Optimization of factors to obtain cassava starch films with improved mechanical properties

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Abstract. In this study, was investigated the optimization of the factors that significantly influenced the mechanical property improvement of cassava starch films through complete factorial design 2^3. The factors to be analyzed were cassava starch, glycerol and modified clay contents. A regression model was proposed by the factorial analysis, aiming to estimate the condition of the individual factors investigated in the optimum state of the mechanical properties of the biofilm, using the following statistical tool: desirability function and response surface. The response variable that delimits the improvement of the mechanical property of the biofilm is the tensile strength, such improvement is obtained by maximizing the response variable. The factorial analysis showed that the best combination of factor configurations to reach the best response was found to be: with 5g of cassava starch, 10% of glycerol and 5% of modified clay, both percentages in relation to the dry mass of starch used. In addition, the starch biofilm showing the lowest response contained 2g of cassava starch, 0% of modified clay and 30% of glycerol, and was consequently considered the worst biofilm.

1. Introduction

Thermoplastic starch is a biodegradable plastic material biologically based which can be obtained from the melting of the native starch granules extracted from a variety of widely available cultures. Due to the chemical structure of the anhydroglucose repeat unit, the two macromolecules constituting the starch (amylose and hyperbranched amylopectin) are highly hydrophilic [11].

Cassava starch is therefore subject to water absorption and plastification by water molecules. This sensitivity of starch to water makes it poorly competitive for the substitution of thermoplastics derived from petroleum in the production of packaging. Moreover, even if the use of a non-volatile plasticizer in the thermoplastic process of starch, such as glycerol, allows the formulation of soft and non-cracking materials by a "stabilization" of the starch, increased molecular mobility may favor the recrystallization of the starch and progressive embrittlement in its structure [9, 10].

An approach to overcome such limitations is the introduction of modified clay nanoparticles in the presence of a quaternary ammonium salt to reinforce the biopolymer structure, such approach showed good results to the corn starch film that had a marked improvement in its mechanical properties [2, 4]. Based on the above and making use of a complete factorial design 2^3, we investigated the individual and interactive effects of three factors that may affect the optimization of the mechanical properties of cassava starch films.

2. Materials and methods

2.1. Ion exchange
The ion exchange was performed according to the methodology proposed by Lee et al. [6]. In the first step was formed a solution of 1% by weight of bentonite clay in deionized water. This solution was kept under stirring and heated at 30 ° C in a thermostat until to obtain swollen slurry. In another Becker, the quaternary ammonium salt was dissolved in 20 mL of ethyl alcohol to form a 0.06 M solution. The two solutions were then mixed and kept under stirring for 12 h at 30 ° C. After stirring, the solution was filtered and washed to remove excess salt. The material retained in the filtration was brought to the oven at 60 ° C and held for 24 h. After drying, they were macerated with mortar and pistil, and then sieved in ABNT No. 200 sieve ($\varphi = 0.074$ mm).

2.2. Preparation of biopolymer film
The film was prepared according to the methodology proposed by Cyras et al. [3]. Initially, 10 solutions were prepared each one containing the cassava starch mass and the percentage of glycerol in relation to the dry mass of the polymer, as shown in Table 2. The mixture was heated at 70°C for 15 min until complete homogenization. Then, 10 solutions were prepared with different percentages of modified bentonite clay, in relation to the polymer dry mass, dispersed in distilled water according to Table 2. Each solution was placed in an ultrasonic bath at room temperature. The solutions of starch and clay were mixed and placed in an ultrasonic bath for 30min to facilitate dissolution. The prepared filmogenic solutions were arranged in rectangular plates and dried at 40°C for 6 hours.

2.3. Statistical analysis
Table 1 shows in quantitative terms the ten experimental tests carried out for the factorial analysis of the tensile strength of cassava starch biofilm. Three variables associated to the formation of the nanocomposite were considered as factors that could influence the improvement of the mechanical properties of the starch film, being these the contents of cassava starch (A), glycerol (B) and modified clay (C). Table 1 too establishes the quantitative analysis of the three factors in terms of the minimum, maximum and central levels.

The tensile strength was determined with the average of three experiments in parallel. The order in which experiments were performed was random to avoid systematic errors. The results were analyzed with Statistica 8 software, and the main effects and interactions among factors were determined. The central point was adopted to verify whether or not there is a lack of fit in the empirical model, which would be impossible by analyzing only two levels. The repeats at the central point have two purposes: to provide a measure of the pure error and to stabilize the expected response variance [1, 5].

Table 1. Shows the matrix of the contrast coefficients of factorial design 2^3.

