Study of factors affecting hardness behavior of biopolymers based on potato and plantain peels: a factorial experimental evaluation

H F Castro1, H I Farfán1, I V Abril1, R A Paredes1, and K L Roa1,2
1 Universidad Pedagógica y Tecnológica de Colombia, Sogamoso, Colombia
2 Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada CICATA-IPN, Ciudad de México, México

E-mail: hariana.farfan@uptc.edu.co

Abstract. The environmental impact caused by generation of plastic wastes at a global level is significant, during the last year, production of plastic increased by 40% due to the Covid-19 pandemic, demanding in an accelerated way the massive use of disposable personal protection elements. This situation has changed drastically the pattern of human behavior, introducing a lifestyle with greater hygiene that makes necessary to use plastic packaging to cover products, utensils, and food, avoiding any risk of transmission. To combat the massive use of plastic it is necessary to activate the transition towards circular economies that make use of environmentally friendly plastics; this is the case of biopolymers, materials that can be synthesized from organic waste rich in starch. Therefore, in this work, the factors that affect the hardness of polymers made from potato and plantain peels are studied through a factorial experimental design. The design establishes the combination of urea, glycerine, acetic acid, and water, to identify the best combination of plasticizer and their effect on the hardness of the material. Using Minitab, the multivariate linear models of hardness behavior were assessed to achieve the highest hardness values.

1. Introduction
Relating the current situation of the planet to the sustainable development goals, it was identified that the problems that could be mitigated through the deployment of this project with respect to counteracting climate change, water sanitation, sustainable agriculture and production, sustainable cities, and human settlements, as well as protecting and reversing land degradation. One of the main causes of these environmental issues is pollution from the massive use of single-use plastics [1,2].

Plastics have become indispensable in human daily activities [3-5], especially during the current COVID-19 pandemic, which increased its production by 40%, and thus increased the generation of medical waste (mainly plastic) by 340% from 40 tons to 240 tons per day [6]. This situation caused a negative environmental impact considering its degradation time, remaining up to 100 or more years in the earth, depending on the environmental conditions in which the plastic material is found [7,8]. This situation is intensified if they are improperly disposed of, incinerated and/or accumulated, releasing substances such as phosgene and dioxides both in the open field and in the sea [9,10]. These residues decompose into nano and micro plastics at a scale of 0.1 mm and 5 mm respectively [11,12], these have been found lately in considerable proportions in the ocean [13,14], in fresh water, in the terrestrial...
environment [15,16] and organisms [17,18] being catalogued as the second most important scientific problem in the field of environment and ecology [19].

The above, encourages scientific research in the development of new substitute materials for single-use plastics, among the sustainable alternatives to the use of hydrocarbon-based polymers, are biopolymers. These materials are made from organic materials such as starch, the second most important agricultural source polysaccharide [20], which is present as an energy reserve in various proportions in roots, tubers, aquatic plants, and fruits [21]. The use of starches represents lower costs in the manufacture of biopolymers due to their abundant presence in nature [22]. Some abundant sources of starch are found in by-products and wastes from the food industry and agroindustry; commonly, the massive disposal of these wastes generates significant logistic costs [23]. Taking advantage of them will give them an added value and will prevent them from ending up in the environment, contaminating water sources, soils, among others [24]. Therefore, the present work seeks to identify, by means of a factorial experimental design, the appropriate proportion of starch to achieve the maximum hardness in biopolymers as materials that can potentially replace the extensive use of plastic.

2. Materials and methods

2.1. Starch extraction

The process is based on previously reported wet starch extraction [25,26]. First, organic wastes are collected from local restaurants in the Municipio de Sogamoso, Colombia. The process is shown in Figure 1, where the raw materials are washed, disinfected with a hypochlorite solution, then crushed, hydrated, and flocculated to release the starch particles from the dry fiber. Subsequently, they are filtered to obtain the starch by sedimentation. Finally, the humidity of the resulting starches is eliminated in an electric oven at 40 °C for 24 h for their respective milling.

![Figure 1. Starch extraction from potato and plantain peels for biopolymer synthesis.](image-url)

2.2. Polymerization

The polymerization method is detailed in Figure 2 and is based on previously reported studies [27,28], modifications were made to the temperatures, selection of plasticizers and order of incorporation of the components to the biopolymer according to the results of previously performed tests, this due to reactions that may occur between the mixtures of starches, plasticizers, and acetic acid, thus, optimizing the polymerization process in a shorter time. First, at room temperature the urea pellets are dissolved in water together with the milled starches, and then the temperature of the mixture is increased to 40°C. This is because the polysaccharide gelatinizes with increasing temperature and in the presence of water. Next, the mixture is close to gelatinization maturation, in this step glycerine is added to provide elasticity. Once a temperature of 60 °C is reached, acetic acid is added to facilitate the release of amylose during the final phase of gelatinization.
2.3. Model description
Experiments were developed to analyze the performance of processes and systems, considering the inputs, outputs, controllable and non-controllable factors according to the general model presented in Figure 3, thus, with the result to be able to implement improvements, standardize and favor its quality in terms of hardness [29].

