Optimization of Hydrophobic Coating Production by Pechini Method on Modified Aluminum Surface

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To fabricate a hydrophobic coating using the sol-gel method (Pechini), an experimental design using the drying time and chemicals ratio as variables was developed. The coating was deposited on an aluminum substrate (AA6061-T6) treated by acid solution or anodization method. The surface wettability was measured using a goniometric instrument. Coatings were fabricated using different numbers of layers, heating rates, and drying temperatures, and their morphologies were observed using visual analysis and scanning electron microscopy. The use of anodization treatment with a furnace ramp of 1 °C min^{-1}, a drying temperature of 220 °C ± 10 °C, and single-layer application, produced a coating free of visible flaws and apparent damage. The coating was obtained with a 15:1 glycerin:citric acid ratio and sample pre-polymerization in the drying oven for 1 hour at 100 °C resulted in the highest contact angle, 62° ± 2°, which meets the ASTM D-7334-08 standard for a hydrophobic surface.

Graphical abstract
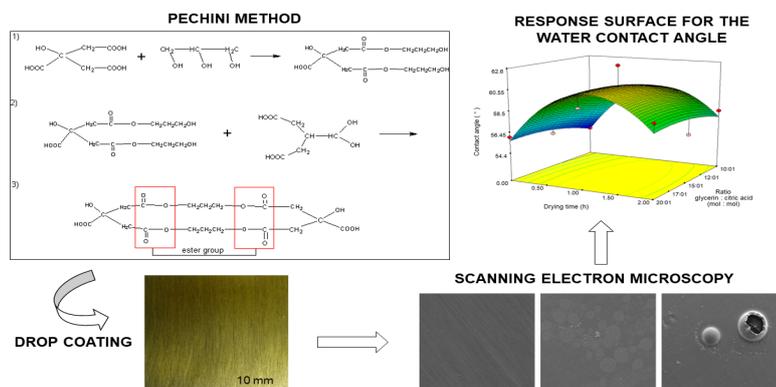
1. Introduction

Hydrophobic coatings are increasingly being utilized to protect windows, car windshields, solar panels, building exteriors, wind turbine blades, and other outdoor surfaces [1–6]. For those applications aluminum alloys is an attractive material due to its light weight, low density, flexibility, thermal conductivity, and corrosion resistance [7–13]. To provide efficient durability and avoid costly repairs, the development of coatings with high hydrophobicity for most applications is required, considering that one of the most problems is the

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presence of humidity [14–18].

Various preparation methods to increase or decrease the wettability of a surface have been developed, including vapor deposition, sol-gel, chemical etching, laser engraving, and electrospinning processes among others [19–24]. The sol-gel method is the preferred route to produce these coatings, because the desired properties such as hardness, roughness, surface energy, transparency can be easily adjusted through the formulation [25–29].

The Pechini process is a variation of the sol-gel method that consists of the formation of chelates between metal cations and carboxylic acids and subsequent polymerization using a polyesterification reaction with a polyalcohol [30,31]. Ethylene glycol is the most used polyalcohol, but glycerol can also be used as an alternative. Among the advantages of using the Pechini method, it can be mentioned: that the implementation of this technique only requires cheap chemicals, a beaker, a stirrer, a hot plate and an oven. This technique is also not sensitive to the presence of water (for rare exceptions); it does not require an inert atmosphere and, even without careful control of the time and conditions of gel processing, it should be possible to obtain samples of excellent homogeneity [32].

To produce hydrophobic coatings by the Pechini method, most authors have analyzed single parameters in isolation, for example, the molar ratio of the reagents [33,34] and the time intervals for the addition of the reactants to the mixture [35]. However, such simple optimization methodologies do not consider the combined effects of different parameters. The use of an experimental design that combines mathematics and statistics to analyze the relative importance of the different operational parameters [36,37] can be used to discover the ideal conditions for various reactions, and thus reduce the time, energy, and cost [38].

In this work, a hydrophobic coating on aluminum substrate (6061-T6 AA) prepared by acid solution or anodization was developed using a Pechini method. To obtain a quality coating, the number of applied layers, furnace ramp, and drying temperature were first studied, and then an experimental design was developed to investigate the effect of the drying time and reactant ratio, with contact angle as response.

