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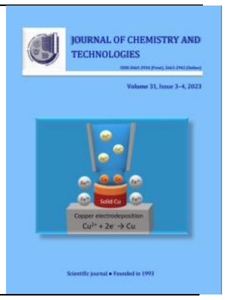

UDC 628.483

INFLUENCE OF THE COMPOSITION OF MODIFIED LIGNIN-EPOXY COATING ON CORROSION RESISTANCE USING RESPONSE SURFACE METHODOLOGY

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Abstract

Bisphenol A epichlorohydrin (BPA-EC) as a resin, and cycloaliphatic amine (CAA) as a curing agent, are conventionally used for formulating epoxy coatings for industrial applications. However, due to its noticeable toxicity, alternative curing agents such as aminopropyl triethoxysilane (APTES) can be used instead of CAA. Moreover, BPA-EC can be partially replaced by kraft lignin. In this study, the influences of APTES, BPA-EC, and kraft lignin on corrosion resistance were analyzed using the robust statistical analytical capabilities of the existing optimization models. Response surface methodology and the Box–Behnken design model were used to investigate the respective and cumulative effect of each element. Initially, the model has a P value of 0.0037, with some of the terms not significant. Thus, a modified model has been introduced keeping only the significant terms. Finally, a P-value of 0.0004 has been achieved. Although the model showed a non-linear association for all the constituent elements, no cumulative relation has been found. However, statistics showed that BPA-EC is a necessary element for the coating to be corrosion-resistive, as corrosion resistance of the coating is proportional to the quantity of BPA-EC in the coating. Thus, the study concludes that in an attempt to decrease toxicity from the proposed APTES-cured coating matrix, BPA-EC cannot be completely replaced by lignin.

Keywords: aminopropyl triethoxysilane; Bisphenol A epichlorohydrin; Box–Behnken design model; carbon steel; lignin; organic coating.

ДОСЛІДЖЕННЯ ВПЛИВУ СКЛАДУ МОДИФІКОВАНОГО ЛІГНІНО-ЕПОКСИДНОГО ПОКРИТТЯ НА КОРОЗІЙНУ СТІЙКІСТЬ З ВИКОРИСТАННЯМ МЕТОДУ ПОВЕРХНІ ВІДГУКУ

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Анотація

Епіхлоргідрин бісфенолу А (BPA-EC) як основа і циклоаліфатичний амін (CAA) як затверджувач зазвичай використовуються для створення епоксидних покриттів для промислового застосування. Однак, через його помітну токсичність, замість CAA можуть бути використані альтернативні затверджувачі, такі як амінопропілтриетоксисилан (APTES). Крім того, BPA-EC можна частково замінити лігніном. У цьому дослідженні було проаналізовано вплив APTES, BPA-EC та лігніну на корозійну стійкість з використанням надійної статистичної аналітики сучасних оптимізаційних моделей. Методологія поверхні відгуку та розрахункова модель Бокса-Бенкена були використані для дослідження індивідуального та кумулятивного впливу кожного елемента. Початково модель мала значення P 0.0037, а деякі члени моделі не були значущими. Таким чином, було запроваджено модифіковану модель, в якій залишились лише значущі члени. В результаті було досягнуто P-значення 0.0004. Хоча модель показала нелінійну асоціацію для всіх складових елементів, кумулятивного зв'язку не було виявлено. Статистика показала, що BPA-EC є необхідним елементом для корозійної стійкості покриття, оскільки остання пропорційна кількості BPA-EC в покритті. Таким чином, в дослідженні зроблено висновок, що в спробі зменшити токсичність запропонованої матриці покриття, отвердженого APTES, BPA-EC не може бути повністю замінений лігніном.

Ключові слова: APTES; розрахункова модель Бокса-Бенкена; BPA-EC; вуглецева сталь; лігнін; органічне покриття.

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Introduction

The investigation of durable organic coatings derived from epoxy-lignin compositions has been a topic of research for a considerable period [1–3]. However, lignin normally has poor solubility in the lignin-based coating, which can limit the performance of lignin-based products [4–6]. Thus, the coating often is addressed as mediocre [5]. Moreover, epoxy-lignin coatings are prone to migration of moisture and oxygen in case they are gouged or damaged [7]. This phenomenon results in the acceleration of corrosion in the affected areas, undermining the overall effectiveness of the coating. Moreover, the developed coatings often lack adhesion strength, and the strength evaluation is limited only to ASTM D3359 and ASTM D3363 standards [8–10]. Moreover, the materials and processes used to synthesize the coatings can sometimes be environmentally harmful. The study of Binbin Zhang et al. [11] is one of the few studies addressing these aspects. Thus, a different approach has been taken by the current study in the formulation of the coating.