The criteria established for the test tubes are presented below, considering previously reported studies [30,31].

- pH reading between 4 and 8: this pH range generates an optimal environment for gelatinization, establishing a slightly acidic medium that facilitates the breakdown of the starch granules, so that they swell in a stable manner and a homogeneous paste is achieved. Likewise, a low pH prevents the proliferation of microorganisms.
- Each specimen is considered by means of organoleptic tests as suitable or unsuitable to fail the hardness test.

2.3.1. Experimental design structure. Table 1 specifies the experimental design factors and their levels selected for the multivariate linear models. The hypotheses stated in the experimental design are described as $H_0$: the components cause significant difference in hardness and $H_a$: the components do not cause significant difference in hardness. From where, if $H_0$: $p < 0.05$, the null hypothesis is accepted, otherwise, if $H_a$: $p > 0.05$, the null hypothesis is rejected.
Table 1. Experiment design matrix.

| Level/Factor | Glycerin (g) | Urea (g) | Acetic acid (g) |
|--------------|-------------|----------|-----------------|
| 1            | 2.50        | 1.25     | 1.25            |
| 2            | 3.00        | 1.50     | 5.25            |

2.4. Description of the hardness test

The method described in ASTM D2240 [32] is used based on the penetration of a specific type of indentation, depending on the strength in the biopolymer under specific conditions. The indentation hardness presented in Figure 4, is inversely related to the penetration, and depends on the elastic modulus and viscoelastic behavior of the material [32]. This property is measured with the digital hardness tester reference 511A PTC Shore A Scale e2000, the Shore scale is used because it is the most used to measure hardness in soft and semi-hard materials such as rubbers, elastomers, and plastics.

![Model of the indenter used in the hardness test according to ASTM D2240, 2015 [32].](image)

3. Results and discussion

The hardness test of the synthesized biopolymer presented gelatinization points close to the theoretical ones between 65 °C and 77 °C [33,34]. Considering the temperatures recorded in the other phases, the highest hardness values were obtained in this phase; this result is directly proportional to the use of a native starch and the degree of association of the molecules inside the starch granule [35] affecting the resistance they present when breaking.

Based on the model proposed and considering the number of iterations between levels of the factors of the amount in grams of glycerin, urea and acetic acid, the design was entered into the Minitab program, yielding the results presented in Table 2.

| Source                  | DF | Adj SS   | Adj MS  | F-Value | P-Value |
|-------------------------|----|----------|---------|---------|---------|
| Model                   | 7  | 3104.04  | 443.43  | 67.69   | 0.000   |
| Linear                  | 3  | 1357.16  | 452.39  | 69.05   | 0.000   |
| Glycerin (g)            | 1  | 214.80   | 214.80  | 32.79   | 0.000   |
| Urea (g)                | 1  | 5.23     | 5.23    | 0.80    | 0.385   |
| Acetic acid (g)         | 1  | 1.137.13 | 1137.13 | 173.57  | 0.000   |
| 2-Way interactions      | 3  | 1.716.51 | 572.17  | 87.34   | 0.000   |
| Glycerin (g)*Urea (g)   | 1  | 1.636.80 | 1636.80 | 249.85  | 0.000   |
| Glycerin (g)*Acetic acid (g) |       | 43.20    | 43.20   | 6.59    | 0.021   |
| Urea (g)*Acetic acid (g) | 1  | 36.51    | 36.51   | 5.57    | 0.031   |
| 3-Way interactions      | 1  | 30.37    | 30.37   | 4.64    | 0.047   |
| Glycerin (g)*Urea (g)*Acetic acid (g) | | 30.37    | 30.37   | 4.64    | 0.047   |
| Error                   | 16 | 104.82   | 6.55    |         |         |
| Total                   | 23 | 3208.86  |         |         |         |
When observing the significance of the linear terms in the analysis of variance, it can be inferred that glycerin and acetic acid influence the hardness value, since their p-values are less than the 0.05 significance level. On the other hand, the p-value of urea represents a null effect on the hardness, which can be attributed, on the one hand, to the fact that glycerin provides visco-elasticity to the material, affecting its elastic modulus, and on the other hand, to the fact that acetic acid, once it finishes breaking the starch granules in the final stage of polymerization, facilitates the obtaining of a homogeneous and more fluid biopolymer.

