IOP Conf. Series: Journal of Physics: Conf. Series **885** (2017) 012002 doi:10.1088/1742-6596/885/1/012002

Statistical analysis of the factors that influenced the mechanical properties improvement of cassava starch films

Mayra Monteiro[1*], Victor Oliveira[2], Francisco Santos[2], Eduardo Barros Neto[1], Karyn Silva[1], Rayane Silva[1], João Henrique[1], Abimaelle Chibério[3]

[1] Universidade Federal do Rio Grande do Norte, UFRN, Natal – RN, Brazil.
[2] Universidade Federal Rural do Semi-Árido, UFERSA, Mossoró – RN, Brazil.
[3] Universidade NOVA de Lisboa, Lisboa, Portugal.

mayra.kerolly@gmail.com

Abstract. In order to obtain cassava starch films with improved mechanical properties in relation to the synthetic polymer in the packaging production, a complete factorial design 2^3 was carried out in order to investigate which factor significantly influences the tensile strength of the biofilm. The factors to be investigated were cassava starch, glycerol and modified clay contents. Modified bentonite clay was used as a filling material of the biofilm. Glycerol was the plasticizer used to thermoplastify cassava starch. The factorial analysis suggested a regression model capable of predicting the optimal mechanical property of the cassava starch film from the maximization of the tensile strength. The reliability of the regression model was tested by the correlation established with the experimental data through the following statistical analyse: Pareto graph. The modified clay was the factor of greater statistical significance on the observed response variable, being the factor that contributed most to the improvement of the mechanical property of the starch film. The factorial experiments showed that the interaction of glycerol with both modified clay and cassava starch was significant for the reduction of biofilm ductility. Modified clay and cassava starch contributed to the maximization of biofilm ductility, while glycerol contributed to the minimization.

1. Introduction

The wide application of biodegradable polymers in the production of packaging and as a coating of fruits and vegetables has been receiving more attention by numerous researchers in recent years due to its sustainable character [11].

Starch is a natural polymer that is cheap and readily available. However, its high sensitivity to water limits its use in the production of flexible packaging [13]. Recent research focuses on the incorporation of layered silicates along the biopolymer matrix, especially the chemically modified sodium montmorillonite in the presence of organic surfactants, which could be used as a filling material that enhances the ability of the biopolymer structure to withstand a charge applied, the clay thus serves as a barrier to traction [3, 6].

In this perspective, a very low level of modified montmorillonite loading can form nanocomposites with improved mechanical, thermal, electrical and barrier properties in relation to the physicochemical properties of the original biopolymer. The central issue discussed in the whole preparation of nanocomposites is the dispersion of the nanoparticle of clay influenced by the content of the plasticizer material that thermoplasticizes the cassava starch [1, 4].

IOP Conf. Series: Journal of Physics: Conf. Series **885** (2017) 012002 doi:10.1088/1742-6596/885/1/012002

Based on the above and making use of a complete factorial design 2^3, was 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. [7]. 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 12h 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 (φ = 0.074 mm).

2.2. Preparation of biopolymer film
The film was prepared according to the methodology proposed by Cyras et al. [5]. 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 performed for the factorial analysis of the tensile strength of the cassava starch biofilm, as well as table 2 that establishes the quantitative analysis of the three factors in terms of minimum, maximum and central levels, are shown in [8]. The breaking 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.

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 [5].

3. Results and discussion

3.1. Factorial analysis

Selected the three important factors, the next step was to quantitatively evaluate their influence on the response of interest, with the minimum of experiments using a full factorial design 2^3. Therefore, the effect of one factor depends on the level of the other, and it is possible to calculate the value of the interaction effect between them. In terms of the effects were obtained the correlation coefficients of the statistical model used to describe the response of the complete factorial planning. The T-value indicates the contribution of each effect on the observed response. The P-value indicates that the observed result has more than 95% confidence. Table 1 shows all the statistical parameters cited above having the tensile strength as a response variable.

Table 1. Shows the estimated effects of the three investigated factors, the correlation coefficients of the model and the statistical parameters for the tensile strength response.