Bisphenol A epichlorohydrin (BPA-EC) stands as a versatile fusion of synthetic polymers, finding extensive utilization in the production of epoxy resins and coating applications. However, the report from the safety data sheet suggests that the toxicity level of BPA-EC is not insignificant. LC_{50} is a testing criterion for toxicity, where the amount of any compound responsible for the annihilation of 50% of the population within 96 hours represents the toxicity level of that compound. The amount of BPA-EC in this aspect is 1.3mg/l [12] and of Cycloaliphatic amine (CAA) is 3.6mg/l [13] for Oncorhynchus mykiss (OM) for 96 hrs. Thus, the toxicity of both BPA-EC and CAA cannot be neglected. On the contrary compounds like lignin and aminopropyltriethoxysilane (APTES) have significantly less toxicity, requiring >100mg/l [14] and >934mg/l [15] to get the 50% population decrease, respectively. The Fig. 1 shows the equivalent toxicity of CAA, lignin, and BPA-EC; in respect of APTES . It is manifested that BPA-EC and CAA are 718.46 and 259.44 times more toxic than APTES, respectively. The presented data demands to fully replace the BPA-EC and CAA with lignin and APTES. However, the influence of BPA-EC in enhancing corrosion resistance has yet to be investigated. Functionalization of lignin by APTES is not a rare practice. The successful methods of An et al. [16] and Qi Yuan Ng et al. [17] have inspired the current study to develop a less complicated method for forming an organic coating with BPA-EC, and lignin, cured by APTES. Thus, the current study focused on the influence of the composition on the mitigation ability of the coating, utilizing the existing optimization model.

Inspired by the study of Jamshid Behin et al. [18] on the enhancement of the adhesion strength of lignin/epoxy coating, by optimization approach, the current study attempted to use Box–Behnken design model in response surface method. The study of Xintian Liu et al. [19] played a crucial role in deriving the outcome of the optimization model, where the Box–Behnken design model has also been used to enhance the contact angle and heating rate of the graphene oxide dopped epoxy coating. The contribution of the current study is listed as follows –

I. Although An et al. [16] has synthesized one polycomposite with successful bond formation between polyurethane and APTES functionalized lignin, no published studies havebeen found on the development of a coating containing epoxy resin (BPA-EC) and APTES-cured lignin..

II. Based on the review of the author, the composition of the developed organic coating has not been analyzed from a statistical point of view. Consequently, not a single model has been developed that takes into account the effect of the composition on the corrosion resistance of the developed coating.

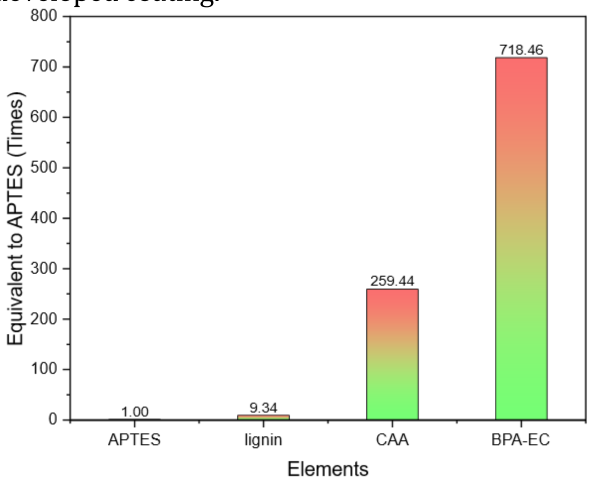

Fig. 1. The equivalent toxicity of coating elements in respect of APTES.

Materials and Methods

Materials

BPA-EC was purchased as a form of epoxy resin (EP, epoxy value: 5.1 mmol/g), APTES (purity 98 %) and kraft lignin (alkali, low sulfur content) were purchased from Sigma-Aldrich. Ethanol 99.7% (denatured) (molecular mass 46.07 gram per mole) was purchased from R&M Chemicals.

Preparation of the substrate

The substrates used in the study, have an area of around $1cm^2$ carbon steel blocks, obtained from the A333 carbon steel pipeline, as shown in Fig. 2 (A). The preliminary observation revealed that based on standard ISO 8501 1, followed for the coating implementation on carbon steel, the substrates were ready for coating implementation

Preparation of the coating

The preparation method was inspired by the formulation of Qi Yuan Ng et al. [17], where they used APTES as lignin functionalizer to work as a curing agent for organic polymer. Initially, different quantities of BPA-EC, ranging from 1.305 grams to 1.0875 grams, were dispersed in a 10 ml solution of 99 % ethanol solvent and subjected to mechanical shaking for 10 minutes using an IKAKS 260 compact flat orbital shaker. Kraft lignin weighing 1.305 grams was then added to the solution for all compositions, followed by an additional 10 minutes of mechanical shaking and 15 minutes of sonication. Next, APTES in varying volumes ranging from 0.27 ml to 89.14 ml were added dropwise using a micropipette and quickly sonicated for 15 minutes at 60 °C.

Thus, the resulting coating in the form of a semi-transparent liquid was uniformly implemented dropwise on the substrate. 100 µl of the drop has been found to be enough to form a coating of 60 microns (± 40 microns) thickness. The freshly applied coating was heated for 20 minutes under 60 °C temperature, followed by 3 days curing under room temperature (Fig. 2(C)).

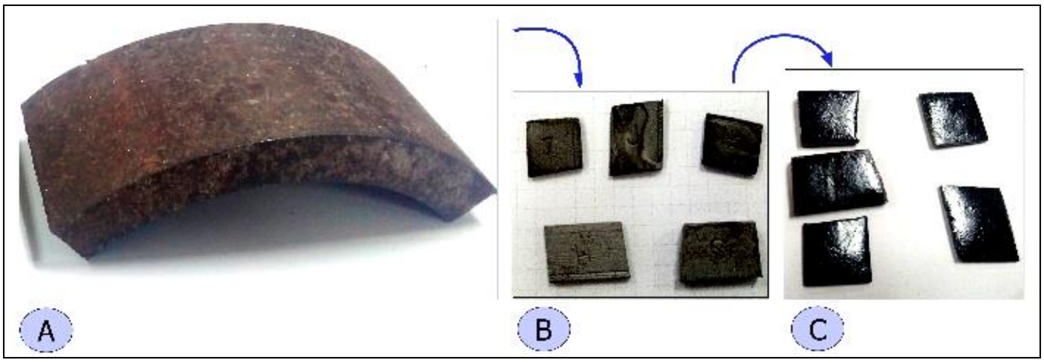

Fig. 2. A portion was cut off from the A333 carbon steel pipe (A). The small blocks were extracted from the block by a band saw machine and hack saw (b). Furthermore, the blocks were punched with markings for easy tracking (B). Eventually, the blocks were sandblasted and coated through micro pipetting (C).