The second order iterations are significant, however, the iteration between plasticizers urea and glycerin, presented a greater effect than the biopolymers synthesized with acetic acid. In the third order interactions, it is observed that the three factors interact with each other, therefore, they influence the hardness value, and the p-value is less than 0.05 indicating that there is statistical significance. The R-squared of 96.73% indicated that the model fits the data, considering that it is a value close to 100% which indicates a good correlation. The adjusted R-squared showed that the variables urea, glycerin, and acetic acid independently have an impact on the correlation (see Table 3). Finally, the hypothesis test accepts the null hypothesis considering that the p-value of the iteration between the three components was less than the significance value 0.05.

| Table 3. Model summary. |
|-------------------------|
| S          | R-sq      | R-sq (adj) | R-sq (pred) |
| 2.55954    | 96.73%    | 95.30%     | 92.65%      |

In the residuals plot presented in Figure 5 it is possible to verify that the assumptions of normality and independence are met, likewise there are no extreme or atypical data because the standardized residuals are ±2. In this sense, it means that they are within 2 standard deviations of the mean. The main effects graph is shown in Figure 6, where can be observed that the factors glycerin and urea had a positive effect on the hardness values; on the other hand, acetic acid has a negative effect defined by the sign that accompanies the coefficients of the regression equation.

Levels 1 influence to obtain a higher hardness in glycerin and urea, however, it can be corroborated that urea does not have a significant effect. At the same time, it can be observed that acetic acid has a greater effect on the hardness of the biopolymers because the levels reflect extreme values with respect to it. The graph of interactions presented in Figure 7 shows that only significant interaction occurs between urea and glycerin because they cross each other, where level 1, in both plasticizers, causes greater hardness with respect to the amounts of level two, relating inversely.
Figure 7. Interactions in the biopolymer hardness model.

Figure 8 shows the optimum levels that have the greatest effect on the maximum hardness, in this case 2.5 g of glycerin, 1.25 g of urea and 5.25 g of acetic acid, the latter being the decisive factor in the response variable, being above the mean of the resulting maximum hardness.

| Optimal D: 0.9128 | Glycerin | Urea (g) | Acetic-acid |
|-------------------|----------|----------|-------------|
| High Cur Low       | 3 2.5 2.5 | 1.5 1.25 1.25 | 5.25 5.25 1.25 |

Figure 8. Optimum representation to obtain the maximum hardness in biopolymers.

4. Conclusions

Through the analysis of the solution of the factorial models, the optimum combination of materials was established to obtain the highest hardness of 49.43 Shore A, with the following quantities: 12.5 g of water, 2.5 g of glycerin, 1.25 g of urea, 5.25 g of acid, 7.5 g of potato starch and plantain. Acetic acid is the component that causes the greatest effect on hardness, unlike urea, which has no effect on the hardness value; however, the interactions of plasticizers with acid are less significant compared to the interaction between glycerin and urea.

The future scope is focus on characterizing the biopolymer through test for stress, degradation, density, etc., to find its mechanical, physical, and structural proprieties, applying multivariate linear models to the results, to validate which type of packaging can replace. In addition, mix it with other biomaterials to reinforce physical characteristics and generate added value to them.
References

[1] Alexander A, Delabre I 2019 Greening of Industry Networks Studies ed N Yakovleva et al. (London: Springer) chapter 7 pp 95-111
[2] Razza F, Guerrini S, Impallari F 2018 Acta Hortic 1252 77
[3] Lebreton L, Andray A 2019 Palgrave Communications 5(1) 1
[4] Amsaveni D, Ghayathri D, Venkatesan S 2020 Materials Today: Proceedings 21(1) 257-262
[5] Malik J, Bhadauria M 2020 Environmental and Human Health Impacts of Plastic Pollution (Indonesia: IGI Global) chapter 18 pp 370-387
[6] Vanapalli K, Sharma H, Ranjan V, Samal B, Bhattacharya J, Dubey B and Goel S 2021 Sci. T. Environ. 750 141514
[7] Herron M, Thompson R 2010 Marine Pollution Bulletin 60(12) 2279
[8] Rajmohan K, Ramya C, Viswanathan M, Varjani S 2019 Curr. Opin. Env. Sci. Health 12 72
[9] Krueger M, Harms H, Schlosser D 2015 Appl. Microbiol. Biot. 99(21) 8857-8874
[10] Prata J 2018 Environ. Pollut. 234 115
[11] Souza A, Kloas W, Zarfl C, Hempel S, Rillig M Global Change Biol. 24(4) 1405-1416
[12] Rochman C 2018 Science 360(6384) 28
[13] Sereni J 2016 Mat. Sci. Eng. A-Struct. 1 1
[14] Ilyas R, Sapuan S, Ishak M, Zainudin E 2018 Carbohydr. Polym. 202 186
[15] Sadegh F, Nafchi S, Dehaghi J 2014 Int. J Biol. Macromol. 71148 3
[16] American Society for Testing and Materials (ASTM) 2015 Standard Test Method for Rubber Property—Durometer Hardness, ASTM D2240 (United State of America: American Society for Testing and Materials)