Test	Real Value			Response
	A	B	C	Tensile Strength (MPa)
1	2	10	0	82.873
2	5	10	0	87.235
3	2	30	0	74.793
4	5	30	0	78.729
5	2	10	5	131.412
6	5	10	5	138.329
7	2	30	5	118.600
8	5	30	5	124.842
9	3.5	20	2.5	104.602
10	3.5	20	2.5	104.524

2.4. Characterizations

2.4.1. Visual aspect
At this stage, the biofilms selected showed the best visual aspects, absence of cracks or zones with tendency to rupture, without insoluble particles and uniform color.

2.4.2. Thickness
The thicknesses of the films were measured using a Mitutoyo micrometer (Model MDC-25M, MFG / Japan). The measurements were taken at five different points throughout the film.

2.4.3. Mechanical properties
The mechanical properties were determined using a Testing Machine DL5000 / 10000 Series EMIC 23, EMIC (Parana, Brazil), which operates according to standard ASTM D882-83 method at a test speed of 5 mm / min with application of total force of 5KN. The samples follow the same standard and are evaluated with length of 50mm, width of 5mm and obeying the maximum thickness of 0.25mm [8].

3. Results and discussion

3.1. Factorial analysis

3.1.1. Estimation of optimal design conditions by the desirable function method
Figure 1 shows, according to HANK et al., 2014 [5] the quantitative measurement of each factor to obtain the best and the worst biofilm of cassava starch, based on the regression model proposed by the factorial analysis.
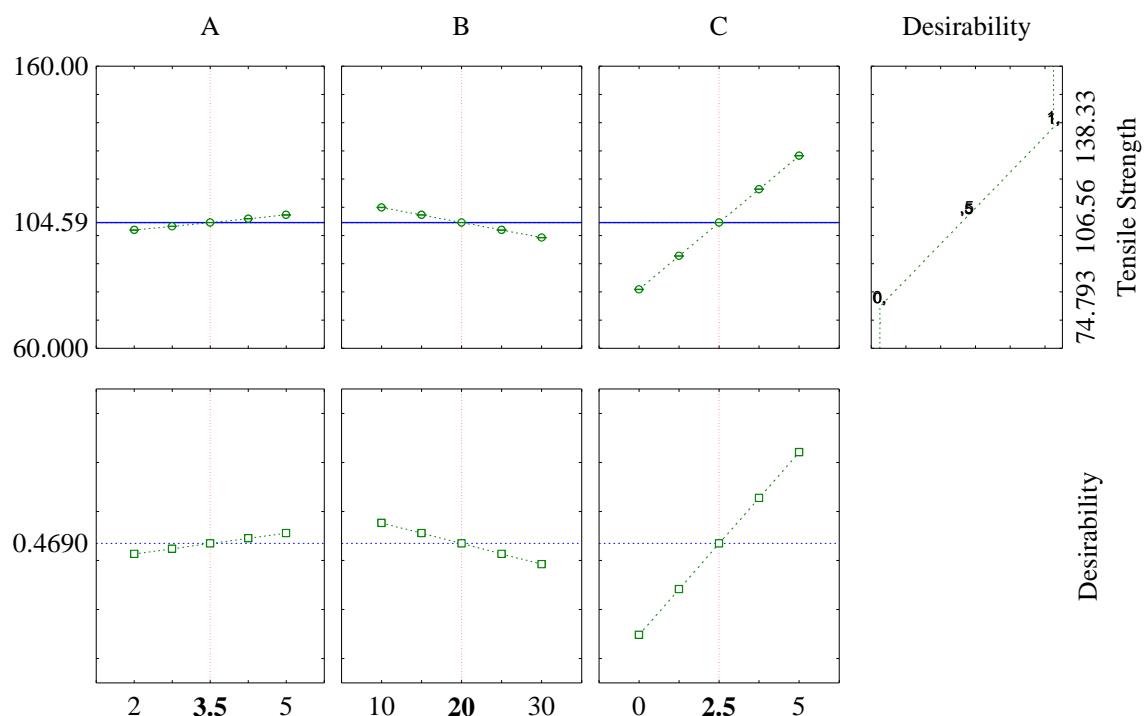

Figure 1. Desirable function for optimizing the response.

The preference function method was used to obtain cassava starch biofilm with the highest tensile strength, that is, with the best mechanical properties. The optimum condition, that is, the best combination of factor configurations to reach the best response was found to be: with 5g of cassava

starch, 10% of glycerol and 5% of modified clay, both percentages in relation to the dry mass of starch used. In addition, the biofilm that showed the least tensile strength contained 2 g of cassava starch, 0% of modified clay and 30% of glycerol, and was consequently considered the worst biofilm. The regression model for the factorial analysis performed, which predicts the observed desirability function, is found in [7].