2. Results and Discussion

Substrate treatment, drying, and deposition of the coating

The appearance of the coatings is shown in Fig. 1. From these images, it is possible to view the interaction between coating and the substrate after the acid (a) and anodization (b) treatments.

As shown in Fig. 1a, acid etching of the aluminum surface did not provide acceptable results; the coating was not fully adhered to the surface, resulting in some exposed areas. However, Fig. 1b shows that the adhesion of the coating was apparently uniform over the entire surface of the sample treated with anodization. This may have occurred due to the anchoring of the polyester film to the generated porous surface, since in anodizing the aluminum oxide produced in the process consists of two layers, that is, a very thin non-porous layer of the barrier type located close to the surface and a porous layer with a much greater thickness [39].

Images of the samples after drying are shown in Fig. 2. Treatment at heating rates of 0.5 °C min^{-1} (Fig. 2a) and 1 °C

min^{-1} (Fig. 2b) did not result in significant differences in terms of flaws or damage to the coatings. However, the sample heated at 2 °C min^{-1} (Fig. 2c) exhibited deformations and exposed areas (red circles). Thus, a heating rate of 1 °C min^{-1} was chosen for further study to minimize the amount of time and energy consumed during the process.
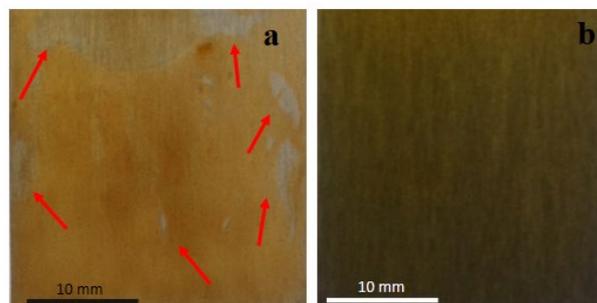
Fig. 1 Surfaces of the samples after the deposition and drying of the coating: initial treatment with acid attack (a) or anodization (b). The red arrows indicate the exposed aluminum areas.
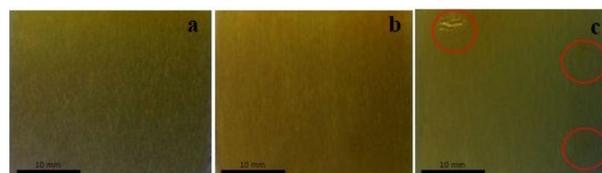
Fig. 2 Samples subjected to furnace heating rates of 0.5 °C min^{-1} (a), 1 °C min^{-1} (b) and 2 °C min^{-1} (c).

Fig. 3 illustrates the coatings obtained using different polymerization temperatures before and after immersion in deionized water for 7 days.

No significant differences were observed in the appearance of the samples subjected to temperatures of 180 °C ± 10 °C (Fig. 3a), 200 °C ± 10 °C (Fig. 3c), and 220 °C ± 10 °C (Fig. 3e) before immersion in water. However, after immersion in deionized water for 7 days, the coating detached from the sample treated at 180 °C ± 10 °C (Fig. 3b). In the sample treated at 200 °C ± 10 °C (Fig. 3d), air bubbles formed under the coating, causing an initial detachment. Thus, these two temperatures were not suitable for drying the coatings, mainly considering the applications of this process, which is generally exposed to environment with high humidity [15, 16].

The sample treated at 220 °C ± 10 °C (Fig. 3f) was the only one that showed no failure or damage after immersion in deionized water. Halpern et al. [40] studied the reaction between glycerol and citric acid at temperatures up to 150 °C and found that the resulting polymer is biodegradable and generates water as the primary byproduct, as the polyester has a large amount of free hydroxyl groups. Thus, the drying temperature of 220°C ± 10 °C provides a reference for describing the behavior of the coatings studied, because below this temperature the produced polyester reacts with water and dissolves. Above this temperature, the polyester has reduced amounts of hydroxyl groups, as they have reacted with the metal substrate to form covalent chemical bonds, making its solubilization in water improbable [19]. It is also important to point out that higher temperatures (230-270 °C) cause to the initial decomposition of the polymeric chains, and the proposed work loses its usefulness, since the main objective is to obtain an organic coating that prevents

