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Transformative Nanosized Organic Coatings with *Euphorbia Condylocarpa*/Poplar Tree Bark/Zircon Silicate Hybrid System for Enhanced Industrial Resilience

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Abstract

This study focused on enhancing the properties of interior coatings by incorporating natural additives to minimize potential health impacts associated with traditional additives. Organic additives such as *Euphorbia condylocarpa*, poplar tree bark, and zircon silicate were employed by utilizing Design Expert for optimization. The optimized formulation demonstrated impressive attributes including the prevention of bacterial and mold growth, high corrosion resistance, effective coverage and adhesion, and resistance to dirt retention. The recommended optimum formulation, *Euphorbia condylocarpa* (1%), poplar tree bark (1%), and zircon silicate (1%) by using the 2FI model, exhibited an R^2 value of 0.9838, indicating a remarkable predictability of the variability in the experimental data. This result emphasized the effectiveness of the proposed model in optimizing the properties of nanosized organic coatings for various industrial applications. Thermogravimetric and differential thermal analysis (TG-DTA) revealed that the additives contributed to the development of flame-retardant properties as the temperature increased and morphology of coating was obtained with optical microscope and scanning electron microscope (SEM). Specifically, *Euphorbia condylocarpa* exhibited antibacterial, flame-retardant, and hydrophobic properties. The study concluded that the incorporation of euphorbia plant, poplar tree bark, and zircon silicate substances positively impacted the performance of coatings offering a more health-conscious and technologically advanced alternative.

Keywords

Euphorbia condylocarpa, zircon silicate, poplar tree bark, interior coating

1 Introduction

Nanomaterials, as a novel class of materials, garnered substantial attention from both governments and researchers since their introduction. The unique properties inherent in nanomaterials indicated a promising array of applications across various fields. The manipulation and modification of matter between 0.1 and 100 nanometers in size was the focus of nanotechnology. The specific physical and chemical characteristics inherent to the nanoscale size contributed to these advancements [1]. Its characteristic led to the integration of nanomaterials in various applications, including optical, thermal, chemical, mechanical, magnetic, and energy conversion/storage applications [2]. The widespread utilization of nanomaterials was evident across diverse sectors including chemical, ceramics, metallurgy, and electronic communication [3, 4] It explored materials with morphological features at the nanoscale, particularly those showcasing unique properties derived from their nanoscale dimensions [5]. The field of nanotechnology presented a promising opportunity for the development of high-performance or even innovative functional coatings often referred to as nanocomposite coatings [6]. The coating industry was quick to leverage the potential of nanotechnology as the addition of nanoparticles to coatings can enhance numerous properties of the coating system resulting in versatile coatings with minimal cost differences. Such coatings, sometimes composed of self-assembling monolayers, found applications ranging from scratch resistance [7]. According to the standards, a "coating" referred to a layer formed from a single or multiple applications of a coating material to a substrate [8]. A diverse range of products permeated in daily lives and critical sectors such as transportation vehicles, aircraft, marine equipment, machinery, as well as the design of residential and commercial spaces, furnishings, and

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information storage appliances. These items often featured thin coatings to shield them from mechanical and chemical impacts, ensuring resilience against weather effects [9]. Coatings played a crucial role in safeguarding materials from environmental factors such as corrosion, gas permeation, tribological effects and thermal barriers all while maintaining an economical advantage. Significant advancements in the development and formulation of industrial coatings and paints were anticipated driven notably by the integration of nanotechnology [5]. The remarkable expansion was closely linked to heightened demand in various consumer sectors such as healthcare, automobile engineering, building materials and construction, electronics, shipbuilding, power industry, water treatment, and packaging [10]. It was crucial to note that in the realm of coatings, the term "nano" referred to the ingredients within the coating, not the coating itself a distinction frequently emphasized [11] and obtained results of suggestion that the multifunctional coating showed high mechanical stability [12]. The development of coating technology hinged on the interplay between the final coating materials and the surface properties of the substrate. This relationship was governed by the meticulous selection of base materials, solvents, and additives in the coating formulation. The incorporation of specific functional additives in the formulation determined the characteristics of the coating system [13]. The multifunctional properties of nanocomposites extended to being anticorrosive, self-cleaning, ecofriendly, wear resistance, heat and radiation effects, friction, antireflection, and flame retardancy, anti-radiation, anti-microbial, barrier, waterproofing, anti-scratch, etc. making them pivotal for surface treatments that contributed superior physical effects to products [14]. Nanocomposite coatings were advanced offering various functionalities from simple barrier protection to smart auto-responsive and self-healing capabilities finding applications in both industrial and domestic settings. Nanocomposite coatings emerged as a modern and high-performance category of materials with exceptional properties that significantly enhanced the mechanical, tribological, and anti-corrosion characteristics of metallic substrates [15]. Traditionally, organic coatings served as a physical layer to insulate materials from the surrounding environment [16]. Coatings offered a plethora of desired and achievable properties on surfaces, including being dirt or water repellent, non-stick, hydrophobic, conductive, colored, transparent, decorative, anticorrosive, with good adhesion, high chemical and temperature resistance, effective diffusion barriers for certain metal ions, easy to clean/self-cleaning, scratchproof, insulating, antimicrobial [17]. The advantages of water-based paint coatings over solvent-based paints were that they were environmentally friendly, contained fewer volatile organic compounds, and had less odor. Water-based paint coatings were generally preferred as a safer and more environmentally friendly option [18, 19]. Corrosion was a phenomenon that threatens the long-term sustainability of industrial structures and causes serious economic losses. The studies carried out examined the costs and environmental effects caused by corrosion and tried to prevent metal structures from being affected by corrosion. Bio-based nanocomposite coatings were environmentally friendly nanomaterials that provided anti-corrosion and mechanical reinforcement [20, 21]. Anti-corrosion pigments in organic coating systems, especially when defected develop through the film, offer effective corrosion protection [22]. In recent years, the fundamental requirements for achieving strong and long-lasting coatings in various conditions are self-cleaning surfaces that could eliminate pollutants to lessen corrosion impacts [23]. The use of various coatings, both inorganic and organic (paints, enamels, and lacquers), was developed because of modern technological advances, with research contributing to these scientific developments conducted on corrosive degradation. Inorganic sol-gel coatings, such as zirconium, titania, and silica, were notable for corrosion mitigation. Zirconia-based coatings with self-healing properties were of interest. These inorganic compounds enhanced the long-term stability of coating materials, resistance to wear, and prevent electrical short circuits when deposited as interlayers in superconducting materials [24]. Zircon silicate was a high temperature material widely used in refractory applications. The reason for this was that it has features such as high melting temperature, high thermal shock resistance, resistance to corrosion and abrasion, high resistance to acidic chemicals, slag and glass, and thermal expansion coefficient close to iron-based materials [25]. Zirconia was modified at high temperatures and provided a fire-retardant effect when used as an additive material. It was preferred to use the powder form of zirconia in intumescent coating for easy dispersion in the coating material [26]. A coating's composition could not endanger human health or the biological systems of the surrounding environment. Therefore, biocompatibility evaluation was a critical factor in coating material selection and had an impact on the antibacterial property of the coating [27]. Natural fibers began to take their place in the industry to create lighter and more durable composite coatings. The use of natural fiber reinforcement in coatings