Electrochemical test & characterization

The corrosion resistance of the coatings was analyzed by Electrochemical Impedance Spectroscopy (EIS) test in the pH 5 solution with 0.2 ppm H_2S concentration at room temperature, to replicate the mild corrosive environment of the observed site of Bakun Hydroelectric Power Plant. A standard setup was selected for the test, and the continuity test was conducted for each sample before the test (Fig. 3). A concentrated solution of 0.2 ppm H_2S solution with a pH level of 5 has been prepared as follows-

First, a stock solution was prepared by dissolving 0.1803 gm of Na_2S into 80 ml of deionized water (DI water) and another stock solution of Na_2SO_4 was prepared by dissolving 12 gm of Na_2SO_4 into 120 ml of DI water. Then from the stock solutions, 30 ml of Na_2SO_4 and 0.368 ml of Na_2S were dissolved into 950 ml of DI water under continuous stirring at 700 RPM. Afterward, pH 5 was achieved by adding a mild concentration of H_2SO_4 dropwise to the solution until the pH meter read pH 5.

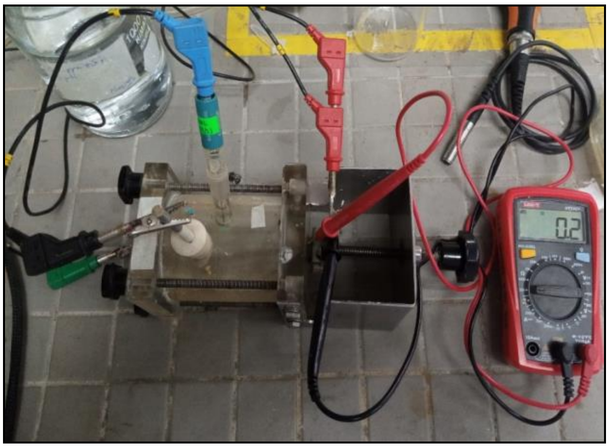

Fig. 3. The coated blocks were connected to the working electrode (red colored plug), a stainless-steel rod was inserted as the reference electrode (black colored plug), and the same counter electrode was used in each EIS test (blue colored plug).

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Experimental Model

Considering the existence of multiple factors, the response surface method (RSM) is a good way to analyze the interaction between those factors. To characterize corrosion resistance, corrosion resistance was introduced as the response. The preparation of the experimental scheme was designed by the Box–Behnken Design (BBD) method using the software Design Expert.

Box–Behnken Design (BBD) model has been assigned with three variables, addressing three elements of the coating, namely APTES, BPA-EC, and lignin. In contrast to a full factorial design, 16 Table 1 experimental runs were performed, which included 4 center points per block, and 1 central point, prescribed by the model. The Natural Log transformation gave the best agreements, considering P-value, R^2, and lack of fit. Initially, the Linear model was selected for analysis with the sequential P value of 0.0037, lack of fit value of 0.3106, adjusted R^2 of 0.5772, and predicted R^2 of 0.333. However, modification of the model gave better agreement with the P value of 0.0004. The variables and their levels selected for this study are presented in Table 1. The range of these three parameters was chosen based on the preliminary experiments and the literature review [20; 21], illustrated in Table 2. The prescribed experimental data point and obtained results are shown in Table 3.

Table 1

Response surface analysis factor level

Code id	Name	Units	Low	High
A	APTES	gm	1	1.5
B	BPA-EC	gm	4	6
C	lignin	gm	4	16

Table 2

The justification of the range assigned in the design model. The letter 'x' indicates any value of APTES, within the range.

A:B: C	Justification
1.5:4:4	The highest percentage of curing agent (A) (15.8 wt.%) was found in the study of Sushmitha Devadasu et al. [20], where APTES was used as a curing agent for the lignin-based coating.
1:6:16	The lowest ratio for the curing agent (4.35 wt.%) was from the preliminary adhesion strength study. The percentage (4.35 wt.%) marginally falls below the minimum adhesion strength of 500 psi for the splash area, as per the coating adhesion standard of PETRONAS Technical Standard (PTS), which is 429 psi.
x:4:16	The ratio has the highest share of lignin at 80 wt.%, excluding the curing agent. From the adhesion study of 1:4:12 and 1:8:12, 689 psi and 685 psi pull-off strength has been found, respectively, addressing negligible differences. Hence, it has been considered that beyond 3 times the amount of BPA-EC for lignin, the variation in strength gets negligible. Thus, the highest share of lignin has been selected 4 times of BPA-EC, to get better confirmation.
x:6:4	The lowest share of lignin with 40 wt.%, excluding the curing agent, was found in the study of Feldman et al. [21] for epoxy/lignin resin composition of 40 wt.%. In the study the 40 wt.% lignin content was found with reasonable adhesion strength of 10MPa. Thus, the highest share of lignin was selected 4 times of BPA-EC, to get better confirmation.

