Effect of Carnauba Wax and Coconut Fiber Contents on Tensile Properties of Corn Starch-Based Biocomposites

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This work aims investigate the changes on tensile properties of biocomposites obtained by addition of carnauba wax and coconut fibers in a corn starch matrix. The influence of carnauba wax and coconut fibers contents on tensile strength, modulus of elasticity and elongation at break was studied using a response surface methodology. A central composite design based on three levels of carnauba wax content (0, 10 and 20 %) and coconut fibers content (0, 10 and 20 %) was elaborated. Empirical models were obtained to describe these properties as function of coconut fiber and carnauba wax contents. Optical microscopy was carried out to visualize the dispersion and interactions between coconut fibers, carnauba wax and starch matrix in the biocomposites. In presence of carnauba wax, the biocomposite became more compact and with a better interaction between the corn starch-based matrix and coconut fibers reinforcement. It was observed that tensile strength and modulus of elasticity rise with the increase in carnauba wax and coconut fiber contents. Moreover, the elongation at break increases with the addition of coconut fiber, while a decrease in the values of this property occurs with the addition of carnauba wax.

Keywords: *surface response methodology, central composite design, tensile strength, modulus of elasticity, elongation.*

1. Introduction

The development and use of biodegradable and renewable materials have attracted the attention of society in view of the problems caused by increased solid waste production, pollution and greenhouse gases, as well as, the shortage of non-renewable raw materials. Synthetic polymers are materials widely used in disposable objects and cause a serious problem due its biological recalcitrance since these materials need hundreds of years to degrade in environment. Also, most synthetic polymers are currently obtained from non-renewable sources like petroleum. Therefore, ecological friendly materials able to substitute artificial polymers are being investigated by researchers around the world[1,2].

An alternative to conventional polymer objects is using biodegradable objects made from biopolymers, like starch. Starch-based materials stand out as promising candidates to replace polymers from petroleum due its biodegradability, low

cost, and to be obtained from a renewable resource. However, these materials have low flexibility, high brittleness and hydrophilicity[1,3]. In order to improve the flexibility of these materials, plasticizers such as glycerol and others polyols can be added to starch matrix. On the other hand, natural fibers have also been used to reinforce starch matrices, resulting more strength materials[4,5,6].

The materials resulting from the combination of a biopolymer matrix, like starch, reinforced with vegetable fibers are known as biocomposites. These can be disposed of without injury to the environment and arise as an alternative to synthetic polymer matrix composites[7,8]. Nevertheless, the high moisture absorption ability of the biocomposites produced from starch, because its high hydrophilic character, compromises its mechanical properties and life cycle[9]. A solution to increase the hydrophobicity of these materials and improving their water barrier properties is add lipids,

such as carnauba wax, to biocomposites matrices. Although adding lipids can improve water barrier properties of starch matrix, mechanical properties of biocomposites are likewise affected[10,11]. Thereby, it is necessary to investigate how the lipids content modify the mechanical properties of biocomposites. Moreover, fibers present in biocomposites can interact with the particles of lipids changing mechanical behavior of these materials.

This work aims investigate the effect of fiber and wax contents in tensile properties of biocomposites constituted by a corn starch-based matrix, reinforced with coconut fibers and added of carnauba wax. A central composite experimental design was carried out with three levels for each factor (fiber and wax contents). A variance analysis (ANOVA) permitted select the significant effects of factors and interactions. Then, empirical polynomial models were fitted to experimental results and a response surface methodology was employed to describe changes in tensile strength, modulus of elasticity and elongation at break of the biocomposites, as function of coconut fiber and carnauba wax contents. Finally, optical microscopy aided to elucidate the morphology of biocomposites and the interactions between matrix, fibers and wax particles at microscopic level.

2. Experimental

2.1 Materials

Carnauba wax type I (Agrocera, Russas-CE, Brazil) and coconut fibers (Fazenda Morada Nova, Mossoró-RN, Brazil) were kindly given away by manufacturers. The corn starch (3 Corações Alimentos S.A., Mossoró-RN, Brazil) and glycerol 99.5 % (Dinâmica Química Contemporânea, São Paulo, Brazil) were purchased from commerce and used without further purification. Osmosed water was used to prepare the precursor mixtures for biocomposites.