affected the hydrophobicity of the product [28]. In natural fiber composites, organic fillers could improve mechanical characteristics and raise the composite's flammability and heat resistance [29]. Additionally hydrophobic coatings, inspired by natural surfaces like the lotus leaf [30], offered unique characteristics such as self-cleaning, water repellence, anti-icing, anti-corrosion, and oil-water separation [31, 32]. These coatings could limit the ingress of water and salt solutions into concrete, contributing to the durability of hydrophobic surface treatments [33]. Nanoparticles in hydrophobic coatings improved penetration into substrate surfaces, making them hydrophobic and water repellent facilitating easy cleaning [34]. In literature, there were some sources of phytochemicals including compounds with antioxidant activity [35]. The family Euphorbiaceae was the largest family of angiosperms and contained acrid and milky or colorless juice. The genus Euphorbia was the best-known species within the plant family Euphorbiaceae which included approximately 2000 species. Studies on *Euphorbia condylocarpa* had revealed the presence of phytochemicals such as flavonoids, tetracyclic triterpenoids and trifoline in different parts of the plant. Antibacterial and cytotoxic activities of various species reported in different studies [36, 37]. Poplar (*Populus euramericana*) was a fast-growing tree with a short growing period and was used primarily to make paper, veneer, and sawn wood. In addition to its use as a raw material, poplar wood was also used to increase mechanical strength and other structural properties [38]. One of the most important characteristics of wood bark was its hydrophobicity, which is in addition to the conventional factors that indicated whether this material was proper for energy purposes. The hydrophobic properties of the bark were due to the nature of hydrophobic extracts, which were bioactive compounds found in the bark. Biomass materials characterized by their hydrophobic nature were highly valued in the sector [39].

The present study was aimed to optimize the effective additive parameters in organic coating by using viscosimeter to improve different properties of interior coatings. *Euphorbia condylocarpa*, zircon silicate and poplar tree bark were examined by utilizing Box Benhken optimization method in the Design Expert program.

2 Materials and method

2.1 Materials

Euphorbia condylocarpa plant and poplar tree bark were collected from the plateau of Gündoğmuş district of Antalya. In first step for cleaning of plants, any visible dirt was removed from the collected *Euphorbia condylocarpa* plants, poplar tree barks and rinsed thoroughly with distilled water to eliminate any surface contaminants. In second step, the cleaned *Euphorbia condylocarpa* plants and poplar tree barks in a well-ventilated area were dried. After dried, a proper grinder was used to reduce the *Euphorbia condylocarpa* plants and poplar tree barks into smaller to uniform particles. In sieving step, the ground plant materials were sieved through a series of sieves with progressively finer mesh sizes. Sieving helped to separate larger particles from the desired finer particles by ensuring uniformity in the sample. Zircon silicate (Thermo Fisher Scientific, Dublin, Ireland) was utilized to improve the flame-retardant properties of coating. Chemical composition of reference coating consisted of 1-isopropyl-2,2-dimethyltrimethylene diisobutyrate methylisothiazoline (<3%), N-butyl acrylate (≤0,1%), 5-chloro2-methyl-4-isothiazolin-3-one and 2-methyl-2H-isothiazol-3-one (<0,0015%) and methanol (<0,1%).

2.2 Method

A user-defined trial design was applied to examine the optimization of the desired quality properties of additives and the interactions of independent variables with each other. Design Expert (Stat-Ease v7.0.0 package program) [40] was used to determine the proportions of additives and achieve the best result with minimum number of experiments. Box Behnken experimental design was utilized to determine the experimental points by moving away from the middle levels of the independent variables [41]. Regression analysis was performed to evaluate the experimental data. The analysis was used to determine the relationship of the independent variables (additives) and dependent variable (coating properties). It was evaluated how the additives affected the coating properties using regression analysis, Analysis of Variance (ANOVA) was used to determine whether there was a statistically significant difference between different experimental groups and to determine where the differences between experimental results originated. In industrial applications, the highest rate that could be utilized statically to achieve maximum efficiency in coating additives was 6%. A total of 17 trial patterns were used with 5 repetitions in the center and three-variable pattern. Three levels in Box-Behnken design were coded as −1, 0, 1. After all experiments were prepared, the viscosity of each experiment was measured and recorded. The effect of the coating additives on the coating's viscosity was measured using a rotational viscometer (RM 100 Lamy Rheology, Rotating Springless Viscometer, France). The viscosity of

each solid addition test was evaluated after the viscosity of the reference coating without additives was determined. The coating samples were rotated at 500 rpm for 20 s while kept at room temperature to determine viscosity. The additive coatings, which formulations were indicated from 1 to 17, were applied on iron plates cut into 10 × 10 cm pieces (wall thickness 2 mm) by pulling them with the use of a film applicator with a thickness of 150 µm.

3 Tests

3.1 Cross-cut test

The cross-cut test method was used to measure the adhesion resistance of the coating applied to the surface. Cross-cut testing was a method to determine the resistance with separation from substrates by using a tool to cut an angled lattice pattern into the coating, penetrating down to the substrate. With this method, the success or failure of the sample could be quickly tested. When testing a multilayer system, the determination of the resistance to separation of different layers could be carried out. At the beginning of the test, 6 deep scratches, 3 horizontal and 3 verticals, were made on the reference coating and optimum formulation on the metal surface using a utility knife. Duct tape was firmly applied to the scratches and removed firmly.

3.2 Corrosion test

The salt test method was utilized to test the corrosion resistance of the developed coating. For this purpose, the reference coating, and the optimum formulation, which were drawn onto the plates and waited to dry, were kept in the prepared 5% salt solution for 2 h. Meanwhile, the water was boiled, and the water bath system was filled. A grid was placed in the system filled with water, plates were placed on the grid and the system was covered. The coatings were left in this system for 24 h. At the end of 24 h, the plates removed from the experimental setup were examined and corrosion rates were compared.

3.3 Dirt test

To test the dirt-repellent properties of the coatings, ketchup, cooking water, coffee, tea, and fruit juice were provided. The selected materials were applied sequentially to the reference and optimum formulation, which were drawn onto the plates and dried, and were cleaned with a wipe after waiting for 2 min. By comparing the dirt retention properties of the coatings, the dirt retention capacity of the optimum formulation was determined.