Results and discussion

Analysis of corrosion resistance

The R_{cr} data was optimally fitted using a multivariate regression analysis approach, conducting a response surface regression analysis on the experimental outcomes documented in Table 3. The value of the corrosion resistance of the coating was obtained from the circuit fitting from the NOVA 2.1 software. The polarization resistance was considered as the corrosion resistance for the coating. The EIS results have been illustrated through multiple graphs for better understanding, as the values differ at a high order of magnitude (Fig. 4, Fig. 5, Fig. 6 & Fig. 7). Table 4 displays the results of the variance analysis and the derived empirical, derived from Inverse transformation, presents the regression equation for the R_{cr} fitting. Here, 'Y' represents the R_{cr}. By default, the high levels of the factors are coded as +1 and the low levels are coded as −1. Based on the analysis in Fig. 8(a), the experimental data and predicted values are considerably distributed along a straight line, indicating that the difference between the predicted value and the real value is small. Fig. 8(b) shows that the residual error of the experiment is distributed along a straight line, which is a good accuracy. Fig. 8(c) shows the relationship between the residual and the predicted value R_{cr}. The distribution of data points is random and uniform, considering the model to be able to predict the experimental results accurately in theory. As can be seen in Fig. 8(d), the

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residuals of each data point are in the range of (−3.78, +3.78), indicating that the data or model operation error is small. Therefore, it can be judged that the model fits the experimental data well.

Table 3

BBD matrix and results

Run	A: APTES	B: BPA-EC	C: lignin	R_{cr}	Run	A: APTES	B: BPA-EC	C: lignin	R_{cr}
	gm	gm	gm	degree		gm	gm	gm	degree
1	1.25	4	4	26148.00	9	1.25	5	10	24314.00
2	1.5	6	10	75285.00	10	1.25	5	10	2354.90
3	1.5	5	16	902.2	11	1	5	4	21189.00
4	1.5	5	4	8211.00	12	1.25	6	4	27000000
5	1.25	6	16	808000.00	13	1	5	16	123.40
6	1	4	10	122.26	14	1.25	5	10	2760.40
7	1	6	10	6073.90	15	1.5	4	10	1361.40
8	1.25	4	16	133.00	16	1.25	5	10	37786.00

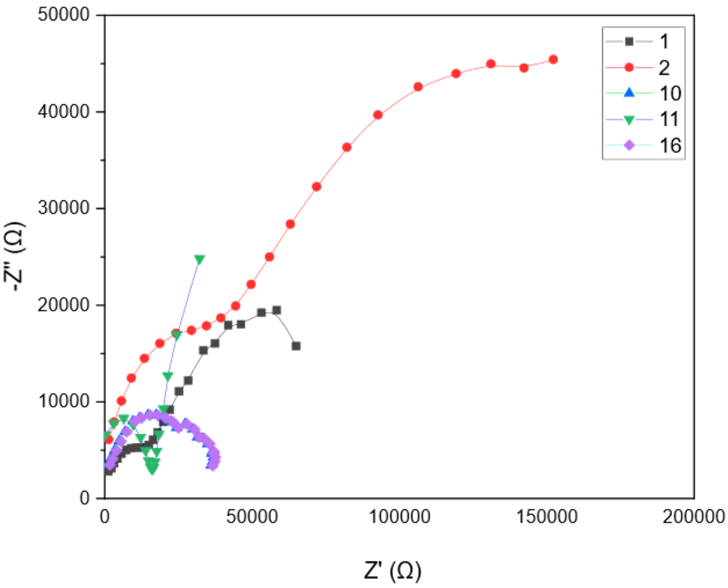

Fig. 4. The Nyquist plots of the sample 1, 2, 10, 11, 16.

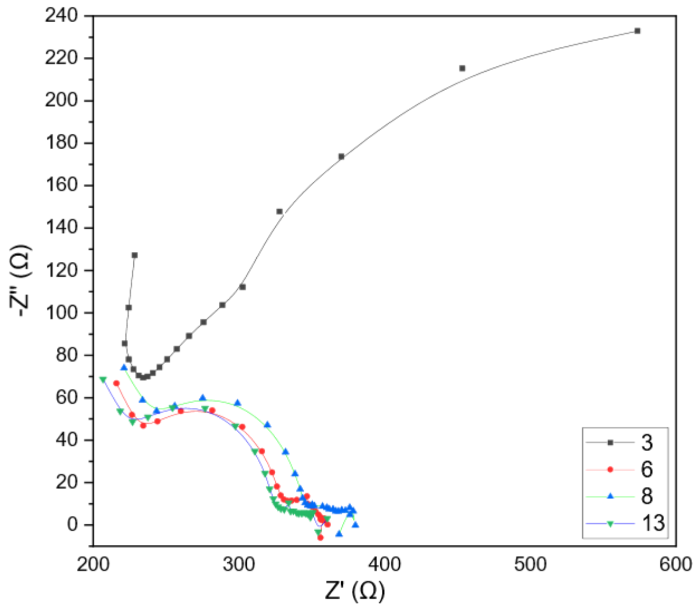

Fig. 5. The Nyquist plots of the sample 3, 6, 8, 13.

