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A Bio-Phase Change Material from Poly(butylene succinate) to be used in Concrete

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Abstract: the objective of this research is to test different variables combinations and show which Poly (cutylene succinate)-based (PBS-based) material OBS material has the best properties to be added as a Bio-phage-change material in concrete matrices. In this experimental study, a novel PBS-based phase change material (PCM) was synthesized to be applied in concrete systems to increase thermal resistance. Box-Behnken design was followed to produce a total of 14 samples with different reaction times, catalyst concentrations, and glycerin concentrations (which acted as additives). All of the samples were able to decrease the regular melting point of PBS from 110ºC to around 68ºC, showing a significant improvement that allows the use of this material to improve the thermal properties of concrete systems.

Keywords: Box-Behnken Design, Experimental Design, Polymer, Concrete, Phase-change material, Poly (butylene succinate),.

Adherence to the BJEDIS' scope: This work is closely related to the scope of BJEDIS as it presents an experimental design that helps to understand the behavior of the studied variables in the samples.

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1. INTRODUCTION

According to Del Veccio and collaborators, the costs needed to repair or substitute concrete structures are enormous, promoting both economic and environmental problems. Because of this, new technologies are needed to promote the improvement of concrete structures life cycle, promoting many benefits to society (1).

Many researchers study polymeric materials to develop such technologies, since they can allow the improvement of concrete materials. Sakhakarmi and collaborators proved that polymeric materials can repair structures previously damaged, making it unnecessary to substitute it, thus extending its lifetime (2).

One of the possible polymer applications to improve concrete lifetime is using phase-change materials (PCMs). A PCM is an additive that helps improve the thermal properties of a given material, as shown by Pomianowski and Jensen (3). A phase-change material acts by absorbing and liberating heat instead of concrete, changing its physical state and avoiding damage to its structure, extending both lifespan and performance, as proved by Arivazhagan (4). A PCM can store and liberate heat many times, promoting continuous heating-cooling cycles, as found by Uthaichotirat and collaborators when they studied the behavior of a PCM added to a concrete matrix (5).

According to Naresh and collaborators, Bio-PCMs are PCMs made of renewable sources (6). They tend to have better properties than regular PCMs, since they are more accessible, are less inflammable, can adjust their properties depending on the formulation, and are capable to withstand thousands of temperature cycles, as confirmed by a comparative study done by Sam and collaborators (7). Bio-PCMs are already studied to act improving the thermal properties of concrete, as found by Olawoore (8). It is biodegradable and its production is cheaper than its oil derivate counterparts, even though it is produced using renewable sources (10–17). It can be produced by polycondensation of 1,4-butanediol and succinic acid/anhydride using many different catalysts (18). PBS also has similar properties to polypropylene and low-density polyethylene, making commercial application promising (19).

Since PBS tends to have much higher molar mass values than those needed as a Bio-PCM, the addition of small glycerol ($C_3H_8O_3$) amounts, which tends to decrease molar mass values by ending chain growth (20). Thus, as low molar masses are achieved, we renamed PBS as OBS (Oligo (butylene succinate)). We also used phosphoric acid (H_3PO_4) as a catalyst, because it does not present any heavy metal, is highly available, and is a well-known catalyst (21).

The objective of this work is to test different variables combinations and show which OBS material has the best properties to be added as a Bio-PCM in concrete matrices. Considering that this research presents a deep statistical study exploring the effects of different variables in an experimental study regarding the production of a novel, renewable and relevant material for the construction industry, we believe it is highly relatable to this special edition of the Brazilian Journal of Experimental Design, Data Analysis and Inferential Statistics dedicated to ConBraPA 2020.

2. Material and Methods

In this section, we present the materials used in the study, as well as the methods experimentally performed.

2.1. OBS Synthesis

To synthetize Oligo (butylene succinate) (OBS), we used 1,4-buthanediol (99%, VETEC) and succinic acid (≥99%, VETEC). H3PO4 (85% v/v, VETEC) was used as the catalyst and glycerin (99,5%, VETEC) was used to reduce molar mass (13). 14 samples were made, with reaction times taking 1 to 3 hours, depending on the sample. All reactions happened at the same time and were performed at 130ºC. Aluminum foil was used to ease heat propagation. Figure 1 shows the prepared reactional system.