3.4 Antibacterial test

Molds on the wall coating were collected to perform the antibacterial test. The collected molds were weighed, and masses recorded. Then, the weighed mold samples were placed in small pieces on the plates. The system was covered and left to stand for 24 h. The aim was to provide proper conditions for the collected molds to multiply and to measure the capacity of the coatings to prevent the growth or survival of molds. After waiting for 24 h, the mold samples on each plate were weighed, and as a reference, the weights of the samples that were not kept in the water bath were measured. Samples taken from each sample were prepared for examination with a microscope. The samples taken from the plates were placed in methylene blue and shaken well to stain the bacteria and made easier to observe.

3.5 SEM

Scanning electron microscopy (SEM) was used to take 500x, 1000x, 5000x and 10000x images (Zeiss brand EVO LS 10, Carl Zeiss, Germany). The microscope was operated at 10.00 kV. Regions in the range of WD = 11 ± 1 mm were selected from the images (where WD (working distance) was space between the specimen surface and the bottom of the objective lens and it played a pivotal role in determining the quality of the SEM image). In analysis method, coating samples were placed in the device by coating gold under vacuum to prevent glare and reflection.

3.6 TG-DTA

Thermogravimetric and differential thermal analysis (TG-DTA) analysis was performed to characterize samples with nitrogen gas at 10 °C/min increments from 25 °C to 600 °C. TG-DTA was performed on TA Instruments, SDT Q600 device (METTLER TOLEDO, New Castle, DE, USA).

4 Results and discussion

The Box Behnken approach was used to determine the optimum formulation depending on the viscometer response. The measured viscosity values were proceeded into Design Expert program, and it was decided that experiment number 11 was the optimum formulation considering the values of 1-2 Pa s which was the most suitable viscosity range for an ideal coating. The levels were accepted as equal to 0.00 (0%), 1.00 (1%), −1.00 (2%) (Table 1). A: *Euphorbia condylocarpa*, B: poplar tree bark, C: zircon silicate ($ZrO{\cdot}SiO_2$). The proposed model, together with the R^2 values and other information found for each model, were

Table 1 Rates of independent variables and measured viscosity values

No	A (%)	B (%)	C (%)	Viscosity (Pa s)
1	1	2	0	1.837
2	0	0	1	0.784
3	1	2	2	1.799
4	2	0	1	1.172
5	1	1	1	1.470
6	0	1	2	1.126
7	1	1	1	1.477
8	1	0	0	1.069
9	1	1	1	1.519
10	2	1	0	1.810
11	1	1	1	1.505
12	1	0	2	1.077
13	0	1	0	1.088
14	1	1	1	1.526
15	2	2	1	2.332
16	0	2	1	1.474
17	2	1	2	1.893

shown in Table 2. The model recommended for optimum formulation number 11 was the 2FI model. The R^2 value of the model was found to be 0.9838 indicating that 98.38% of the variability in the experimental data could be explained by this model. The adjusted R^2 value was found to be 0.9741 indicating a high agreement rate between predicted and experimental values. The expected R^2 value of 0.9291 showed that this model could explain 92.21% of the variability in the prediction of new observations. Since the difference between the expected R^2 value and the corrected R^2 value was small, it showed acceptable compatibility with each other. Therefore, this appropriate model was found sufficient to predict new observations (Fig. 1) [42].

The model *F* value of 101.46 indicated that the model was significant. $p < F$ values less than 0.05 indicated that the model terms were significant. In this case, A, B, AB were meaningful model terms (where AB showed the combined effect of A and B parameters on viscosity). Values greater than 0.1 indicated that model terms were not significant. When the coefficients and response surface graphs (Fig. 1) of the variables in the regression model created for the viscosity of coatings with additives were examined, it was observed that as the ratio of zircon silicate and poplar tree bark (B) contained in the coating increased due to the negative effects of the zircon silicate ratio (C) and the poplar bark/zircon silicate ratio (BC). The 2FI regression model determined for viscosity was shown in Eq. (1).

$$\text{Viscosity} = +1,468.18 + 342.00 \cdot A + 417.38 \cdot B + 11.37 \cdot C + 117.25 \cdot AB + 11.25 \cdot AC - 11.50 \cdot BC \quad (1)$$

The visual results of the analyses for the optimum and reference coatings were shown in Fig. 2. It was concluded that the corrosion resistance of the optimum formulation was higher than the reference. Viscosity determined the fluidity of a coating material. Lower viscosity coatings were more fluid and easier to apply. Coatings with higher viscosity could formed a thicker layer, but application difficulties could be encountered. In this case, the viscosity of a coating material considered along with other properties such as corrosion

Table 2 Statistical parameters and variance analysis findings for viscosity model compatibility

Model	Standard deviation	R^2	Adjusted R^2	Expected R^2	PRESS*
Linear	85.59	0.9607	0.9517	0.9207	1.922E+005
2FI	62.61	0.9838	0.9741	0.9291	1.719E+005
Quadratic	64.61	0.9881	0.9729	0.8250	4.244E+005
Cubic	24.95	0.9990	0.9959		+
Source of Variation	Sum of squares	*F*-value	*p*-value		
Model	2.386E+006	101.46	<0.0001		
A-A	9.357E+005	238.70	<0.0001		
B-B	1.394E+006	355.51	<0.0001		
C-C	1,035.13	0.26	0.6185		
AB	54,990.25	14.03	0.0038		
AC	506.25	0.13	0.7268		
BC	529.00	0.13	0.7210		
Residual	39,200.72	-	-		
Lack of fit	36,711.52	9.83	0.0222		
Pure error	2,489.20	-	-		
Total	2.426E+006	-	-		