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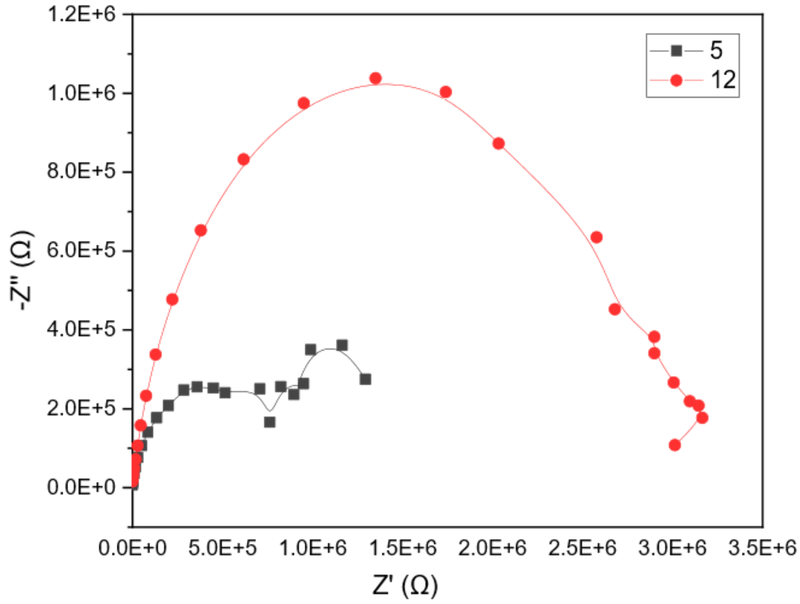

Fig. 6. The Nyquist plots of the sample 5, 12.

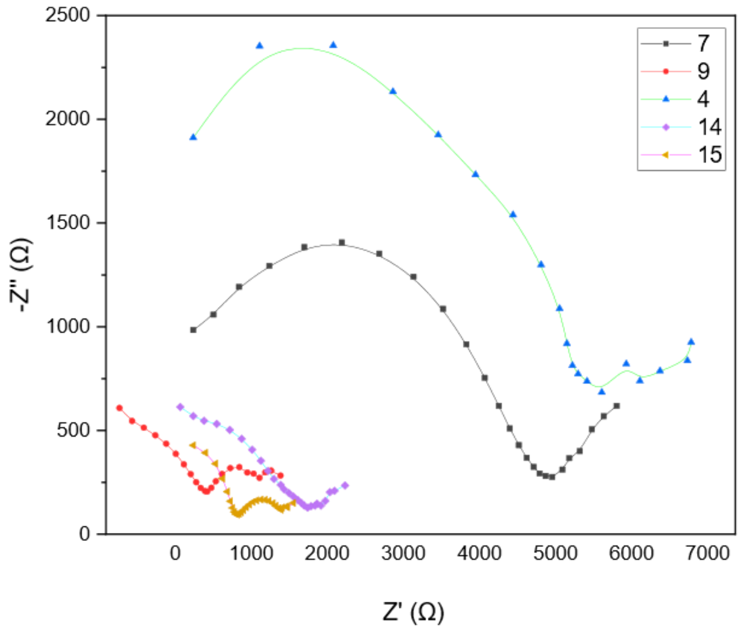

Fig. 7. The Nyquist plots of the sample 4, 7, 9, 14, 15.

Table 4

Variance analysis of response surface experiments of Rcr, using the linear model, with Natural Log Transformation

Source	Sum of Squares	df	Mean Square	F-value	p-value	Effect
Model	84.94	3	28.31	7.83	0.0037	**significant**
A-APTES	4.45	1	4.45	1.23	0.2890	
B-BPA-EC	56.54	1	56.54	15.63	0.0019	
C-lignin	23.95	1	23.95	6.62	0.0244	
Residual	43.41	12	3.62			
Lack of Fit	37.18	9	4.13	1.99	0.3106	**not significant**
Pure Error	6.24	3	2.08			
Cor Total	128.36	15				

P-values less than 0.0500 indicate model terms are significant. In this case, *A* is not a significant model term. Values greater than 0.1000 indicate the model terms are not significant. The F-value of the fitting model is 7.83, which implies the model is significant. The probability that such a large F-

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value may occur due to the noise is only 0.37 %. In the model, elements with a P-value less than 0.05 are significant at a 95 % confidence level. The Lack of Fit F-value of 1.99 presents that the lack of fitting is not significant relative to the pure error. There is a 31.06 % chance that an F-value of this magnitude could occur due to noise.

$$Y = 8.8973 + 0.7461A + 2.6585B - 1.7302C \quad (1)$$

However, compared with the quadratic model A^2 was found to be a significant term. Thus, the model has been modified and reanalyzed to achieve better agreement, reducing the relatively nonsignificant terms from the equation. Table 5 displays the results of the variance analysis and the derived empirical of the modified model, derived from Inverse transformation, presents the regression equation for the R_{cr} fitting. There is only a 0.04 % chance that an F-value of 13.53 large could occur due to noise. From Table 5, *B, C* & A^2 are significant model terms. The Lack of Fit F-value of 1.23 presents the lack of fitting is not significant relative to the pure error. There is a 48.13% chance that an F-value of this magnitude could occur due to noise. The Predicted R^2 of 0. 5727 is in reasonable agreement with the Adjusted R^2 of 0. 7148. with the difference being less than 0.2. Adeq, Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable, which is 11.7803 in this aspect (Table 6).