the contact of water with the metallic substrate [41].
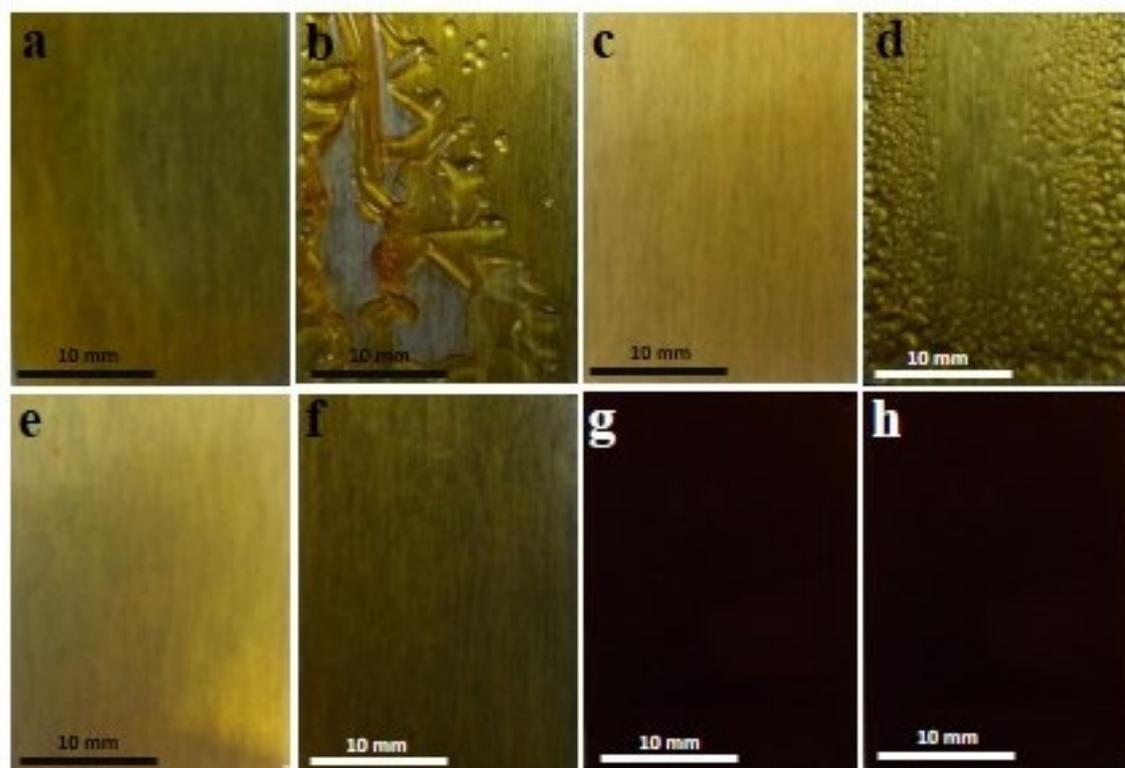
Fig. 3 Samples polymerized at different temperatures, before and after immersion in deionized water for 7 days. (a) and (b): 180 °C ± 10 °C; (c) and (d) 200 °C ± 10 °C; (e) and (f) 220 °C ± 10 °C; (g) and (h) 240 °C ± 10 °C.

The sample in Fig. 3g exhibited darkening compared to those treated at lower temperatures, indicating the degradation of the coating. This behavior reduces or makes impractical the applicability of this coating, mainly when it is necessary to consider the visual impact [17]. Nevertheless, the sample in Fig. 3h behaved similarly to that in Fig. 3f, with no visible flaws or damage to the coating.