* PRESS: Predicted Residual Error Sum of Squares

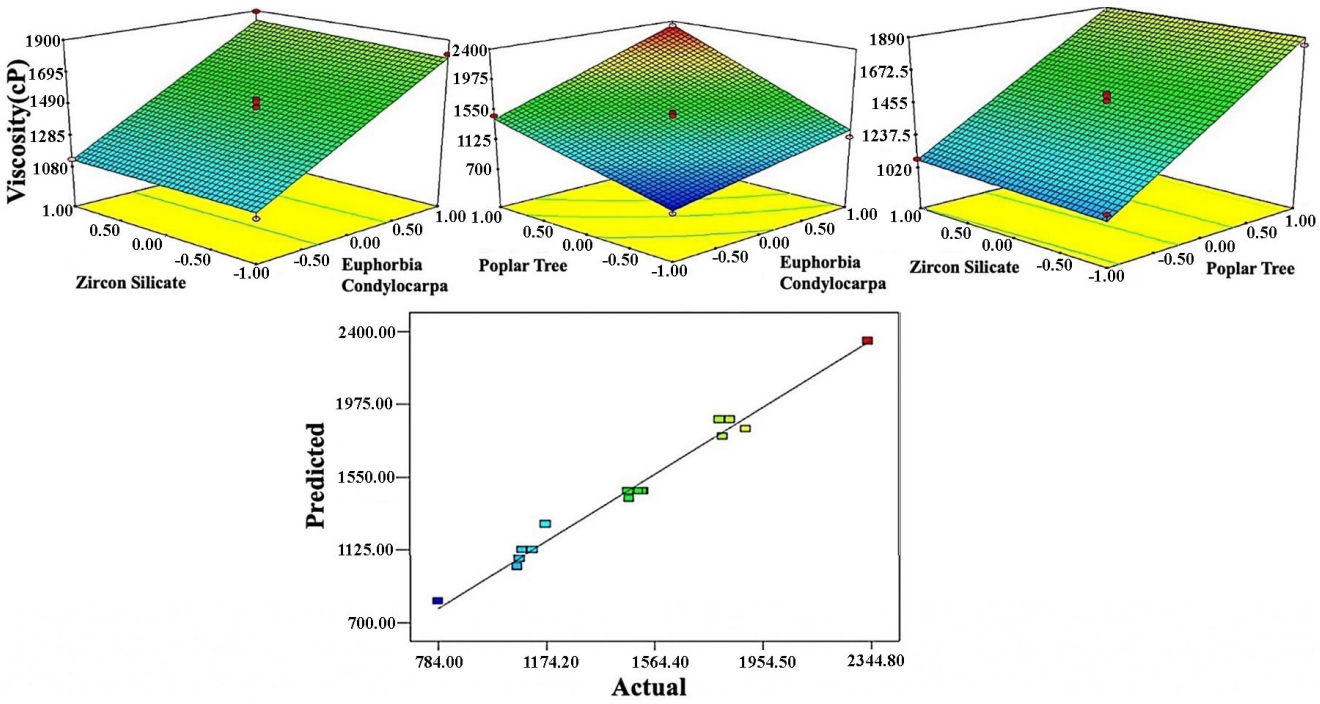

Fig. 1 3D response surface plots for viscosity and comparison of predicted values with experimental values

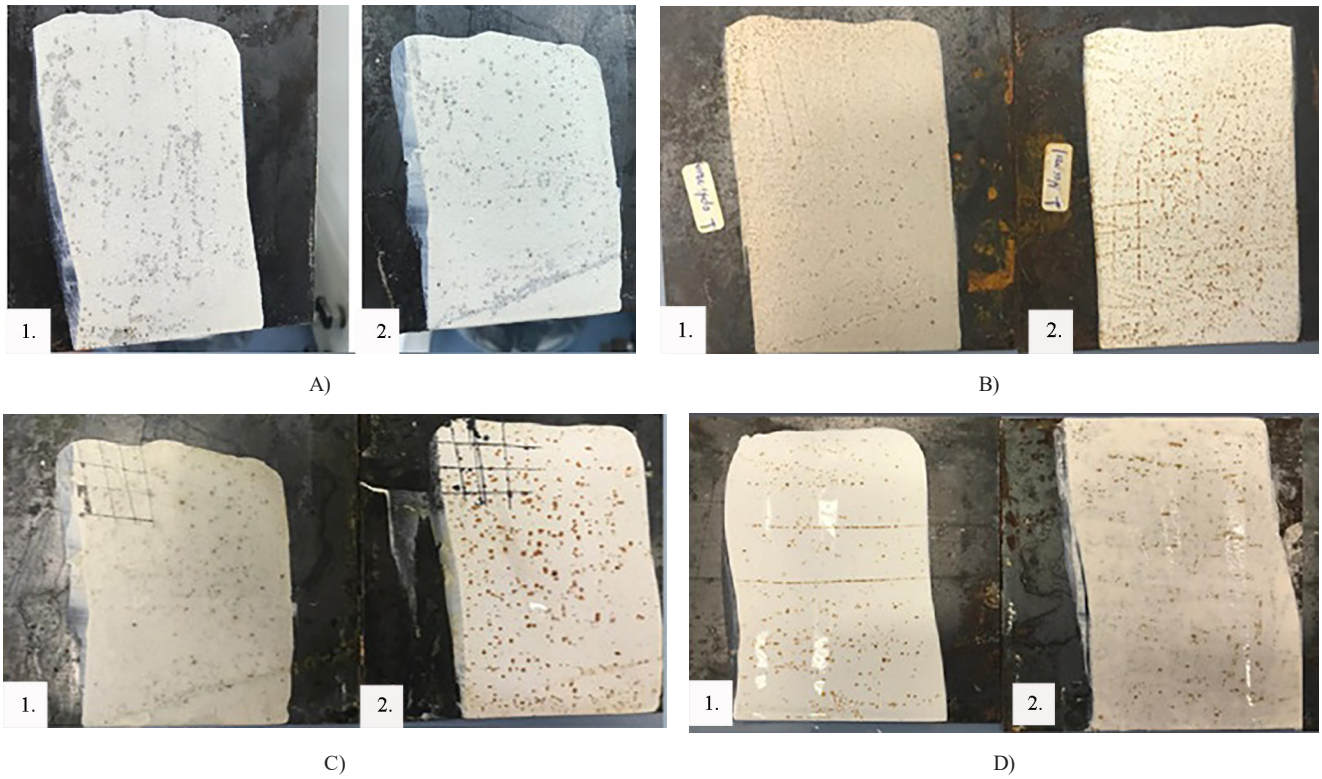

Fig. 2 Optimum and reference coatings drawn on the plates: A) drying test, 1. optimum, 2. reference; B) corrosion test, 1. optimum, 2. reference; C) adhesion test, 1. optimum, 2. reference; D) hydrophobicity test, 1. optimum, 2. reference

resistance and antibacterial properties. If the coating was not applied properly to the surface, corrosion resistance could decrease, and the metal surface could corrode over time. Therefore, viscosity could affect the uniform application of material to the surface and thus the corrosion resistance. A high viscosity coating could form a rough coating on the surface, which could allow bacteria to grow and take hold and reduce the effectiveness of antibacterial properties.

As a result of the cross-cut test, the surface adhesion resistance of the optimum formulation was higher than the reference. The weights of the mold samples on the plates and the samples that were not kept in the water bath were weighed as a reference. As a result of weighing, it was seen that the decrease in the weight of the optimum formulation was greater than the weight decreasing in the reference.

Samples taken from each sample were examined under a microscope to measure the coatings' ability to inhibit the growth or survival of molds. The samples taken from the plates were placed in methylene blue and shaken well to stain the bacteria.