Table 5

Variance analysis of response surface experiments, using the modified model with Natural Log transformation

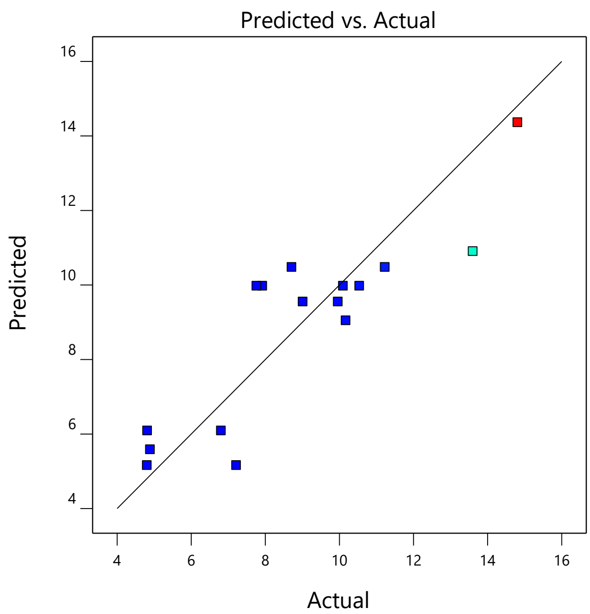
Source	Sum of Squares	df	Mean Square	F-value	p-value	Effect
Model	99.07	3	33.02	13.53	0.0004	**significant**
B-BPA-EC	56.54	1	56.54	23.16	0.0004	
C-lignin	23.95	1	23.95	9.81	0.0087	
A^2	18.58	1	18.58	7.61	0.0173	
Residual	29.29	12	2.44			
Lack of Fit	23.05	9	2.56	1.23	0.4813	**not significant**
Pure Error	6.24	3	2.08			
Cor Total	128.36	15				

Table 6

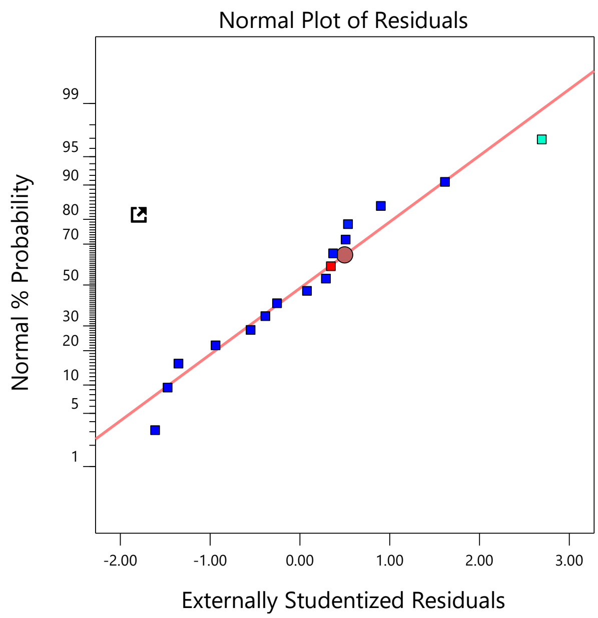
Fit Statistics of the Modified Model

Std. Dev.	Mean	C.V. %	R^2	Adj. R^2	Pred. R^2	Adeq. Precision
1.56	8.90	17.56	0.7718	0.7148	0.5727	11.7803

$$Y = 9.97486 + 2.6585B - 1.7302C - 2.1551A^2 \quad (2)$$



(a)



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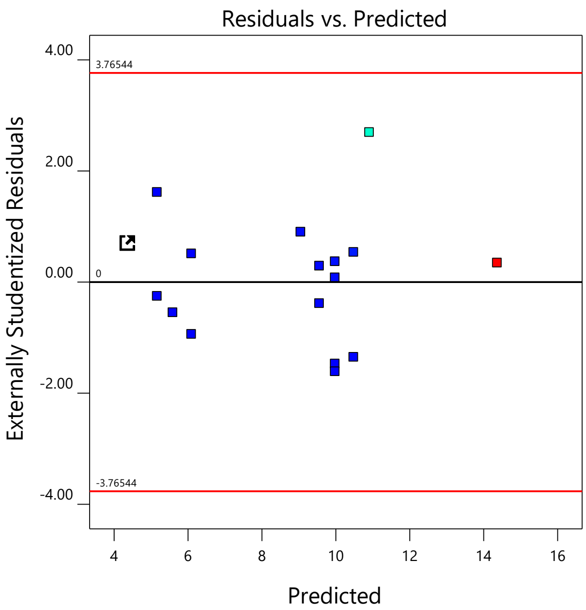

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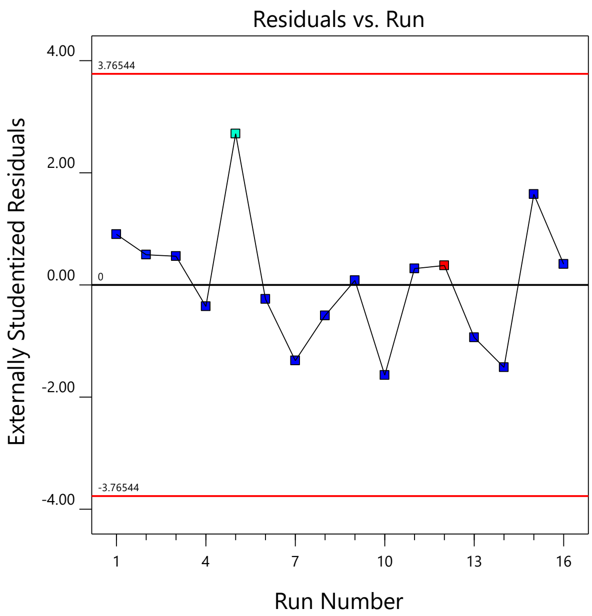