2.2 Methods

2.2.1 Experimental design and statistical analysis

A Central Composite Design (CCD) with two independent variables ($n = 2$, number of factors) was used to studied the effects of coconut fiber (CF) and carnauba wax (CW) contents on tensile properties of corn starch-based biocomposites. A total of 13 experiments were run, being sufficient to calculate the coefficients of a second-order polynomial regression model for two variables. The number of runs corresponding at four (2^n) factorial points added of four ($2n$) axial points and five replicates at central point. Each factor was investigated at three levels: -1, 0 and +1, in coded values; corresponding at 0, 10 and 20%, in real values. The dependent variables (responses) evaluated were tensile strength (TS), modulus of elasticity (ME) and elongation at rupture (El). The behavior

of each response was explained by an empirical polynomial model as showed in Equation 1.

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad (i = 1, 2 \text{ or } 3) \quad (1)$$

Here, Y_i represents dependent variables, where Y_1 was tensile strength in MPa, Y_2 modulus of elasticity in MPa, and Y_3 was elongation at rupture in percentage; X_1 and X_2 were the independent variables, coconut fibers and carnauba wax contents, respectively, expressed in percentage; b_0 was intercept, b_1 and b_2 linear coefficients, b_{11} and b_{22} quadratic coefficients and b_{12} the interactive coefficient.

A variance analysis (ANOVA) and F test were performed to verify if the models were statistically significant at $p < 0.05$. For the models in which the $F_{calculated}$ was superior to the $F_{tabulated}$ and $R^2 \geq 0.75$, the response surfaces were represented as three-dimensional contour plots. During the adjustment of the models, non-significant effects were ignored. All Statistical analysis of data obtained through the experimental design was performed, using the software Statistica® version 13.5 (TIBCO softtware Inc., USA).

2.2.2 Preparation of biocomposites

The biocomposites were manufactured by casting methodology. Precursor blends were prepared with a mass of dry matter total fixed at 20% (w/w) using osmosed water as solvent. Dry matter mass was considered as the sum of masses for the corn starch, coconut fibers and carnauba wax. The masses of coconut fibers and carnauba wax varied in accord with contents stablished in the experimental design for each essay, as described at Table 1. The mass of corn starch was determined by difference between the mass of dry matter total and the masses of fibers and wax used in each run. The mass of plasticizer (glycerol) was calculated in order to maintain its content fixed at 15% (w/w) of the biopolymer mass. Previous the preparation, coconut fibers were cut and its lengths uniformized at 6.55 ± 0.71mm. The first step in process of blend preparation was the dispersion in water of corn starch, glycerol and coconut fibers, according the calculated amounts for each run. This mixture was heated and the temperature kept constant at approximately 90 °C, under constant mechanical stirring until complete starch gelatinization. A change in mixture aspect from opaque to translucid indicates the complete starch gelatinization, which occurs in about 25 minutes of heating. The carnauba wax was added after starch gelatinization and enough stirring to ensure mixture homogeneity. The temperature and stirring conditions required in experiments were got by a mechanical homogenizer (TE-099, Tecnal) and a thermostatic bath. Once prepared, 1000g of each precursor mixture were deposed in trays (20cm x 30cm) and dried in oven with air recirculation (TE-394/1, Tecnal) at 60°C during 48 hours.

Table 1. Central composite design matrix with real and coded (in parentheses) values for independent variables, with X_1 = coconut fiber content (CF) and X_2 = carnauba wax content (CW); and means for response variables, with Y_1 = tensile strength (TS), Y_2 = modulus of elasticity (ME) and Y_3 = elongation at break (El).

Run	X_1 (CF) %	X_2 (CW) %	Y_1 (TS) MPa	Y_2 (ME) MPa	Y_3 (El) %
1	0 (-1)	0 (-1)	2.57	77.1	1.32
2	10 (0)	0 (-1)	1.65	48.6	4.03
3	20 (+1)	0 (-1)	1.99	53.5	5.28
4	0 (-1)	10 (0)	1.64	80.0	1.60
5	20 (+1)	10 (0)	3.08	77.3	5.50
6	0 (-1)	20 (+1)	0.63	55.6	1.25
7	10 (0)	20 (+1)	2.67	94.2	2.95
8	20 (+1)	20 (+1)	3.46	87.3	3.18
9	10 (0)	10 (0)	2.23	125.2	2.08
10	10 (0)	10 (0)	2.51	123.5	2.09
11	10 (0)	10 (0)	2.69	128.0	2.30
12	10 (0)	10 (0)	2.40	116.1	2.26
13	10 (0)	10 (0)	1.98	139.4	1.55