Figure 1: Synthesis of multiple Bio-PCM samples.

2.2. Statistical Design

This methodology was based on Box-Behnken design, a statistical model in which some criteria must be met: (1) each variable is divided in three spaced values; (2) the design needs to fit a quadratic model (contain squared terms, products of two factors, linear terms and intercept; (3) the ratio of experimental points should be reasonable; (4) the estimation variance should depend mostly on the distance from the center value (22).

Based on these conditions, a series of proposed reactions were made, which originated 14 different samples, all of them detailed in Table 1:

Table 1: Composition and reaction time of Bio-PCM samples

Sample	Time (h)	Glycerin (%)	Catalyst (%)
OBS1	1	2	0.0
OBS2	1	2	0.3
OBS3	1	3	0.1
OBS4	2	1	0.3
OBS5	2	1	0.0
OBS6	2	2	0.1
OBS7	2	2	0.1
OBS8	2	2	0.1
OBS9	2	3	0.3
OBS10	2	3	0.0
OBS11	3	1	0.1
OBS12	3	2	0.3
OBS13	3	2	0.0
OBS14	3	3	0.1

All sample total weight was around 4.5g. Samples OBS6, OBS7 and OBS8 were made with the same variables, since they are the central sample.

2.3. Simultaneous Thermoanalysis

Samples were analyzed by STA, a technique in which thermogravimetry (TGA) and differential calorimetry (DTA) are done at the same time to evaluate the sample thermal stability and exothermic events by the method of a heating ramp. The equipment used was a Perkin Elmer STA 6000 in N_2 atmosphere (purge gas—40 mL.min^{-1}) at temperatures between 30 and 700°C (heating rate = 20°C/min). A 3-min isotherm at 30 °C was used to stabilize the initial mass and temperature during the run.

3. Results and Discussion

Table 2 presents data taken from the thermoanalysis. OBS7 was chosen as the standard sample, since it was one of the center samples and the middle sample. Further discussion is made in Figures 2 and 3. Table 3 presents statistical measurements of the samples. Table 3 presents statistical measurements of the samples.

Table 2: Melting point of Bio-PCM samples

Sample	Melting Point (ºC)
OBS1	67.77
OBS2	68.34
OBS3	69.31
OBS4	68.20
OBS5	67.98
OBS6	68.33
OBS7	68.43
OBS8	68.35
OBS9	68.32
OBS10	68.98
OBS11	67.99
OBS12	68.48
OBS13	68.51
OBS14	68.14
OBS15	69.64

Table 3: Statistical measurements of Bio-PCM samples

Measurement	Results
Mean	68.76
Standard Error	0.13
Standard Deviation	0.49
Sample Variance	0.25
Range	1.79
Kurtosis	- 0.38
Skewness	- 0.08
95% Confidence limit	0.28

Standard deviation describes the dispersion from the sample values related to the mean, while standard error how far the sample is likely to be from the population mean. Since all samples presented such close results, both values were considerably small. The same happened with the 95% confidence interval, which is used to confirm whether estimation is trustworthy or not.

If the kurtosis (flattening the curve of the probability distribution function) data is more than twice the standard error, the data may have something uncommon with it (23). If the standard error is more than twice the skewness (the lack of symmetry in a frequency distribution), it may also mean uncommon data (24). Since the second case is true here, the present set of results present very different results from what one would expect, as will be further discussed in the present document.