The hydrophobicity test was performed by visual inspection. For the hydrophobicity test, firstly, two drops of water were dropped on the coatings dried on the plates with a Pasteur pipette. The plates were slowly brought to an upright position and the flow of water on the coating was examined. It was observed that there were no negative consequences such as softening, lifting, deterioration or color change on the surface of the samples.

By comparing the dirt-holding properties of the coatings, the dirt-holding capacity of the optimum formulation was determined and shown in Fig. 3. According to results, the dirt retention test of the optimum formulation could compete with the reference coating. With the optimum formulation, fruit juice, coffee, tea, and ketchup stains could be cleaned easily and without leaving any traces. However, the cooking water stain was a little difficult to clean and left a mark. Natural coatings were utilized not only in colouring textile products, but also in many other areas such as pharmacy, cosmetics, and food. Advantages such as being obtained from edible sources, being compatible with nature and being easily degraded, protection from UV rays, and antibacterial properties made natural coatings as attractive. Natural coating applications went beyond known traditional applications because of scientific and technological developments and interdisciplinary studies between different branches of science such as chemistry, physics, biology, biotechnology, electrical and electronics [43].

The optimum formulation, the molds on the reference coating on the plate, and the mold that was not kept on the plate as a reference were examined separately and the resulting images were recorded. As a result of the examination, spores indicating the growth of bacteria were clearly observed in the mold sample. When the sample kept on the plate on which pure coating was examined, it was shown in Fig. 4 that the spores on the mold were fewer, and the spores on the mold on which the optimum formulation were almost absent.

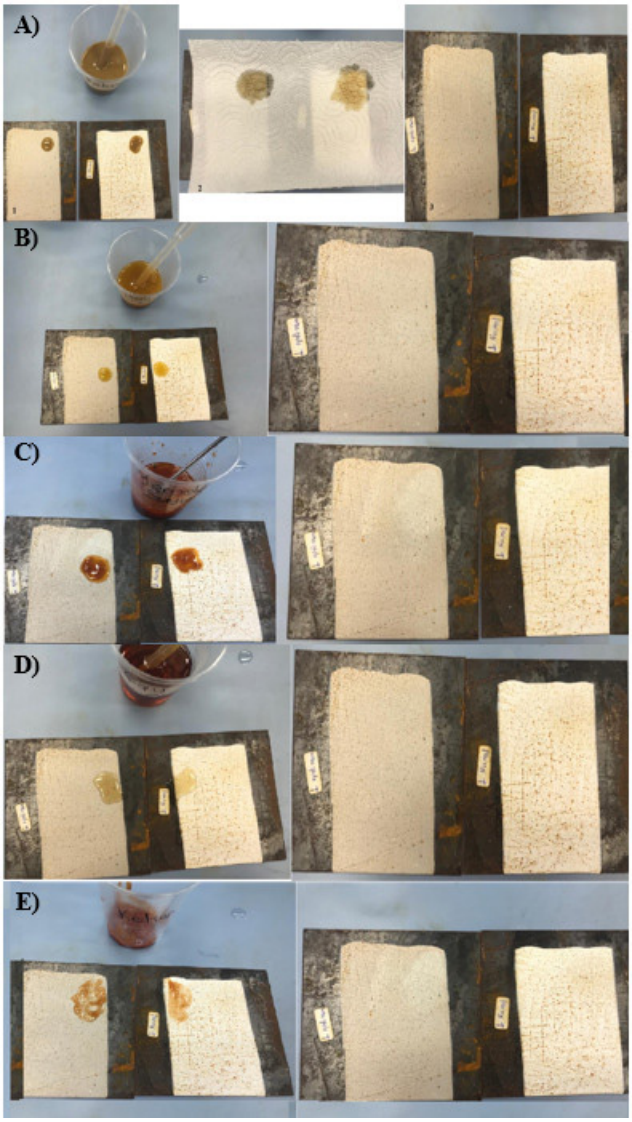

Fig. 3 Results of dirt retention test: A) coffee stain; B) fruit juice stain; C) cooking water stain; D) tea stain; E) ketchup stain

Samples were examined with SEM analysis at 10 kV and 1000x, 1000x and 500x respectively given in Fig. 5. Thermogravimetry measured the change in the mass of the substance to be examined depending on temperature or time using a thermal balance. In the differential thermal analysis, the heat absorbed in the system was observed by measuring the temperature difference between a chemical system and an inert reference compound. In the analysis, the temperatures of the system and the reference were increased at a constant rate. The temperature difference between the examined sample and the reference was examined as a function of temperature [44, 45]. TG-DTA results were given in Fig. 6. In thermogravimetric analysis, the sample to be examined was heated at a constant rate in nitrogen atmosphere and the change in its weight was recorded depending on time

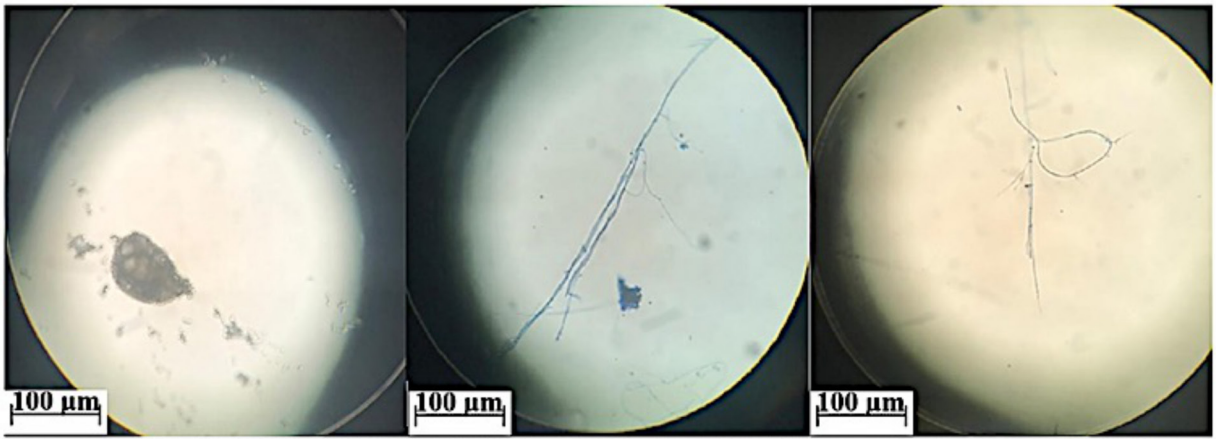

Fig. 4 Samples examined under the microscope (reference, sample kept in normal coating, sample kept in optimum formulation), respectively