2.2.3 Preparation and conditioning of test specimens

After manufacture of biocomposites, test specimens were cut with dimensions of 100 mm x 20 mm. Then, test specimens were conditioned in a hermetically sealed vessel at a constant relative humidity of 49%. The humidity was maintained constant using a saturated saline solution of potassium carbonate (K_2CO_3), prepared according to ASTM E104[12]. The mass of test specimens was measured periodically until equilibrium conditions be attained and verified by have no changes in their masses over time. The Figure 1 shows test specimens of biocomposites prepared according to coconut fibers and carnauba wax contents specified by experimental design stated in Table 1.
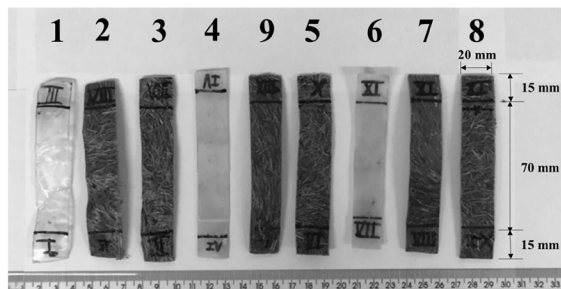

Figure 1. Test specimens of biocomposites for the different essays of the experimental design (digits at the top correspond to essay number in Table 1)

2.2.4 Measurement of thickness

The thickness of test specimens was measured at five random points with an EDA analogical micrometer with 0.01 mm resolution. The averages of these values were used to determine the mechanical properties of each specimen.

2.2.5 Optical Microscopy

Optical microscopy was carried out to visualize the dispersion and interactions between coconut fibers, carnauba wax and starch matrix in the biocomposites. The equipment used was the Nikon SMZ18 Stereo Microscope assisted by the NIS Elements D software for viewing, capturing and storing images.

2.2.6 Mechanical Testing

The characterization of the biocomposites was carried out by means of a tensile test according to ASTM D3039[13]. The equipment used to perform the test was the Universal Testing Machine, model DL10000 of EMIC, with capacity 100kN, load cell of 5 kN and software TESC for data acquisition. The test was performed at a temperature of 23 ° C and relative humidity of 49%. Five specimens were tested for each run of the experimental design.

3. Results and Discussion

3.1 Optical microscopy

Figure 2 shows the morphology and interfacial adhesion of some biocomposites prepared with corn starch matrix reinforced with coconut fiber and with carnauba wax as additive.

The biopolymeric matrix of corn starch is shown in Figure 2 (a), where it is possible to observe the cross-sectional area of the sample that has a homogeneous and smooth morphology, possibly indicating a fragile fracture. This is because the matrix contains a low glycerol (plasticizer) content, what provides greater intermolecular interaction and, consequently, a lower mobility of the macromolecules,
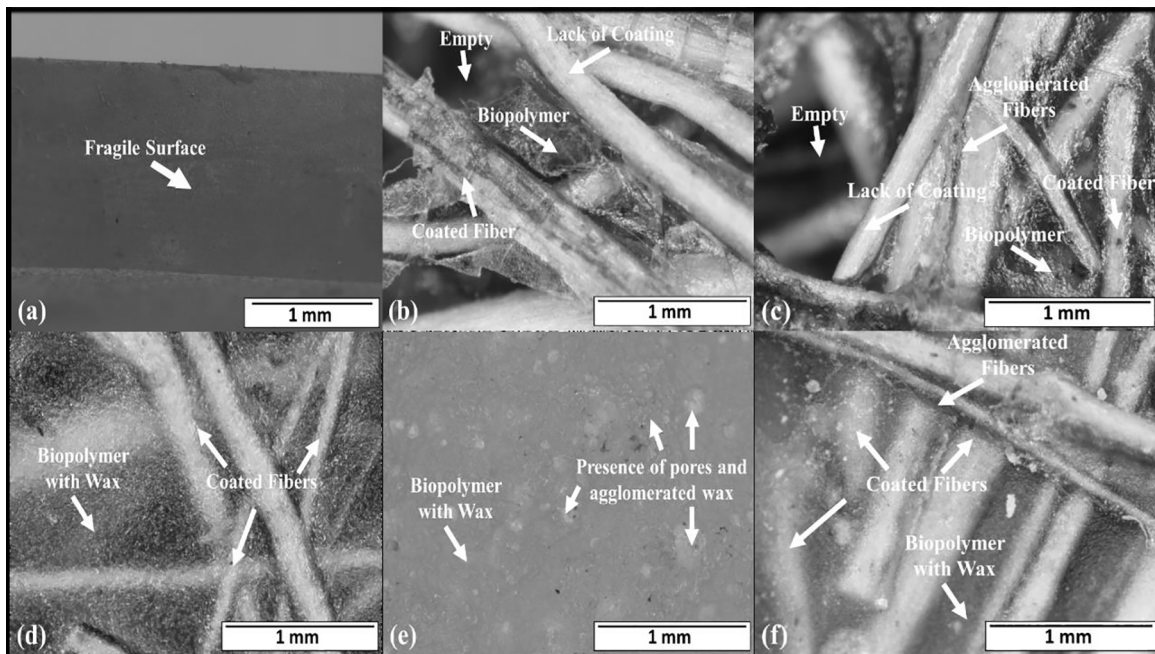
Figure 2. Optical microscopy of (a) Matrix of corn starch; (b) Biocomposite with 10% coconut fiber and (c) 20% coconut fiber; (d) Biocomposite with 10% coconut fiber and 10% carnauba wax; (e) Biocomposite with 20% carnauba wax; (f) Biocomposite with 20% coconut fiber and 20% carnauba wax.