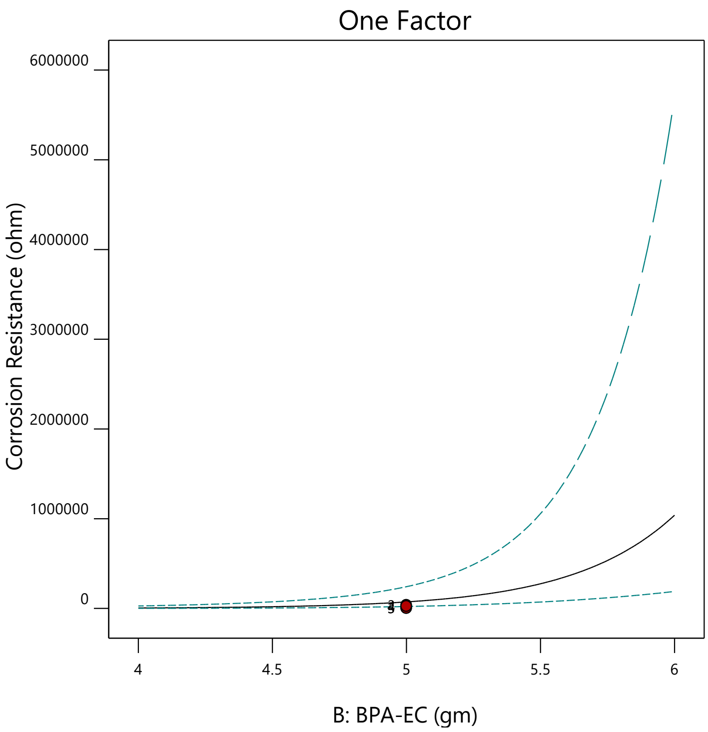
(d)

Fig. 8. (a) Predicted vs experimental R_{cr}; (b) normal % probability and externally studentized residual plot; (c) externally studentized residuals vs the predicted R_{cr}; and (d) outlier t plot.

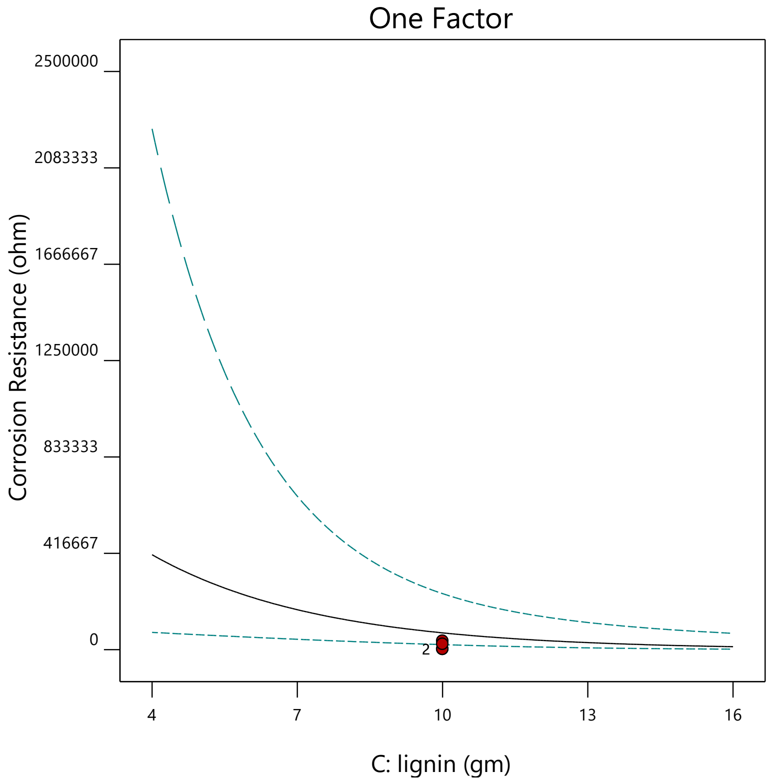
Interactions and verification of parameters

The degree of interaction between different factors can be reflected in a 2D plot. There are no special requirements for the weight, and the value is set to 1. In Fig. 9 (a), for BPA-EC, the R_{cr} increases with the increment of the values, and the slope increases with the increase of the ratio of BPA-EC. In Fig. 9 (b), lignin showed anti-proportionality with the R_{cr}. The effect can be prominent from 4 to 10. Fig. 9 (c) shows that 1.25 is the optimum value for APTES with respect to $R_{cr.}$ Thus, in terms of corrosion resistance lignin is undesirable and BPA-EC is unavoidable from the recipe, resulting in the content of BPA-EC and lignin being dependent on the level of toxicity and the degree of corrosion resistance, considered by the respective applications.