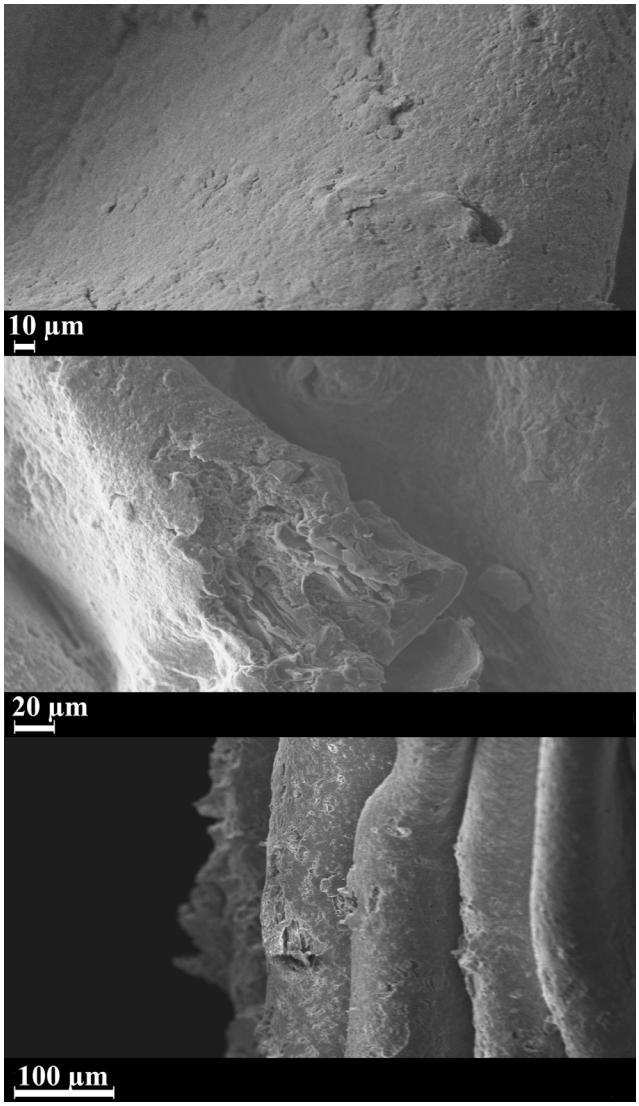

Fig. 5 SEM analysis for optimum formulation

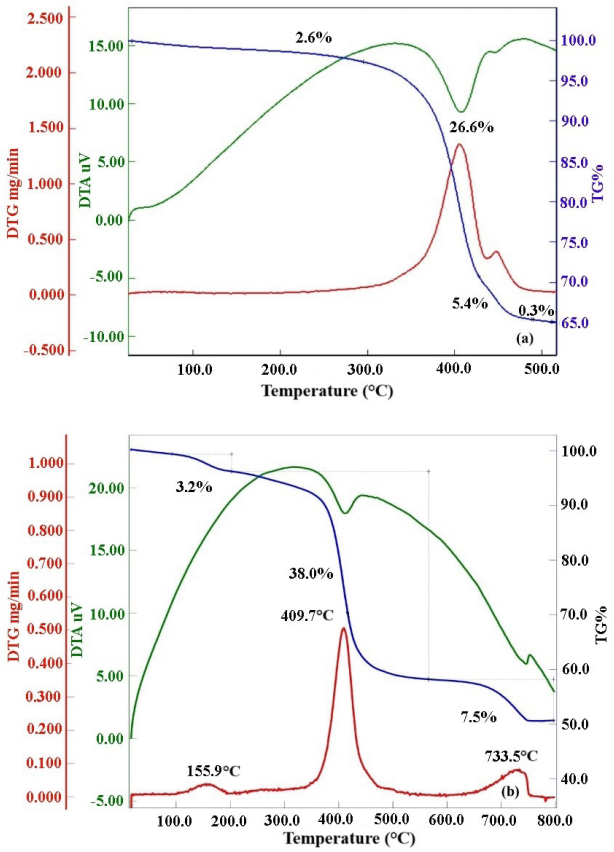

Fig. 6 TG-DTA analysis: A) Water-based reference coating, B) Water-based coating containing optimum formulation

or temperature. When the TG-DTA graphs obtained for the optimum formulation and the reference coating were compared, in the TG graph, 65% of the sample was degraded at 500 °C in the reference coating, while 50% of the sample was degraded at 800 °C in the optimum formulation. In the optimum formulation, the decrease in the amount of substance started at 400 °C, while in the reference it started at approximately 350 °C. The DTG curve indicated that the mass loss rate was a function of temperature and time [46]. In both samples, the highest peak in DTG was observed at 400 °C. After this temperature, a sharp loss of substance

amount was observed in both graphs. When the DTA curves were examined, both samples underwent a reversible endothermic transition around 350 °C. For the optimum formulation, the second endothermic transition was observed at 450 °C, while in the reference coating it was also observed around 450 °C. In line with these results, the flame-retardant property of the optimum formulation was better than that of the reference coating and the targeted flame retardancy enhancement feature was achieved.

5 Conclusion

The study aimed to improve interior coating properties by using natural additives as *Euphorbia condylocarpa*, poplar tree bark, and zircon silicate. The optimized formulation showed impressive properties as bacterial and mold prevention, effective coverage, and dirt retention. The corrosion results demonstrated that the corrosion resistance of the optimized formulation surpassed that of the reference. The additives also contributed to flame-retardant properties as temperature increased. In reference coating, 65% of the sample degraded at 500 °C, whereas in optimum formulation, 50% of the sample degraded at 800 °C The study concluded that these natural additives offered a more health-conscious and advanced alternative to traditional additives. Sample 11, which 1% *Euphorbia condylocarpa*, 1% poplar tree bark, and 1% zircon silicate, was found to be optimum. The 2FI model identified formulation 11 as the recommended optimum showcasing a remarkable predictability of experimental data variability with an R^2 value of 0.9838.

Author contribution

All authors contributed to the study conception and design. All authors read and approved the final manuscript.

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Data availability

The datasets generated during and/or analysed during the study are available from the corresponding author on reasonable request.