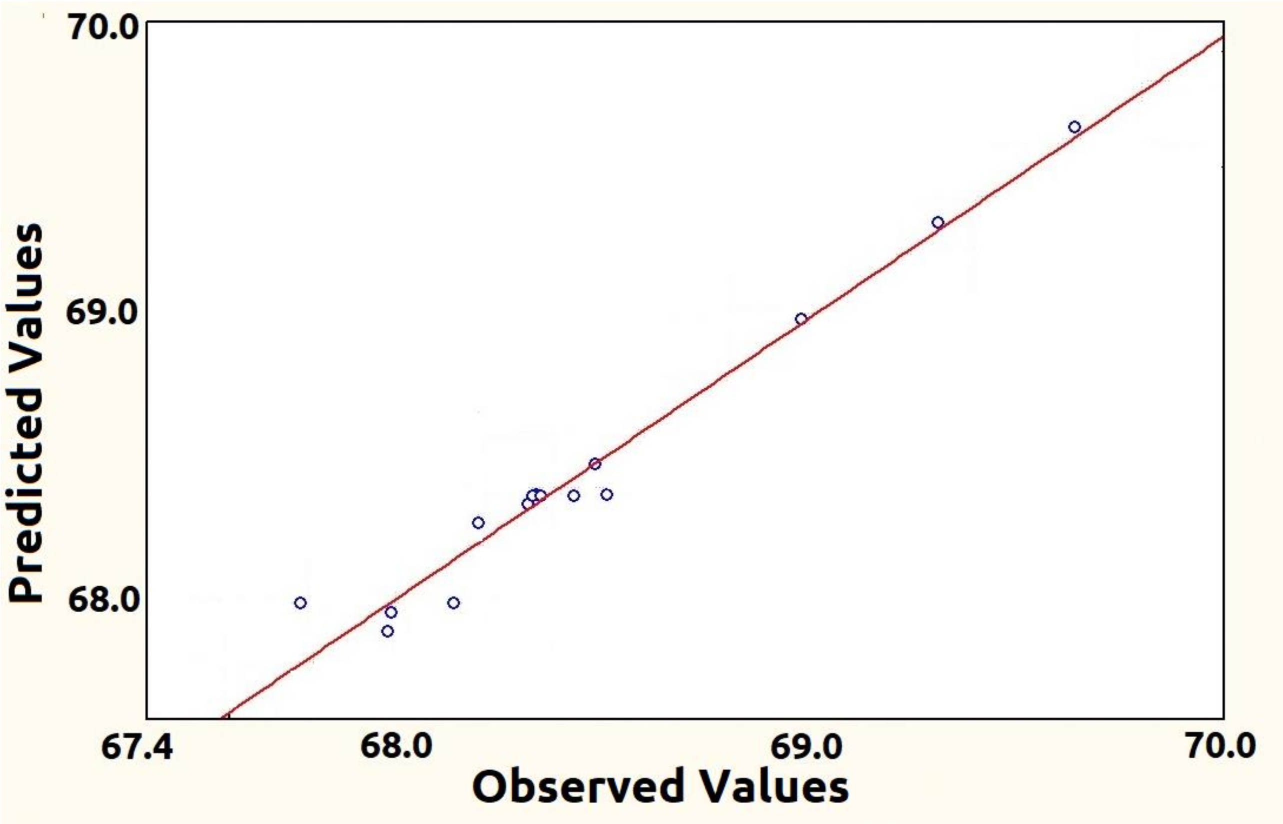

Figure 2: Observed versus predicted values

The results in Table 1 show that most samples were in the 67.7 - 68.6 ºC range, whereas the three samples increased to around 69ºC. No correlation occurs between the sample variables and the improved results. None of the materials presented a significant discrepancy between predicted and observed values.