(a)



(b)



(c)

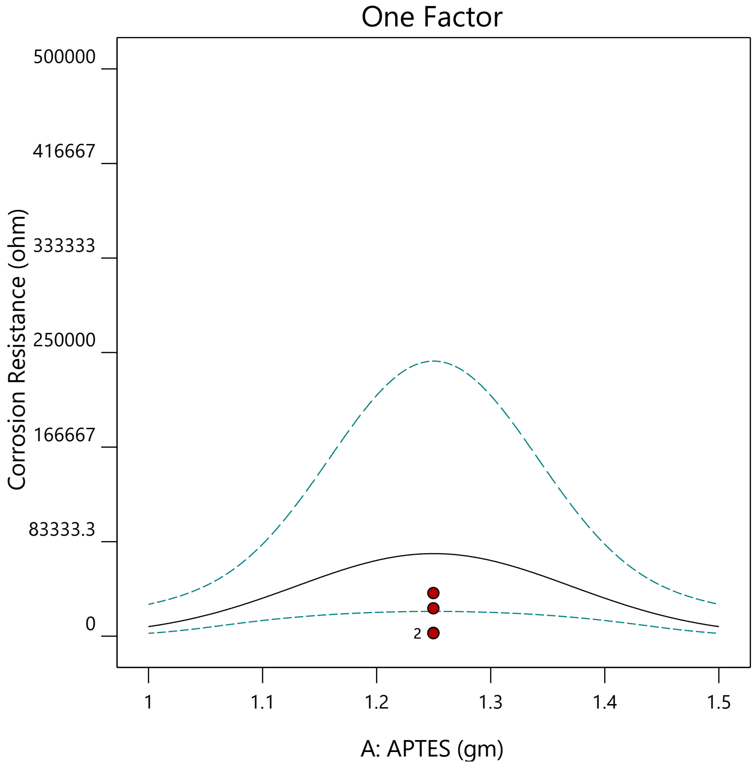


Fig. 9. Response surface plots (a)–(c) showing interaction effects of R_{cr}.

Table 7

Evaluation of compositional parameters

Predicted Mean	Std Dev	95 % PI low	Data Mean	95 % PI high
72784.7	235651	1456.47	31432.9	316772

Morphological Study

To understand the mechanism for ensuring the composition's resistance to corrosion, the morphology of the coating surface was observed. The FESEM images show regular dispersion of white dot-like microparticles, which also has been observed by Ali Rezazad et al. [22] (Fig. 10). Although the lignin has effectively dispersed into the matrix, the prominent separate phase of BPA-EC might have not been effectively assimilated into the coating matrix compared to lignin (Fig. 10). Although the lignin has effectively dispersed into the matrix, the prominent separate phase of lignin might have not been effectively assimilated into the coating matrix compared to BPA-EC (Fig. 10). This phenomenon might explain the reason for the lignin to be inversely proportional to the R_{cr}.

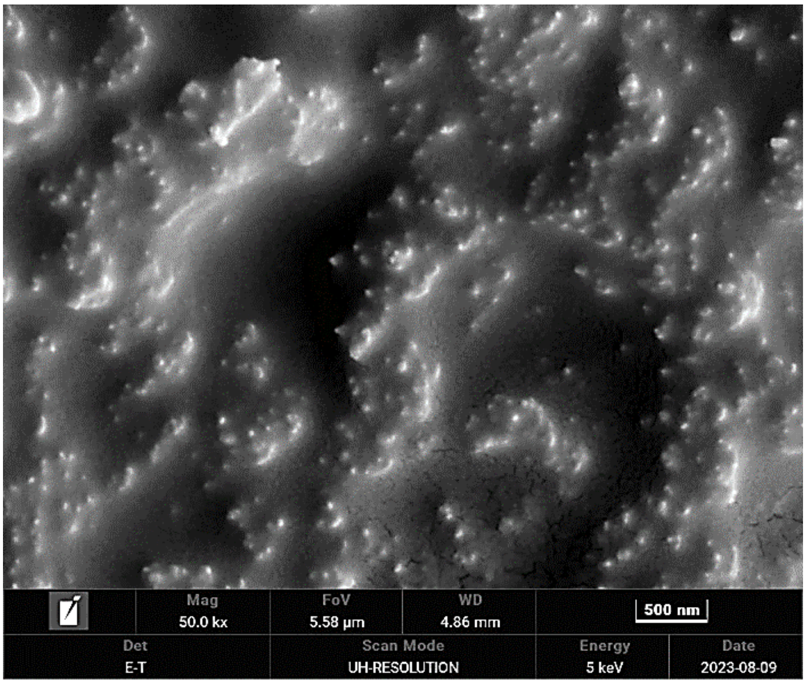


Fig. 10. The FESEM image shows the dispersion of lignin at 50K magnification.

Conclusions

The obtained model has been found reliable enough to predict the outcome with considerable accuracy. From the statistical analysis, it is evident that the compositions do not cumulatively contribute to R_{cr}. However, unlike lignin, BPA-EC plays a positive role in this aspect, considering the individual P values (Table 4). Eventually, the effects of the elements conclude that BPA-EC should not be fully eliminated from the standpoint of toxicity. Therefore, the study suggests that BPA-EC should not be completely replaced by lignin in terms of lowering toxicity and the content of lignin should be kept limited to preserve the protective properties of the coating. Moreover, to evaluate the coating performance in openair conditions, a salt spray test using RSM should be performed to compare the dependency of the composition on the corrosion resistance under different conditions.

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Declaration of conflicting interests

The authors have stated that there are no conflicts of interest regarding the research, authorship, and publication of this article.

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