The SEM study to determine the number of layers to be applied is shown in Fig. 4.
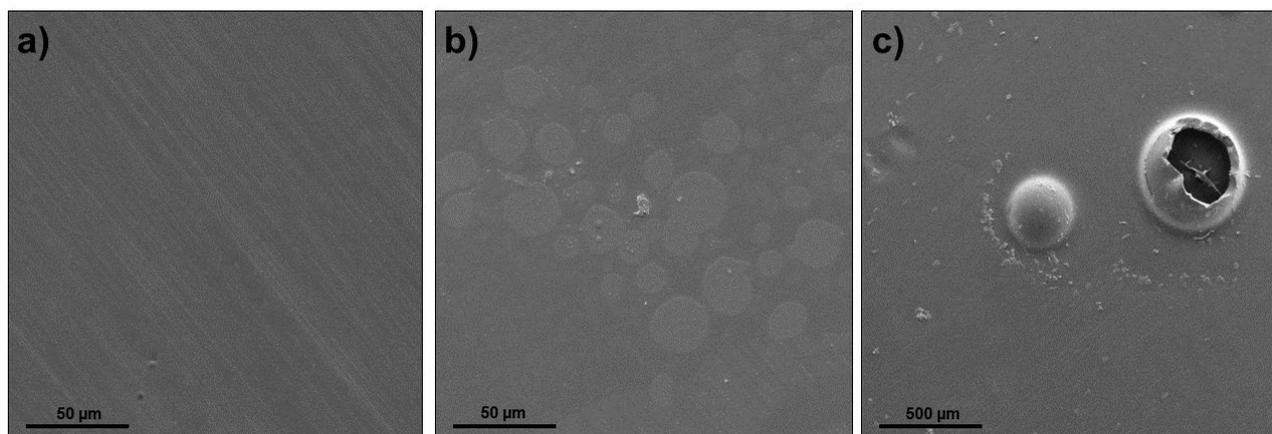
Fig. 4 SEM images of the samples with (a) one and (b) two layers of coating (1000x magnification), and (c) detail of the bubbles formed with two layers (100x magnification).

As can be seen from the images in Fig. 4a and 4b, the application of a second layer caused the coating to become less homogeneous and form bubbles. For this reason, the application of two or more layers was not considered further, because the presence of bubbles (Fig. 4c) leads to the formation of microholes that compromise the performance of the coating and allow exposure of the substrate to the aggressive environment. The formation of chelates between metallic cations and carboxylic acids, favors the adsorption of the coating to the surface, on the other hand, the bonding of the film to the surface with a polymeric layer was weakened [30,31].

Based on the analysis of the results, the conditions used

for sample preparation in further experiments were an anodized substrate, the application of a single coating layer, and drying at 220 °C ± 10 °C with a heating rate of 1 °C min^{-1}.

Wettability

Table 1 shows the contact angle measurements of water droplets under the conditions specified by the experimental design. In general, the measurements showed a difference of about ± 2°. In Figure 5, the images emitted by the goniometric equipment are shown, for the tests 1 to 9 of drop 1.

Table 1. Responses (water contact angles) for the various experimental design conditions.

Test	Drop 1 (°)		Drop 2 (°)		Average (°)	Deviation (°)
1	53.427	55.981	53.213	55.341	54.490	1.38
2	58.318	60.255	58.912	58,173	58.914	0.95
3	56.336	57.265	59.328	57.529	57.614	1.12
4	54.324	54.588	54.626	56.929	55.116	1.21
5	62.819	62.447	61.607	63.435	62.577	0.76
6	55.353	57.152	57.265	55.561	56.333	1.02
7	55.818	57,467	55.596	55.056	55.984	1.04
8	61.583	59.108	57.381	59.442	59.378	1.72
9	58.583	59.108	57.381	59.442	58.628	0.90
Polished aluminum	44.621	43.452	41.186	43.000	42.721	1.59
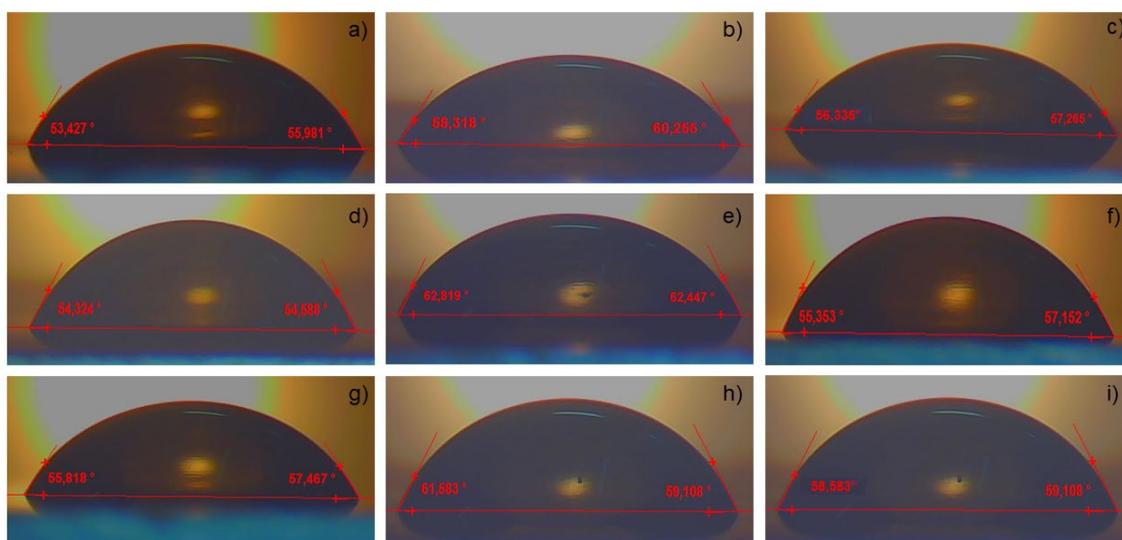
Fig. 5 images obtained by the goniometric equipment, for tests 1 to 9 (a to i, respectively) of drop 1.

