Study of waterborne eco-sustainable paint with plant, shells and cuttlefish bone powder based additives.

S. Rossi[1,*], N. Khongsay[1], L. Benedetti[1], A. Cristoforetti[1], N. Mattei[1]

[1] Department Of Industrial Engineering, University of Trento, Trento, 38123, Italy

**Corresponding author email: stefano.rossi@unitn.it*

ABSTRACT

In paint production, there is increasing demand for eco-sustainable products made from natural or recycled materials. Paints must offer not only corrosion and abrasion resistance but also good aesthetic properties. This study investigates two bio-based fillers: one plant-derived and one animal-derived. The plant-based filler was Tagua, a seed from *Phytelephas macrocarpa* known as "vegetable ivory." The animal-derived fillers came from waste shells and cuttlebone, composed mainly of calcite and aragonite. These materials were micronized and used as alternatives to synthetic fillers in water-based acrylic paint. Four types of powders—Tagua, shells of *Acanthocardia tuberculata* and *Mytilus galloprovincialis*, and cuttlebone—were added at 3% wt. concentration to paint applied on carbon steel panels. A paint without filler served as the reference. The modified paints were evaluated for mechanical resistance and corrosion protection. Abrasion resistance was tested using a Scrub test, showing that cuttlebone powder provided the best performance. Aesthetic stability under artificial weathering was assessed via xenon light exposure, monitoring gloss and color changes. Corrosion resistance was tested using salt spray chamber exposure and electrochemical impedance spectroscopy in NaCl solution. Results highlighted that while Tagua powder improved abrasion resistance, it also increased water uptake, reducing corrosion protection. In contrast, cuttlebone fillers enhanced both abrasion and corrosion resistance. This study demonstrates the potential of using food and plant waste as functional fillers in sustainable coatings.

Keywords: Plant-based fillers, Animal-based fillers, Organic coating, Corrosion protection.

INTRODUCTION

Waterborne coatings have gained significant popularity in recent years and are widely applied across various industries due to their ability to reduce the use of volatile organic compounds (VOCs) [1]. Increasingly strict environmental regulations largely drive this shift and the growing demand for sustainable alternatives to traditional solvent-based anticorrosive paint systems [2]. Despite these advantages, waterborne coatings still face performance limitations, particularly in terms of long-term protection. One major challenge is degradation at the coating–substrate interface due to water penetration [3], which compromises adhesion and overall protective properties. As a result, continued research is essential to improve their functional performance, particularly regarding corrosion resistance and adhesion enhancement, and degradation properties [4].

To address these limitations, waterborne coating formulations commonly incorporate additives such as corrosion inhibitors, defoamers, and dispersing agents [5]. These additives play a vital role in improving adhesion, enhancing corrosion resistance, and providing protection against UV degradation [3]. Both organic and inorganic inhibitors are widely used to suppress electrochemical reactions and prolong coating durability.

In recent years, the increasing cost of raw materials, driven by global economic trends and population growth, has resulted in heightened fuel consumption and CO_2 emissions, further exacerbating environmental concerns [6]. This situation underscores the importance of recycling and reusing waste materials as a sustainable solution. Environmentally friendly, biobased coatings not only align with regulatory goals but also offer a viable alternative to conventional systems [2]. One sustainable approach involves using pigments and fillers derived from waste sources, such as food waste, which require minimal processing and reduce both energy consumption and production waste [7] Recent research has increasingly focused on incorporating fillers derived from food waste and natural materials, aiming to reduce production costs and promote circular material use [8].

Titanium dioxide (TiO_2) is a key mineral additive widely used to enhance water-based paint formulations due to its high refractive index, which provides excellent opacity and brightness [9]. However, it is also one of the most expensive and resource-intensive components. In contrast, calcium carbonate ($CaCO_3$), particularly in the form of calcite, offers a significantly more cost-effective alternative [10]. $CaCO_3$'s production process is simpler and involves fewer chemical treatments than TiO_2's, making it both economically and environmentally advantageous. As a result, $CaCO_3$ represents a promising substitute for TiO_2, contributing to reduced formulation costs and improved sustainability in paint manufacturing [11].

A prominent example is calcium carbonate ($CaCO_3$) extracted from chicken eggshells [10], which has demonstrated excellent performance in coatings without compromising protective properties, while also lowering cost [11]. Similarly, seashell-derived $CaCO_3$ has shown potential in enhancing the functional properties of waterborne paints [11].

In this study, we explore the use of recycled biomaterials—Tagua powder derived from wood buttons production waste, as well as powders obtained from the shells of *Acanthocardia tuberculata* and *Mytilus galloprovincialis* (Mediterranean mollusks and food industry by-products), and Cuttlebone powder—as biobased fillers in waterborne acrylic paints. The objective is to evaluate the influence of these materials on key performance metrics such as water absorption, solar radiation resistance, and overall durability. The broader aim of this research is to develop an eco-friendly, high-performance waterborne coating for steel substrates, while contributing to sustainability and waste reduction through the valorisation of raw materials by products.

METHODS AND MATERIALS

Materials

Seashells (*Acanthocardia tuberculata*), Mussels (*Mytilus galloprovincialis*), and Cuttlebone, from food waste Adriatic Sea origin) are ground into powder using an MGS ball mill (MGS, Fiorano Modenese, MO, Italy). The milling process employed 10 mm diameter aluminous porcelain spheres, which were stirred within the milling jar containing the sample for 10 minutes. Each type of material was processed separately and then sieved to obtain a micrometric powder.