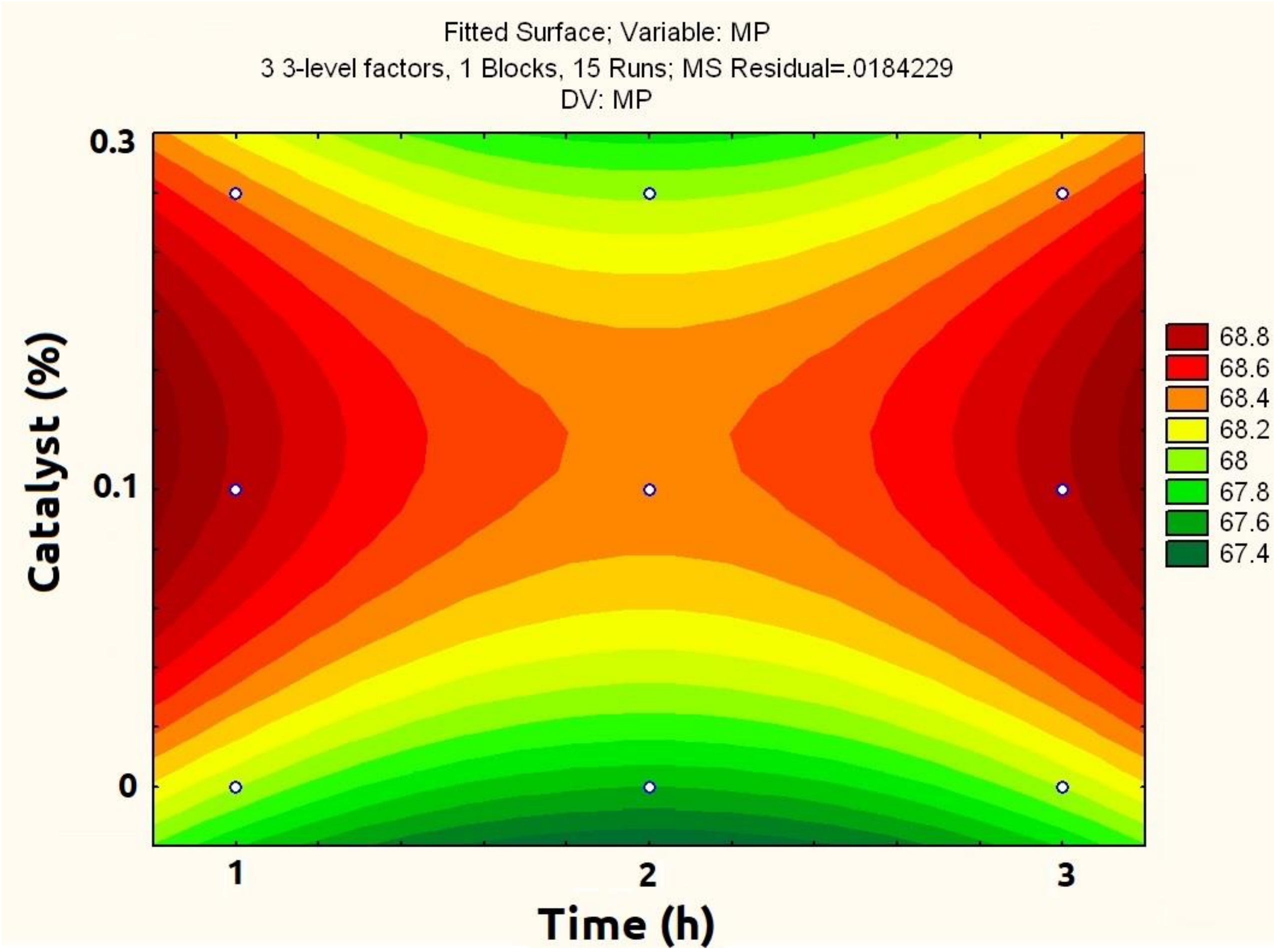

Figure 3: Correlation between the catalyst percentage and the reaction time.