According to the ASTM D-7334-08 standard [42], angles lower than 45° are characteristic of hydrophilic surfaces, and angles equal or higher than 45° are characteristic of hydrophobic surfaces. Thus, polished aluminum is characterized as a hydrophilic surface. The coated surfaces showed improved hydrophobic properties, with angles greater than 45° being obtained in all tests.

Using the contact angle values produced in response to the experimental design, the analysis of variance was used to determine the interaction between the factors and the corresponding level values. Among the several models tested, the quadratic model exhibited the best fit of the obtained data, generating the following equation:

$$\text{Contact angle (°)} = 60.63 + 0.50 * 1.16 * A + B - A * B\ 0.12 * - 0.51 * A2 - B2 * 3.93$$

The independent and dependent variables were examined and adjusted to the equation in terms of fit quality. Based on the ANOVA of the obtained values, it was possible to list all variables, their interactions, the respective effects, and the p-values. ANOVA was used to assess the adequacy of the model used, and the results are shown in Table 2.

Table 2. Summary of the ANOVA results.

Source	Sum of squares	degree of freedom	Mean Squares	f-value	p-value Prob> F
Model	41.05	5	8.21	2.54	**.2362**
A	1.47	1	1.47	0.46	.5478
B	8.13	1	8.13	2.52	.2106
AB	0.058	1	0.058	0.018	.9022
A^2	0.51	1	0.51	0.16	.7163
B^2	30.87	1	30.87	9.57	0.0536
Residual	9.68	3	3.23		
Total	50.73	8			
	R^2 = 0.809			**Adequate precision** = 4.237	

The mean values of the quadratic model, the independent variables, and their interactions differ significantly. This comparison can be made using the value of the average of the square of B (8.13) with the interaction between the factors A and B (0.058). This shows that the treatment of the experimental design affects the results and that, in principle, the model can be used to optimize the contact angle.

The data in Table 1 also shows that in the statistical model used, no factors or interactions had significant effects with p-values less than 0.05. Other statistical models were also tested; although none could suitably explain the interaction between factors, the quadratic model exhibited the lowest p-value. Thus, any combination of values of the factors can be used to continue the work, because the values obtained from the experiments showed no differences.

The value of the correlation coefficient (R^2) measures the extent to which the variability of the obtained response values can be explained by the experimental factors used beyond their interactions. To better predict the responses, the R^2 value should be close to 1.00. The obtained value of 0.809 indicates that the model explained only 80.9% of the responses within a 95% confidence limit. Nevertheless, this model had the largest R^2 among those tested.

The adequate precision value was greater than 4.000, indicating that the model can be used to explore different responses and indications for future studies to improve the polymeric coating deposition process on aluminum in order to increase the water contact angle. Such study could be performed using the response surface generated by ANOVA and shown in Fig. 6.
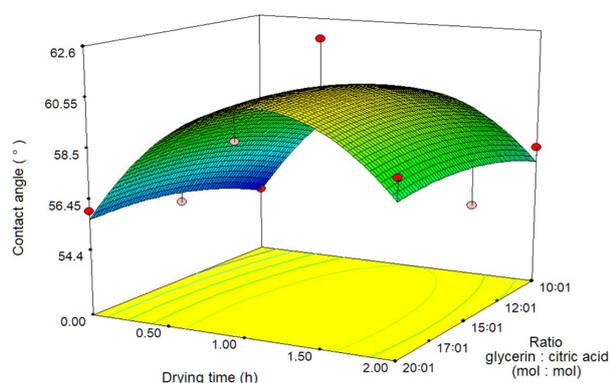
Fig. 6 Response surface for the water contact angle on the polymeric film coating as a function of the drying time and the glycerin:citric acid ratio.