resulting in a more fragile structure, as also observed by Ramírez et al.[9] and Jouki et al.[14].

In Figure 2(b) it is possible to verify the corn starch-based biocomposite reinforced with coconut fiber without carnauba wax additive, where there is the presence of defects (voids) promoted by the poor dispersion of the coconut fibers in starch matrix. In addition, it is observed the absence of matrix coating around the fiber, characteristic of a poor interfacial adhesion between the fiber and matrix.

Figure 2(c) shows the morphology for a biocomposite which have a higher concentration of coconut fiber in relation to material showed in Figure 2(b). There are frequent defects in the biocomposite, possibly due to higher volume of fiber used, promoting a high agglomeration of the coconut fibers, and the lack of coating of the fibers by the matrix. These defects, also observed by Edhirej et al.[15] at high concentrations of reinforcement, contribute to the presence of stress concentrators that can affect the mechanical properties of the biocomposites.

For the material shown in Figure 2(d) can be observed a random and homogeneous arrangement of the coconut fibers in corn starch matrix, without voids, as was also observed by Ramírez et al.[9]. In this case, the matrix is compact and dense, possibly due to the presence of the carnauba wax, which causes a decrease in the viscosity and hydrophilicity of the matrix, thus allowing a better dispersion of the coconut fibers during the production process of the biocomposite. It is observed a uniform coating of the fibers by the matrix,

which promotes a better interfacial adhesion resulting in a good transfer of tension from the matrix to the fiber, as also observed by Lopez et al.[16].

Figure 2(e) shows a corn starch matrix with high content of carnauba wax where is possible to observe a heterogeneous and porous surface. This can be attributed to the high amount of carnauba wax added and the inability to properly mix the hydrophobic wax with a starch hydrophilic matrix under such conditions. Thus, high wax contents provoke the formation of hydrophobic agglomerates in the matrix, as was also observed by Mehyar et al.[17]. This results in structural defects in the matrix that influence the mechanical strength and flexibility of the biocomposites, due to the formation of tension concentrators in the material.

Figure 2(f) shows the investigated biocomposite with the highest concentration of coconut fiber and carnauba wax. Herein is seen a well compacted and dense matrix, in which a good part of the fibers is well coated. This should provide an improvement in the mechanical resistance of materials. However, the high percentage of coconut fibers causes them to agglomerate in the matrix due to insufficient amount of polymer disponible to disperse the fibers, as was also observed by Ibrahim et al.[18].

3.2 Response Surfaces

The experimental design with real and coded values for the independent variables, as well the means for the dependent variables investigated can be observed in Table 1.

The regression coefficients, as well as the R^2, $R_{adjusted}$, $F_{calculated}$ and $F_{tabulated}$ for the models can be observed in Table 2. The omitted coefficients were no significant being ignored during model adjustment.

ANOVA was performed ($p < 0.05$) for the responses shown in Table 2 after an adjustment by disregarding some regression coefficients, in order to obtain the subset with highest $R_{adjusted}$. In all cases the R^2 was higher than 0.75 and the $F_{calculated} > F_{tabulated}$ for a confidence level of 95%, indicating that the models were significant. Only statistically significant terms were considered in final models, as indicated.

