293-299.