In Fig. 6, the most satisfactory combination of factors was an intermediate drying time (1 hour) and intermediate glycerin:citric acid ratio (15:1), confirming the results of the experimental design shown in Table 1. Apparently, this combination should correspond to the region in which the largest contact angle values are found. However, the combinations of factors were very similar, as were the contact angle results, indicating that the factors were significantly independent, as evidenced in the ANOVA results.

Fig. 7 shows that the experimental values of most of the tests were close to those predicted using the statistical model. However, in tests 5, 6 and 8, the deviations between the experimental and predicted results were high, indicating that the model did not adequately represent the process or that the variation of the values of the factors did not differ

significantly in the responses obtained using the proposed experimental design. Therefore, the most significant deviation is noticed in test 5, and as seen in the graph in Fig. 6, here again it is shown the direction towards to a probable process optimization. Also, in the graph of Fig. 7, it is also possible to verify that the residual value (error) presented in the ANOVA results table is relatively high.
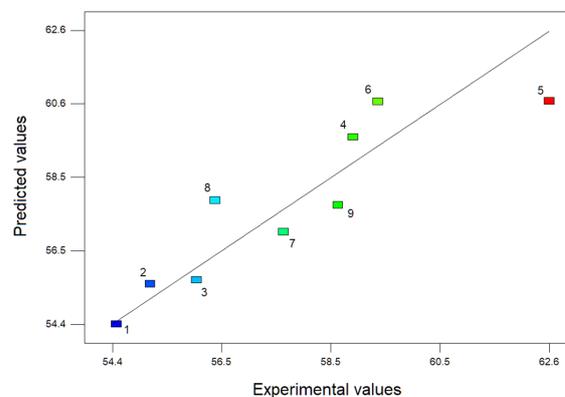
Fig. 7 Relationship between the experimental and predicted values generated by ANOVA of the contact angles of water on the coated anodized aluminum.

The ratio of the reactants used in the Pechini method affects the coating wettability and durability [1]. In the process of developing a hydrophobic coating, there is a risk of sacrificing the coating integrity when the proportions of the reagents are adjusted to obtain a high angle of contact, which in turn can lead to a cracking [35]. Therefore, herein is evidenced the necessity of developing an experimental design to obtain a hydrophobic surface using the Pechini method.

3. Material and Methods

Substrate preparation

An aluminum alloy (Al-Mg-Si AA6061-T6) was cut into rectangular plates with an average area of 32 cm^2 and subjected to a preliminary thermal treatment for recrystallization and relief of the internal stress generated by the cutting process [43]. The samples were treated at 350 °C for 4 hours with a heating rate of 5 °C min^{-1}.

The heat-treated substrate was sequentially polished with #340, #400, #600, and #1200 SiC paper, cleaned with ultrapure water, and dried with a flow of cold air. Then, the samples were immediately subjected to surface preparation by immersion in acid solution or anodization method. The first process consisted in immerse the samples in hydrofluoric acid (Anidrol®, 3 mol L^{-1}) for 5 minutes at 25 °C. For the anodization treatment, a sulfuric acid solution (Neon®, 10% m/v) was used as the electrolyte, and a constant current of 20 mA cm^{-2} was applied for 15 minutes using a Minipa® MPL-3303M power source with digital control. The values of these parameters were chosen based on the optimized conditions in previous studies [44]. The system for this process consisted of the prepared substrate as the anode and a similar plate of aluminum as the cathode, immersed in the electrolyte in a 250 mL polymeric vessel.

Preparation and deposition of the coating

The coatings were prepared by Pechini method, wherein the ethylene glycol normally used was replaced with bidistilled glycerin (Cloroquímica®) [45]. The glycerin:citric acid ((Dinâmica®) molar ratios used to obtain the polymers were 10:1, 15:1 and 20:1; to each 20 mL of bidistilled glycerin was added 0.1 g of aluminum chloride (Dinâmica®)[46]. The preparation consisted of heating the glycerol to 70 °C ± 5 °C, followed by the addition of citric acid with aluminum chloride, up to dissolution. Then, the mixture was allowed to stir for 1 hour at the same temperature. The deposition of the resin on the substrate was performed drop coating.