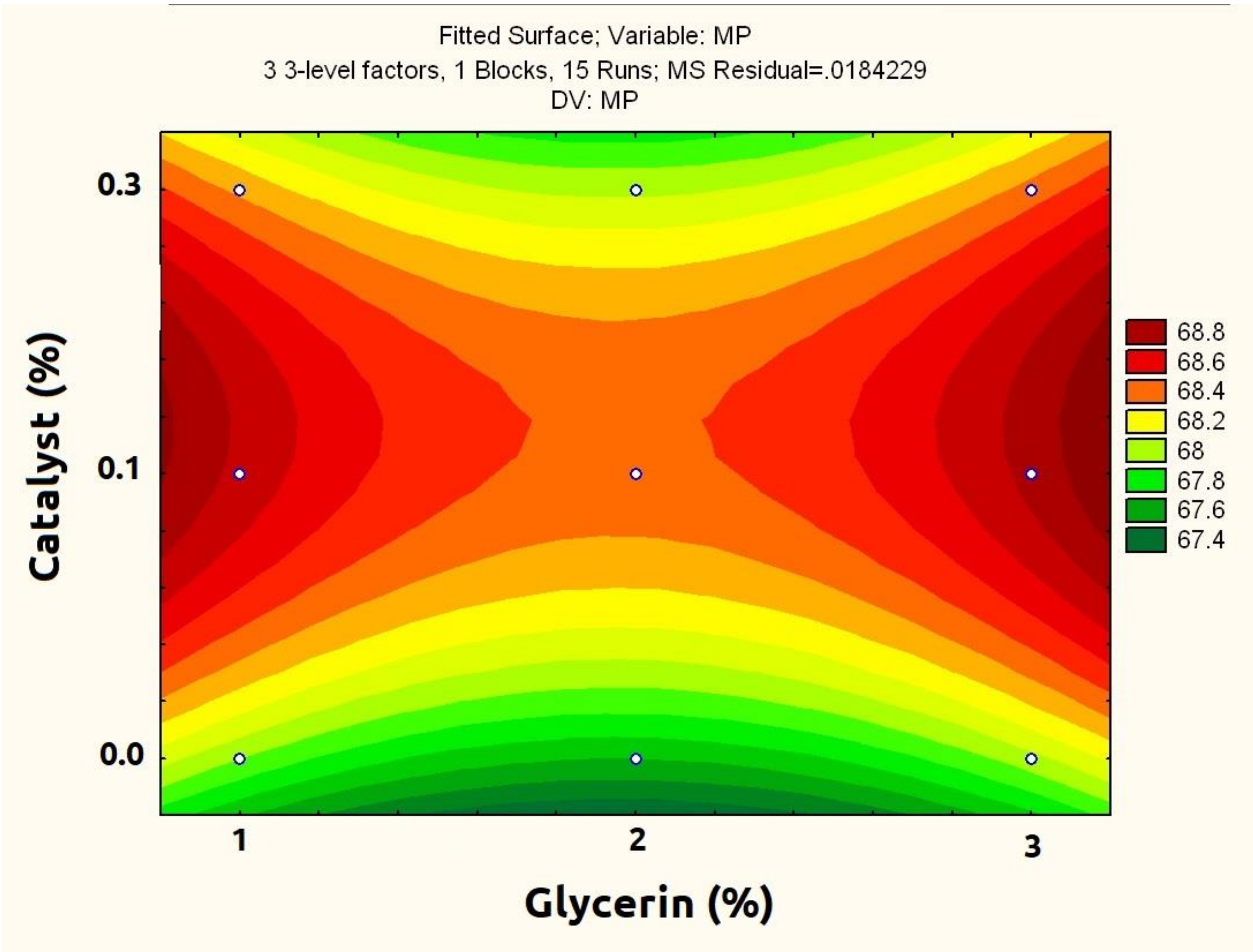

Figure 4: Correlation between the catalyst percentage and glycerin percentage.