3.1.2. Response surface

Figures 2 show across the response surface that an interaction is effective when the change in response from lows to high levels of a factor is dependent on the level of a second factor, this is, when the lines are not parallel [1,5].
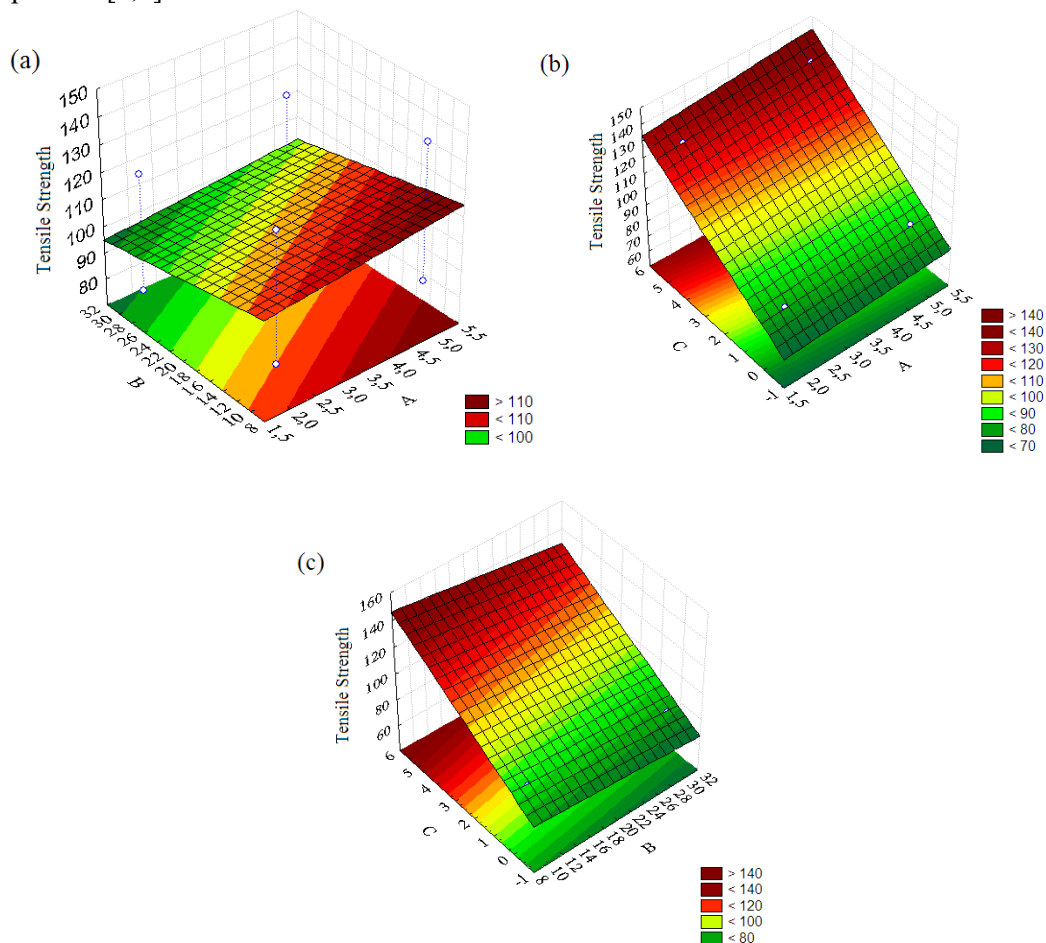

Figure 2. Shows the responses surfaces for the standardized effects: (a) Starch [A] - Glycerol [B], (b) Starch [A] - modified clay [C] and (c) Glycerol [B] - modified clay [C].

The interactions between two factors AB, BC and AC were statistically significant in determining the tensile strength. However, the response surfaces clearly indicated by the slope of the plane representing the statistical model of the observed response variable, that the interaction between B and C was more representative than between A and C, and that the interaction between A and B resulted in the lowest inclination. The AB, BC and AC interactions showed the highest tensile strength at high levels of modified clay, proving that clay is the most significant factor for the improvement of mechanical properties. The effect of C indicated the optimal region of the biofilm strength at the lowest level of A and of B. Therefore, the interaction effects between the AC and BC factors revealed that the nanocomposite with the best mechanical properties were obtained at low A, low B, and high C. These results confirm the observed in the desirability analysis.

4. Conclusion

The statistical design of the experiments combined with regression techniques was applied to optimize the mechanical properties improvement conditions of cassava starch films. The modified clay was the factor of greater statistical significance on the tensile strength of the biofilm observed, being the factor that most contributed to the improvement of the mechanical properties of the biofilm. The factorial experiments showed that the interaction of glycerol with both modified clay and cassava starch was significant for the obtaining of biofilm ductile. The best biofilm contained 5 g of starch, 5% of modified clay and 10% of glycerol; the worst biofilm contained 2 g of starch, 0% of modified clay and 30% of glycerol.

Acknowledgments

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