Drying and application of coating layers

The drying process consisted of placing the samples in an oven at 100 °C for 1 hour followed by treatment in a furnace. As the coating precursors were organic compounds, it was necessary to conduct a series of experiments to determine the optimal heating rate and final temperature. The heating rates tested were 0.5, 1 and 2 °C min^{-1}, and the final temperatures were 180 °C, 200 °C, 220 °C, and 240 °C [40]. For this study, the coated samples produced using each condition were immersed in deionized water for 7 days at 25 °C in order to observe the coating solubility [47].

The best conditions were chosen by visual analysis of the coatings for damaged or degraded regions, as recorded by optical images.

The application of one or two coating layers on the substrate was manually carried out after the oven drying but before the furnace heat treatment. For the application of the second layer, the sample was first cooled in a desiccator in order to make the first coating hard enough to not mix with the second. The number of layers to be applied was determined using scanning electron microscopy (SEM).

Experimental design

To verify the best wettability conditions, an experimental design was developed using the drying time and the glycerol:citric acid molar ratio as variables, as shown in Table 3. These variables can interact to determine the hydrophobicity of the Pechini coating [18]. Thus, a three-level factorial design with four center points was created, and the water contact angle measured on the surface of the coated sample was used as response. Analysis of variance (ANOVA) and response surface methodology (RSM) were used to verify the interaction/influence among the factors studied and for possible process optimization. Table 3 and 4 show the developed experimental design using the software Design Expert® 7.0. The confidence limit was set at 95%, and thus, only p-values below 0.05 were considered significant.

Table 3. Coded parameters levels and values.

Parameters	Symbol	Actual levels		
		-1	0	+1
Glycerin: Citric Acid (mol: mol)	A	10: 1	15: 1	20: 1
Drying time (hours)	B	0	1	2

The surface wettability of the samples was measured using a low-cost system with goniometric characterization via image, which operates with an error of 2% [48]. The evaluation of the water contact angle was based on ASTM D-7334-08 [42], which concerns measurement of the advancing contact angle. A 10 μL volumetric micropipette and distilled water were used to generate droplets on a cleaned and dried surface sample. The contact angle values were obtained from the average of two drops positioned on different regions of each sample surface.

Table 4. Experimental matrix.

Standard order	Order of tests	Coded variables		Real variables	
		A	B	A / mol: mol	B / hours
1	4	-1	-1	10: 1	0
2	1	-1	0	10: 1	1
3	6	-1	1	10: 1	2
4	2	0	-1	15: 1	0
5	5	0	0	15: 1	1
6	3	0	1	15: 1	2
7	8	1	-1	20: 1	0
8	9	1	0	20: 1	1
9	7	1	1	20: 1	2

4. Conclusions

The coating produced on anodized aluminum with the Pechini method was visually free of damage and adhered over the entire surface. The best parameters to obtain an undamaged coating were a heating rate of 1° C^{-1} min, a drying temperature of 220 °C ± 10 °C, and the application of a single coating layer. The surface of the obtained coating was hydrophobic according to the ASTM D-7334-08 standard. A 15:1 glycerin:citric acid ratio and pre-polymerization of the sample in an oven for 1 hour at 100 °C resulted in the best contact angle, 62° ± 2°, among the tested proportions.

Acknowledgments

Author Contributions

Conceptualization, Ariane Aparecida de Lima, Lucas Aparecido Bittencourt, Guilherme José Turcatel Alves; Methodology Investigation, Ariane Aparecida de Lima, Gideã Taques Tractz, Guilherme José Turcatel de Alves. Resources Data curation, Ariane Aparecida de Lima, Lucas Aparecido Bittencourt, Guilherme José Turcatel Alves; Writing-original draft preparation, Ariane Aparecida de Lima, Gideã Taques Tractz Writing-review and editing supervision, Paulo Rogério Pinto Rodrigues, Cynthia Beatriz Fürstenberger; Project administration, Paulo Rogério Pinto Rodrigues, Cynthia Beatriz Fürstenberger.

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