Declarations

Ethical approval is not applicable. Informed consent is not applicable.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Li, J. "Advanced Nanotechnologies Applied in Modern Vehicles", Highlights in Science, Engineering and Technology, 17, pp. 236–244, 2022. https://doi.org/10.54097/hset.v17i.2606

[2] Farooq, S. A., Raina, A., Mohan, S., Arvind Singh, R., Jayalakshmi, S., Irfan Ul Haq, M. "Nanostructured Coatings: Review on Processing Techniques, Corrosion Behaviour and Tribological Performance", Nanomaterials, 12(8), 1323, 2022. https://doi.org/10.3390/nano12081323

[3] Duan, J., Zhang, R., Liu, K., Zhang, Y., Shi, X., Sand, W., Hou, B. "Application of nanomaterials in antifouling: A review", Nano Materials Science, in press. (Accepted for publication March 2024) https://doi.org/10.1016/j.nanoms.2024.01.009

[4] Gohar, O., Khan, M. Z., Bibi, I., Bashir, N., Tariq, U., Bakhtiar, M., Karim, M. R. A., Ali, F., Hanif, M. B., Motola, M. "Nanomaterials for advanced energy applications: Recent advancements and future trends", Materials & Design, 241, 112930, 2024. https://doi.org/10.1016/j.matdes.2024.112930

[5] Chinglenthoiba, C., Ramkumar, K., Shanmugaraja, T., Sharma, S. "Study on Nanotechnology, Nanocoating and Nanomaterial", International Journal of Computer Aided Engineering and Technology, 3(1), pp. 17–25, 2017.

[6] Zhou, S., Wu, L. "Development of Nanotechnology-Based Organic Coatings", Composite Interfaces, 16(4–6), pp. 281–292, 2009. https://doi.org/10.1163/156855409x447101

[7] Patil, N. S., Chaudhari, D. "Review on Nanotechnology & Its Application in Coating Industry", International Journal of Scientific and Engineering Research, 9(4), pp. 1–17, 2018.

[8] Falikman, V. R. "Nanocoatings in modern construction", Application of Nanomaterials and Nanotechnologies in Construction, 13(1), pp. 5–11, 2021. https://doi.org/10.15828/2075-8545-2021-13-1-5-11

[9] Behera, A., Mallick, P., Mohapatra, S. S. "Nanocoatings for Anticorrosion: An Introduction", In: Rajendran, S., Nguyen, T. A., ... Li, Y. (eds.) Corrosion Protection at the Nanoscale, 2020, pp. 227–243. ISBN 978-0-12-819359-4 https://doi.org/10.1016/b978-0-12-819359-4.00013-1

[10] Lucintel "Nanocoating Market Report: Trends, Forecast and Competitive Analysis. Research and Markets", Lucintel, Irving, TX, USA, 2018.

[11] Li, L., Yang, Q. "Coating Materials Nanotechnology", In: Li, L., Yang, Q. (eds.) Advanced Coating Materials, Scrivener Publishing LLC, 2019, pp. 177–233. ISBN 9781119407560

[12] El-Wahab, H. A., Mohamed, S. A. A., Gomaa, I. "New Flame Retardant and Antimicrobial Paints Based on Epoxy Paint Incorporated by Hexachlorocylodiphosphazane Derivatives for Protective Coating", Journal of Coating Science and Technology, 5(3), pp. 85–96, 2019. https://doi.org/10.6000/2369-3355.2018.05.03.3

[13] Mohd Sabee, M. M. S., Itam, Z., Beddu, S., Zahari, N. M., Mohd Kamal, N. L., Mohamad, D., Zulkepli, N. A., Shafiq, M. D., Abdul Hamid, Z. A. "Flame Retardant Coatings: Additives, Binders, and Fillers", Polymers, 14(14), 2911, 2022. https://doi.org/10.3390/polym14142911

[14] Solano, R., Patiño-Ruiz, D., Herrera, A. "Preparation of Modified Paints with Nano-Structured Additives and its Potential Applications", Nanomaterials and Nanotechnology, 10, 2020. https://doi.org/10.1177/1847980420909188

[15] Muresan, L. M. "Nanocomposite Coatings for Anti-Corrosion Properties of Metallic Substrates", Materials, 16(14), 5092, 2023. https://doi.org/10.3390/ma16145092

[16] Deyab, M. A., Eddahaoui, K., Essehli, R., Benmokhtar, S., Rhadfi, T., De Riccardis, A., Mele, G. "Influence of Newly Synthesized Titanium Phosphates on the Corrosion Protection Properties of Alkyd Coating", Journal of Molecular Liquids, 216, pp. 699–703, 2016. https://doi.org/10.1016/j.molliq.2016.01.092

[17] Ulaeto, S. B., Pancrecious, J. K., Ajekwene, K. K., Mathew, G. M., Rajan, T. P. D. "Advanced Nanocoatings for Anticorrosion", In: Rajendran, S., Nguyen, T. ... Li, Y. (eds.) Corrosion Protection at the Nanoscale, Elsevier, 2020, pp. 499–510. ISBN 978-0-12-819359-4 https://doi.org/10.1016/b978-0-12-819359-4.00025-8

[18] Çelik, B., Acaralı, N. "A model-based design for coating materials including perlite-peanut shell-volcanic lava stone ternary system", Journal of Adhesion Science and Technology, 36(10), pp. 1081–1093, 2022. https://doi.org/10.1080/01694243.2021.1958528

[19] Çelik, B., Acaralı, N. "Performance evaluation of coating materials containing Perlite-Volcanic lava Stone-Carrot pulp ternary system", Journal of the Chemical Society of Pakistan, 43(6), 635, 2021. https://doi.org/10.52568/000972/JCSP/43.06.2021

[20] Randis, R., Darmadi, D. B., Gapsari, F., Sonief, A. A., Akpan, E. D., Ebenso, E. E. "The potential of nanocomposite-based coatings for corrosion protection of metals: A review", Journal of Molecular Liquids, 390, 123067, 2023. https://doi.org/10.1016/j.molliq.2023.123067

[21] Gapsari, F., Wahyudi, S., Sumawan, S. "The influence of high content of silicon in austenitic stainless steel to corrosion rate in sulphuric acid", Applied Mechanics and Materials, 493, pp. 727–732, 2014. https://doi.org/10.4028/www.scientific.net/amm.493.727

[22] Asemani, H. R., Ahmadi, P., Sarabi, A. A., Eivaz Mohammadloo, H. "Effect of Zirconium Conversion Coating: Adhesion and Anti-Corrosion Properties of Epoxy Organic Coating Containing Zinc Aluminum Polyphosphate (ZAPP) Pigment on Carbon Mild Steel", Progress in Organic Coatings, 94, pp. 18–27, 2016. https://doi.org/10.1016/j.porgcoat.2016.01.015

[23] Veedu, K. K., Kalarikkal, T. P., Jayakumar, N., Gopalan, N. K. "Fluorine free nanoparticles for superhydrophobic, self-cleaning, and anticorrosive epoxy coatings for steel protection in marine medium", Results in Surfaces and Interfaces, 14, 100195, 2024. https://doi.org/10.1016/j.rsurfi.2024.100195

[24] Gasiorek, J., Mazur-Nowacka, A., Szczurek, A., Babiarczuk, B., Tic, W. J., Guziałowska-Tic, J., Kaleta, J., Krzak, J. "Influence of Zirconia and Organic Additives on Mechanical and Electrochemical Properties of Silica Sol-Gel Coatings", Materials, 14(9), 2389, 2021. https://doi.org/10.3390/ma14092389

[25] Karell, R., Kraxner, J., Chromčíková, M., Liška, M. "Properties of selected zirconia containing silicate glasses", Ceramics, 50(2), pp. 125–130. 2006.