Parameters	Effects	Coefficients	Default Error	T – Value	P – Value
Mean	104.594	104.5937	0.016367	6390.429	0.00E+00
A	5.3642	2.6821	0.036598	146.569	0.000047
B	-10.721	-5.36065	0.036598	-292.946	0.000012
C	47.3882	23.6941	0.036598	1294.82	0.000001
A – B	-0.2749	-0.13745	0.036598	-7.511	0.017266
A – C	1.2151	0.60755	0.036598	33.201	0.000906
B – C	-2.4286	-1.2143	0.036598	-66.357	0.000227
A – B – C	-0.0623	-0.0312	0.036598	-1.701	0.230961

The effects shown in Table 1 can be explained taking into account that the contribution of each factor and the interaction between them on the response obtained was investigated. In this sense, it was observed that both the individual and the interaction effects of cassava starch (A) and glycerol (B) significantly influenced the biofilm tensile strength. The cassava starch contributes to the increase of the tensile strength due to its elasticity from the extensive monomeric chain formed by hydrocarbons and branched by hydroxyl groups from the predominance of amylopectin in its composition [13]. Glycerol contributes to reduce the ductility of the biofilm from the thermoplasticization. This is due to its highly hydrophilic character, which is responsible for reducing the forces that keep the biopolymer matrix cohesive, by breaking the internal hydrogen bonds and the forces of inter and intramolecular attraction between the polymer chains, while increasing the intermolecular space resulting in the fragility of the structure [1]. As a result, the interaction between A and B was also significant for the reduction of film tensile strength.

In this perspective, the individual effects of the three factors were significant on the observed response, with the modified clay (C) contributing the most to the increase. This can be explained because the clay presents a stacked structure of layers interconnected by Van der Waals forces in the presence of free inorganic cations in the interlamellar galleries. Therefore, it becomes organophilized by the ion exchange of inorganic sodium cations by organic cationic surfactants. It has an extensive carbonic chain responsible for increasing the basal distance of the silicate layers, according to [3], [6] and [12], this increase promotes to the thermoplastic biopolymer matrix space for its interlacing that disperses the clay evenly throughout its structure due to compatibility with the functional group of the organic surfactant, thus resulting in a ductile nanocomposite and consequently with the mechanical property of the original biofilm improved. Indeed, in terms of the interaction between two factors, AC interaction also contributed significantly to increased response.

The BC interaction contributed with a negative effect on the resistance of the biofilm, since the glycerol to be depended on the concentration will bind by difference of electronegativity with the crystalline structure of the cassava starch and will make difficult the adequate aggregation of the modified clay [1, 4]. The interaction between the three factors was neglected because they did not significantly influence the ductility of the biofilm, a similar result was found by CHIVRAC (2010) [4] where it is argued that the result is obtained from the deposition of the plasticizer on the starch occurring before the modified clay, this fact leads to the formation of hydrogen bonds between the cassava starch and the glycerol that diminish the attractive forces between the starch and the clay. The mathematical model coded for a complete factorial design 2^3 is represented by:

$$Y = 104.5937 + 2.6821X_1 - 5.3606X_2 + 23.6941X_3 - 0.1374X_1X_2 + 0.6075X_1X_3 - 1.2143X_2X_3 - 0.0312X_1X_2X_3 \quad (1)$$

3.2. Pareto graph

Figure 1 shows the Pareto graph showing which of the individual factors analyzed, as well as which interactions between these factors contribute significantly in the optimization of the mechanical properties of cassava starch biofilms.

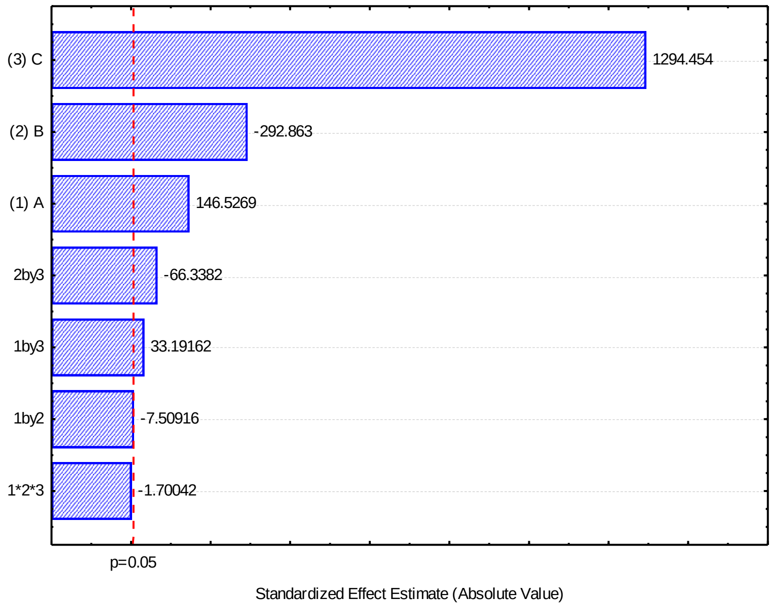

Figure 1. Pareto graph of standardized effects.