The empirical models proposed to describe the tensile strength (TS), the modulus of elasticity (ME) and elongation at rupture (El) of the studied biocomposites are described by Equations 2, 3 and 4, respectively.

$$TS = 2.1416 - 0.003\, CW^2 + 0.008\, CF \times CW \qquad (2)$$

$$ME = 64.671 - 0.254\, CF^2 + 6.408\, CW - 0.341\, CW^2 \qquad (3)$$

$$El = 1.090 + 0.216\, CF - 0.005\, CF \times CW \qquad (4)$$

The response surfaces exhibited in Figure 3 were plotted to demonstrate how coconut fiber and carnauba wax contents affect the (a) tensile strength (TS), (b) modulus of elasticity (ME) and (c) elongation at break (El) of investigated biocomposites.

It can be seen in Figures 3(a) and 3(b) that both carnauba wax and coconut fiber contents influence the tensile strength and modulus of elasticity of the materials, according to indicate by the models (Equations 1 and 2). In these models, a negative quadratic coefficient for the carnauba wax content is observed, which indicates a reduction in the tensile strength with the increase in this factor, as can be visualized in Figure 3(a). This occurs because the carnauba wax has a hydrophobic and antiplasticizing character, resulting in a porous matrix and formation of wax agglomerates, as seen previously in the optical microscopy. These defects cause a decrease in TS, as observed by Mehyar et al.[17]; Chiumarelli and Hubinger[10,19].

The positive interactive coefficient for coconut fiber and carnauba wax contents observed in Equation 01 indicates a synergic effect between these factors in the increase of tensile strength. As can be observed in the micrographs - Figures 1(d) and 1(f), there was a greater compaction of the biocomposites with the concomitant presence of the fiber and the wax, which caused a better coating of the fibers by the matrix. This possibly results in a better interfacial adhesion, which provides a better transfer of tension, considering that there will be a greater interaction between the coconut fibers and the corn starch matrix, which have free hydroxyl groups and can interact by formation of hydrogen bonds. This increase in the tensile strength due to the presence of lignocellulosic fibers was also observed by several authors[9,18,20].

For modulus of elasticity, it was observed that the empirical model presents a positive linear parameter for carnauba wax content, indicating that an increase in this factor causes an increase in that property, as can be seen in Figure 3(b). This is possibly due to increased stiffness of the biocomposites due to the presence, in carnauba wax, of hydroxylated, unsaturated esters from long chain fatty acids, as observed by Mehyar et al.[17]; Chiumarelli and Hubinger[19].

It can be verified through Figure 3(c) that an increase in coconut fiber content rises the elongation at break for the investigated materials. This fact is also evidenced by the positive linear coefficient for the coconut fiber content effect in this response variable, according to the model represented by Equation 03. This is because the biocomposite contains a low percentage of glycerol, resulting in a fragile matrix

Table 2. Regression, determination coefficients and F test for models, as described in Equation 1, for response variables, with Y_1 = tensile strength (TS), Y_2 = modulus of elasticity (ME) and Y_3 = elongation at break (El).

Type of coefficients	Coefficient codes (factors)	Fitted values		
		Y_1 (TS) MPa	Y_2 (ME) MPa	Y_3 (El) %
Intercept	b_0	2.146*	64.671*	1.090*
Linear coefficients	$b_1(X_1)$	-0.019	3.743	0.216*
	$b_2(X_2)$	-	6.408*	-
Quadratic coefficients	$b_{11}(X_1.X_1)$	-	-0.254*	-
	$b_{22}(X_2.X_2)$	-0.003*	-0.341*	-
Interactive coefficient	$b_{12}(X_1.X_2)$	0.008*	0.138	-0.005*
Determination coefficients	R^2	0.851	0.814	0.775
	$R_{adjusted}$	0.801	0.681	0.730
F-values	$F_{calculated}$	17.784	4.163	11.799
	$F_{tabulated}$	3.490	3.106	3.885