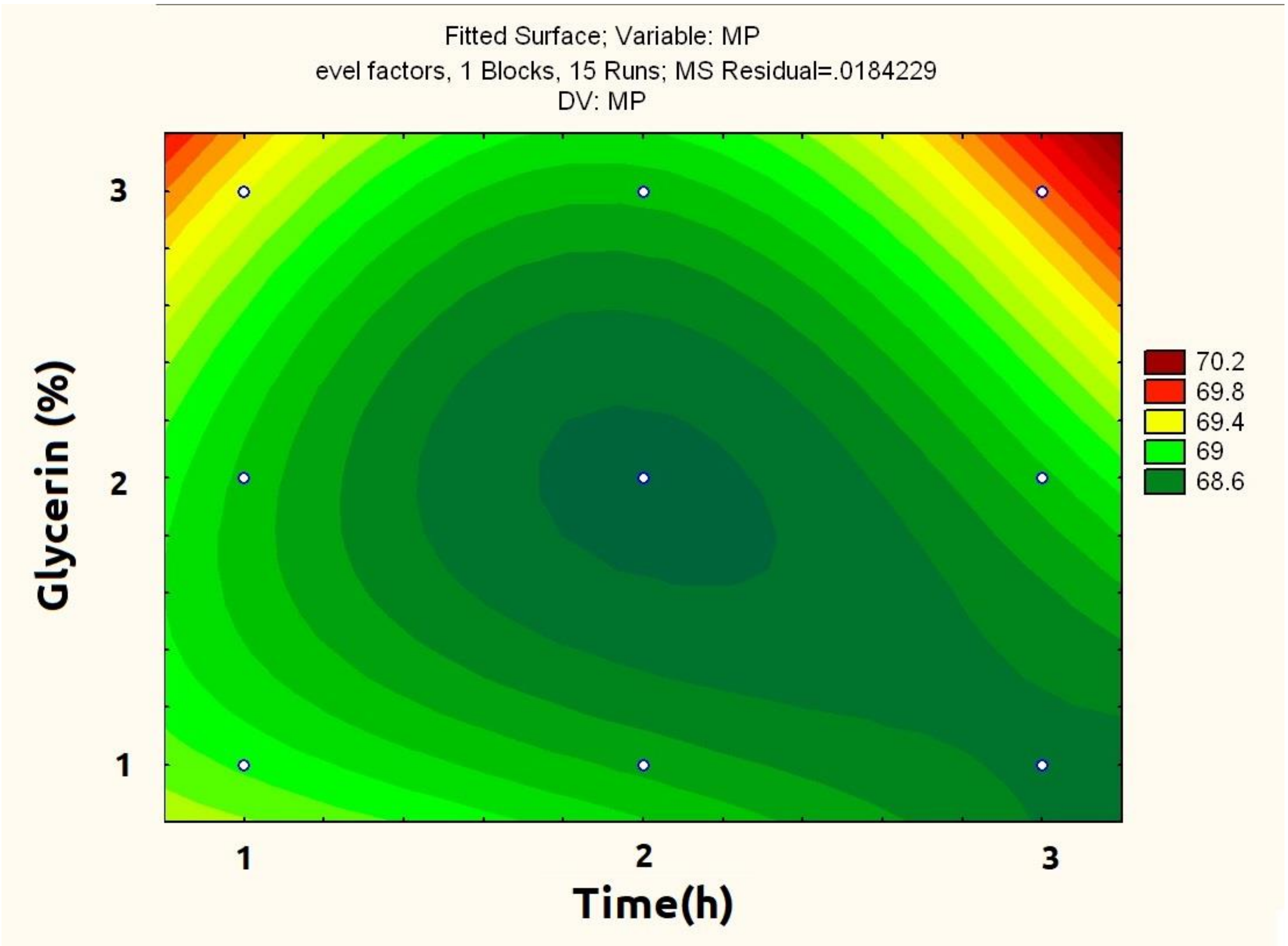

Figure 5: Correlation between reaction time and glycerin percentage.

Figure 3 correlates time elapsed and catalyst percentage. The middle time condition was the optimal one, which leads to believe that the samples that reacted during only one hour were not properly reacting at the time, causing distortions. However, catalyst concentration decreased melting point, contrary to the expected. One possibility is that the H^+ species prevented further polymerization by acting as a mono-functional reactant (25).

Again, Figure 4 shows the atypical decrease in the melting point caused by the increase in catalyst concentration. It is possible to see that the lowest melting point occurred by using the middle condition of glycerin. Further addition of this material would not be needed (26) and, as the data present, counterproductive since it could even help to increase the OBS crystallization through unknown reaction mechanisms. At last, Figure 5 confirms the middle conditions as the optimal for both glycerin concentration and time elapsed.

4. Final Considerations

The synthesized PBS-based phase change material presented an average melting point of 68ºC. As presented before, it is a huge decrease in the thermal stability of the material, which is desirable in this case. It is also worth noting that the melting points of the samples were dispersed, as shown by the response surface method.

By isolating every variable involved in the process, we concluded that the optimal conditions were: 0.3% of catalyst, 2% of glycerin, and 2h of reaction time. The catalyst might have acted as a mono-functional reactant, decreasing the melting point. Excess glycerin might not be useful and could have helped to increase crystallization through an unknown mechanism. The optimal time for the reaction to occur was the middle point, which might mean that, at only 1h of reaction time, the material might have not started to properly polymerize, causing distortions in the results.

The produced Bio-PCM system was a significant improvement from regular PBS, making it possible to further study this material as a possible additive to increase thermal resistance in concrete matrices. With further improvement, this Bio-PCM can decrease its melting point even further to the 30-50 ºC range, in order to have optimal results for this kind of application. These positive results are a step further to study concrete applicable PCMs. With further studies, it is possible to produce a concrete composite capable of having a much longer lifetime and stability, avoiding the production of both economic and environmental problems.

Conflict of Interest: None

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Credit author statement

Vítor Corrêa da Costa: Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation. Fernando Gomes de Souza Junior: Conceptualization, Supervision, Reviewing, Editing and Validation. Fabiola da Silveira Maranhão: Conceptualization, Methodology and Data analysis. Geiza de Oliveira: Reviewing and Validation. Romildo Dias Tolêdo Filho: Reviewing and Validation.

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