For the 95% confidence level and 2 degrees of freedom, the t-critical is equal to 2.920. The value of the t-critical estimated by the student t test was used as the reference line to determine if the calculated effects were significantly different from zero, these values for each effect are shown in the Pareto graph by horizontal columns according to Fig.1, but they are not significant factors [2,9,10]. However, the main factors (A, B and C) and their interactions (AB, AC and BC) that touched the reference line at the 0.05 level were considered significant. The Pareto graph also shows that C represents the individual effect of a greater significant load on the tensile strength, in relation to the interaction between the two factors is BC that presents this characteristic. In addition, only the interaction between the three ABC factors was not significant for the observed response at 95% confidence. The sequence of the degree of statistical significance on the tensile strength in relation to the effects investigated is therefore C> B> A> BC> AC> AB. The individual factors A and C, as well as the interaction between them, AC, show positive effects and contribute to the maximization of the tensile strength of the biofilm. The effects B, AB and BC presented negative effects, leading to the minimization of the response variable. The observed in the Pareto graph confirms the one evidenced in the factorial 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 reduction of biofilm ductility. The evidenced in the factorial analysis was correlated satisfactorily with that observed in the Pareto graph.

References

[1] ALVES, V.D.; MALI, S.; BELÉIA, A.; GROSSMANN, M.V.E. Effect of glycerol and amylose enrichment on cassava starch film properties, Journal of Food Engineering, v.78, p. 941–946, 2007.

[2] BINGOL, D.; TEKIN, N.; ALKAN, M. Brilliant Yellow dye adsorption onto sepiolite using a full factorial design, Applied Clay Science, v.50, p. 315–321, 2010.

[3] CHIU, C.W.; HUANGB, T.K.; WANGB, Y.C.; ALAMANIB, B.G.; LINB, J.J. Intercalation strategies in clay/polymer hybrids. Progress in Polymer Science, v.39, p. 443–485, 2014.

[4] CHIVRAC, F.; POLLET, E.; DOLE, P.; AVÉROUS, L. Starch-based nano-biocomposites: Plasticizer impact on the montmorillonite exfoliation process, Carbohydrate Polymers, v.79, p.941–947, 2010.

[5] CYRAS, V. P.; MANFREDI, L. B.; MINH-TAN, T. T.; VAZQUEZ, A. Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. Carbohydrate Polymers, v. 73, v.55–63, 2008.

[6] KOTAL, M.; BHOWMICK, A. K. Polymer nanocomposites from modified clays: Recent advances and challenges. Progress in Polymer Science, v.51, p. 127–187, 2015.

[7] LEE, S.; PARK, M.; KIM, D.; II KIM; PARK, D. Catalytic performance of ion-exchanged montmorillonite with quaternary ammonium salts for the glycerolysis of urea, Catalysis Today, v.232, p.127–133, 2014.

[8] MONTEIRO, M. K. S.; OLIVEIRA, V.R.L.; SANTOS, F.K.G.; NETO, E.L.B.; SILVA, K.N.O.; SILVA, R.R.; HENRIQUE, J.M.M.; CHIBÉRIO, A.S. Optimization of factors to obtain cassava starch films with improved mechanical properties. Journal of Physics: Conference Series, 2017.

[9] PALANIKUMARA, K.; DAVIM, J. P. Assessment of some factors influencing tool wear on the machining of glass fibre-reinforced plastics by coated cemented carbide tools, journal of materials processing technology, v.2 0 9, p.511–519, 2009.

[10] PONNUSAMI, V.; KRITHIKA, V.; MADHURAM, R.; SRIVASTAVA, S.N. Biosorption of reactive dye using acid-treated rice husk: Factorial design analysis, Journal of Hazardous Materials, v.142, p.397–403, 2007.

[11] REDDY, M.M.; VIVEKANANDHAN, S.; MISRA, M.; BHATIA, S. K.; MOHANTY, A.K. Biobased plastics and bionanocomposites: Current status and future opportunities, Progress in Polymer Science, v.38, p.1653– 1689, 2013.

[12] ROMERO-BASTIDA, C.A.; BELLO-PÉREZ, L.A.; VELAZQUEZ, G.; ALVAREZ-RAMIREZ, J. Effect of the addition order and amylose content on mechanical, barrier and structural properties of films made with starch and montmorillonite. Carbohydrate Polymers, v.127, p.195–201, 2015.

[13] ZHU, F. Composition, structure, physicochemical properties, and modifications of cassava starch. Carbohydrate Polymers. v.122, p.456–480, 2015.