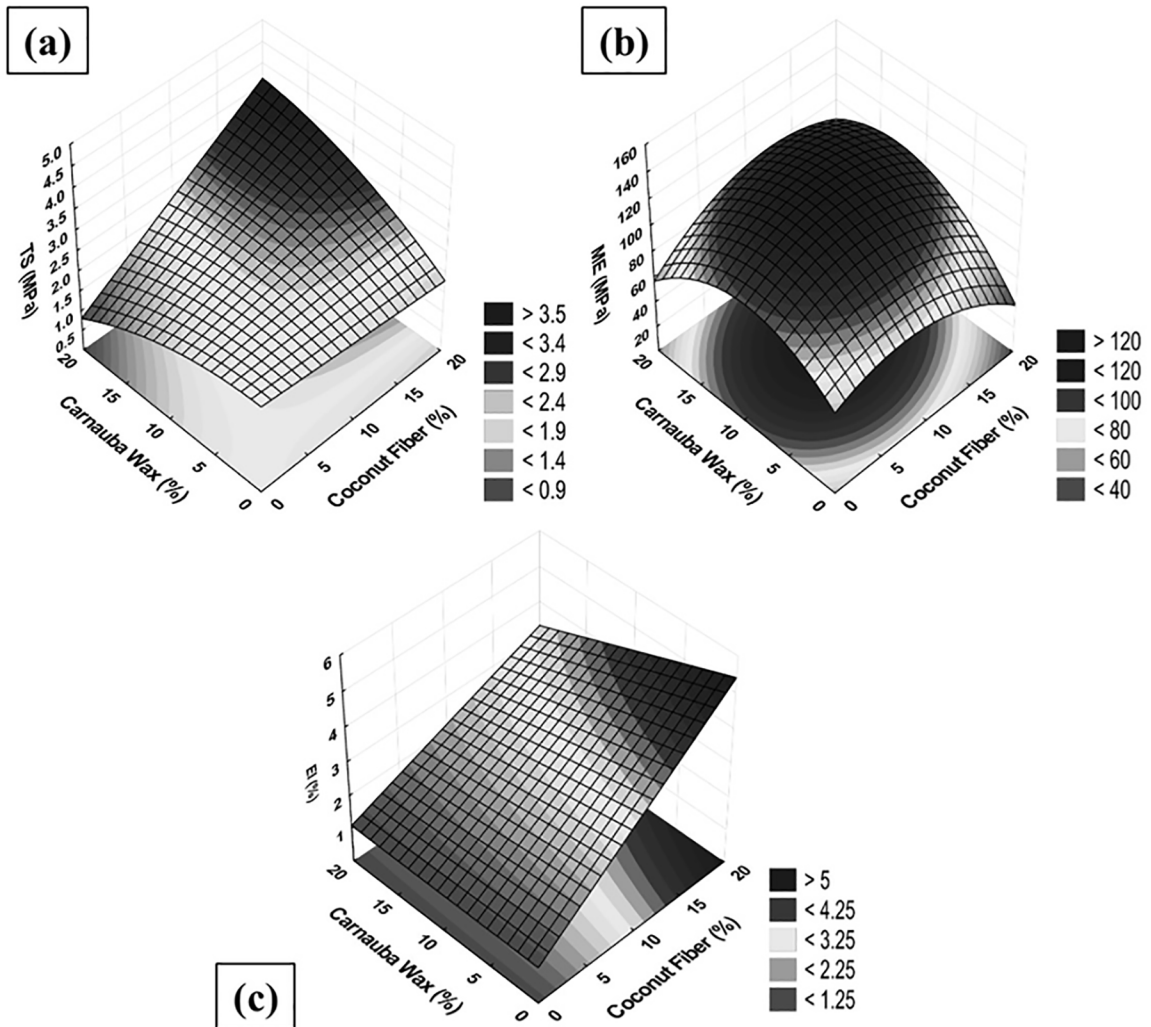*Statistically significant values for $p<0.05$.

Figure 3. Response surfaces for (a) tensile strength (TS), (b) modulus of elasticity (ME) and (c) elongation at break (El) of biocomposites as a function of coconut fiber and carnauba wax contents.

with low flexibility, as show the micrographs in Figures 1(a) and 1(e). The coconut fiber has a great elongation at break, corresponding at approximately 30%, according to Ramesh et al.[21]. So, the presence of coconut fibers in the biocomposites grants higher elongation at break to these materials. The negative linear coefficient of the interaction between the coconut fiber and carnauba wax contents indicates an antagonistic effect of these factors on the elongation variation. This observation can be explained by the structural defects caused by an excessive addition of wax and fibers, such as pores and wax agglomeration, as well as the increase in stiffness, which cause a reduction in elongation at break, as observed by Mehyar et al.[17] and Chiumarelli and Hubinger[10,19].

4. Conclusions

Through optical microscopy it was possible to observe a more compact structure and a better interaction between the corn starch-based matrix and coconut fibers reinforcement in the presence of carnauba wax. The tensile strength and modulus of elasticity rise with the increase in carnauba wax and coconut fiber contents. The elongation at break increases with the addition of coconut fiber, while a decrease occurs with the addition of carnauba wax.

5. Acknowledgment

6. References

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