[26] Ullah, S., Ahmad, F. "Effects of zirconium silicate reinforcement on expandable graphite based intumescent fire-retardant coating", Polymer Degradation and Stability, 103, pp. 49–62, 2014. https://doi.org/10.1016/j.polymdegradstab.2014.02.016

[27] Juliano, H., Gapsari, F., Izzuddin, H., Sudiro, T., Phatama, K. Y., Sukmajaya, W. P., Zuliantoni, Putri, T. M., Sulaiman, A. M. "HA/ZRO_2 coating on COCR alloy using flame thermal spray", Evergreen, 9(2), pp. 254–261, 2022. https://doi.org/10.5109/4793632

[28] Gapsari, F., Darmadi, D. B., Juliano, H., Hidayatullah, S., Suteja, I. W., Rangappa, S. M., Siengchin, S. "Modification of palm fiber with chitosan-AESO blend coating", International Journal of Biological Macromolecules, 242, 125099, 2023. https://doi.org/10.1016/j.ijbiomac.2023.125099

[29] Diharjo, K., Gapsari, F., Andoko, A., Wijaya, M. N., Rangappa, S. M., Siengchin, S. "Flammability and thermal resistance of Ceiba petandra fiber-reinforced composite with snail powder filler", Polymer Composites, 45(6), pp. 4947–4960, 2024. https://doi.org/10.1002/pc.28100

[30] Basha, M. A. M., Srinivasan, S. "Fabrication of Zirconium Silicate Reinforced Superhydrophobic Coating for the Evaluation of Corrosion-Resistance", Acta Chimica Slovenica, 69(1), pp. 1–12, 2022.

[31] Zhang, P., Yin, X., Li, W., Feng, L. "Preparation, Properties and Formation Mechanism of Zirconium-Si Hybrid High Transmittance Hydrophobic Coating", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 631, 127649, 2021. https://doi.org/10.1016/j.colsurfa.2021.127649

[32] Inamuddin, Boddula, R., Asiri, A. M., Ahamed, M. I. "Polymers Coatings: Technology and Applications", Wiley & Sons, 2020. ISBN 978-1-119-65517-6

[33] Jakubíková, K. H., Hodul, J., Hermann, R., Drochytka, R. "Development of a Hydrophobic Polymer Coating in Polyurethane Organic–Mineral Base Containing Waste from Fibreglass Production", Coatings, 13(11), 1934, 2023. https://doi.org/10.3390/coatings13111934

[34] Pérez-Gandarillas, L., Aragón, D., Manteca, C., Gonzalez-Barriuso, M., Soriano, L., Casas, A., Yedra, A. "Highly Hydrophobic Organic Coatings Based on Organopolysilazanes and Silica Nanoparticles: Evaluation of Environmental Degradation", Coatings, 13(3), 537, 2023. https://doi.org/10.3390/coatings13030537

[35] Duangpapeng, P., Ketthaisong, D., Lomthaisong, K., Lertrat, K., Scott, M., Suriharn, B. "Corn Tassel: A New Source of Phytochemicals and Antioxidant Potential for Value-Added Product Development in the Agro-Industry", Agronomy, 8(11), 242, 2018. https://doi.org/10.3390/agronomy8110242

[36] Nasrollahzadeh, M., Sajadi, S. M., Rostami-Vartooni, A., Khalaj, M. "Green synthesis of Pd/Fe_3O_4 nanoparticles using *Euphorbia condylocarpa M. bieb* root extract and their catalytic applications as magnetically recoverable and stable recyclable catalysts for the phosphine-free Sonogashira and Suzuki coupling reactions", Journal of Molecular Catalysis. A: Chemical, 396, pp. 31–39, 2015. https://doi.org/10.1016/j.molcata.2014.09.029

[37] Mohammadi, S., Shandiz, S. a. S., Bigdeli, R., Mahboubi, A., Hedayati, M., Asgary, V. "Evaluation of Anti-Bacterial properties of Euphorbia condylocarpa methanol extract", Archives of Microbiology & Immunology, 01(01), pp. 10–18, 2016. https://doi.org/10.26502/ami.9365002

[38] Yu, Y., Li, A., Yan, K., Ramaswamy, H. S., Zhu, S., Li, H. "High-pressure densification and hydrophobic coating for enhancing the mechanical properties and dimensional stability of soft poplar wood boards", Journal of Wood Science, 66(1), 45, 2020. https://doi.org/10.1186/s10086-020-01892-1

[39] Sobol, L., Sabat, D., Dyjakon, A. "Assessment of Bark Properties from Various Tree Species in Terms of Its Hydrophobicity and Energy Suitability", Energies, 16(18), 6586, 2023. https://doi.org/10.3390/en16186586

[40] Stat-Ease "Design expert, (Stat-Ease v7.0.0)" [computer program] Available at: https://www.statease.com/software/design-expert/ [Accessed: 5 May 2024]

[41] Şahin, F. İ., Acaralı, N. "Extending shelf life and optimizing effective parameters by using clove oil (Syzygium aromaticum oleum)/ orange oil (Citrus aurantium var dulcis oleum) in bread: thermal, morphological and sensory approach", Journal of Food Science and Technology, 60(12), pp. 3002–3013, 2023. https://doi.org/10.1007/s13197-023-05827-8

[42] Yılmaz, K., Acaralı, N. "High Strength Nanosized Organic Coatings for Industrial Applications", presented at Paintistanbul & Turkcoat, Istanbul, Türkiye, Dec 8–9 2021.

[43] Erdem İşmal, Ö. "The Changing Face of Natural Dye Applications and Innovative Approaches", Magazine of Art, Design and Science, 22, pp. 41–58, 2019.

[44] Bulun, G. "Structural and Magnetic Properties of 3d-Transition Metal Ni Doped Zn1-Xnixo and 4f-Lanthanide Gd Doped Zn1-Xgdxo Compounds", PhD Thesis, Çukurova University, 2010.

[45] Şensöğüt, C., Yıldırım, Ö. S., Çınar, İ., Özdeniz A. H. "Statistical Approach to Thermogravimetric Characteristics of Some Domestic Coals", Proceedings of the 13th Turkish Coal Congress, Zonguldak, Türkiye, 2002.

[46] Bülbül, Z. "Production of Composite Materials from Wastepaper Products Coated with Polymeric Materials", PhD Thesis, Süleyman Demirel University, 2018.