Tagua Natural ivory obtained from button production waste was supplied by Mabo (Telgate, BG, Italy). The material was ground into a fine powder using a batch mill (IKA WERKE M20, Staufen, Germany) and subsequently sieved to obtain particles with a maximum size of 40 µm.

Samples Production

Carbon steel panels (Q-panel type R; composition: 0.15% C, Fe balance) with the following dimensions—76 mm × 152 mm × 0.81 mm, 102 mm × 102 mm × 0.81 mm, and 102 mm × 203 mm × 0.81 mm—were used as substrates for coating application. These panels were supplied by Q-Lab (Westlake, OH, USA). The pretreatment involved immersion in a 10 wt% HCl solution at room temperature for 10 minutes. After this step, the substrates were rinsed with demineralized water and dried.

As the primer layer a white commercial 2K acrylic antirust waterborne paint with low organic solvent Ecofiller EQW, (EP Vernici, Solarolo, RA, Italy) was applied. The solids volume is 40 % vol. The primer-coated panels were oven-cured at 50 °C for 30 minutes. In the second step, a topcoat of white waterborne 2K acrylic-based paint, Aquacril satin DTM (Franchi & Kim, Castenedolo, BS, Italy), was applied. The solids volume is 43 % vol. The waste powders were added to the topcoat at a concentration of 3 wt.%. Dispersion of the powder was achieved using a high-speed homogenizer (Ika Ultra-turrax T18, Staufen, Germany) for 10 minutes to ensure homogeneous mixing. Both paint layers were applied by spray deposition at a constant pressure of 5 bar, maintaining a uniform film across the substrate surface. The coated panels were then allowed to dry at room temperature overnight, following the paint manufacturers' recommendations.

Table 1 reports the studied samples.

Table 1. Sample composition with relative nomenclature

Sample Nomenclature	Additives introduced in the paint formulation (3% wt.)
Shell	Seashell powder
Mussel	Mussels powder
Cuttlefish	Cuttlefish bone
Tagua	Tagua powder
Ref.	---

Characterization

Powder, surface morphology, and coating integrity were examined using scanning electron microscopy (SEM, Jeol JSM IT 300, Tokyo, Japan). Powder X-ray diffraction patterns of the pigments were obtained using an X´Pert High Score diffractometer-Rigaku (Tokyo, Japan) with Cu Ka emission source (λ = 1789 Å) and the monochromator working at 30 k*V* and 10 mA. Coating thickness was measured with Phynix Surfix FN thickness gauge (Phynix Sensortechnik, Neuss, Germany), and gloss was measured at 60° angle using a gloss meter-14 (Erichsen 503 glossmeter, Milan, Italy) [12].

Mechanical and Durability Testing

Abrasion resistance was assessed using a scrub test conducted with the Elcometer 1720 Abrasion and Washability Tester (Elcometer, Manchester, UK). Samples were tested to 2000 cycles using a weight loaded on top of 330 g each and an abrasive pad (90.0 ± 0.5 mm × 39.0± 0.5 mm), moving at 37 cycles per minute. Weight loss is measured every 250 cycles. The test was performed in dry mode to prevent solution absorption into the coating, following ASTM D4213-24 [13].

The coating weathering evaluation

Neutral Salt Spray Test (NSST)

The corrosion resistance of the coated samples was evaluated using a neutral salt spray test (NSST 5 wt.% sodium chloride (NaCl) solution) following ASTM B0117-19 [14] in a salt spray chamber (Ascott Analytical Equipment Limited, Tamworth, UK).
Testing was conducted for a total duration of 500 hours. Samples were periodically inspected for visual signs of corrosion, blistering, delamination, or other coating degradation, following blister assessment every 100 hours. In addition to NSST, filiform corrosion (FFC) resistance was experimented exposing the sample for 5 hours in a salt spray chamber for chloride contamination [15], and then at 80% humidity at 40 °C for 500 hours (Figure 8). After, the solar radiation resistance of the samples was assessed via accelerated weathering (Q-Sun| Xe-1 Xenon Test chamber, Westlake, OH, US). The exposed samples were carried out for 500 hours to Xenon radiation. The results were evaluated via visual inspection and retention measurements post-exposure.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was used to evaluate the barrier properties, defect formation, and water uptake resistance of the coatings during immersion in 3% NaCl solution. Measurements were conducted using an Autolab PGSTAT302N potentiostat (Metrohm, Herisau, Switzerland) controlled by NOVA 1.11 software. A sinusoidal AC signal with a 20 mV peak-to-peak amplitude was applied over a frequency range from 100 kHz to 10 mHz. The electrochemical cell exposed a 6.2 cm^2 coated surface area, Ag/AgCl reference electrode and a platinum wire counter electrode were used. Impedance spectra were recorded at predetermined intervals throughout the 13-day immersion period to monitor the evolution of coating performance in a corrosion environment.

RESULTS

1. Filler and coating characterization

Figures 1 and 2 present the SEM images morphological and chemical analyses of the selected bio-based fillers. The Seashell-derived powder (Figure 1) appears as a white, granular material with particle sizes ranging from a few micrometres up to approximately 35 µm. Despite the use of a 40 µm mesh sieve during sample preparation, some granules exceeding 50 µm were observed, likely due to their compact and dense structure, an attribute commonly reported in shell-based by-products [11, 16]. SEM coupled with chemical analysis of X-ray diffraction (XRD) (Figures 1 and 2) confirmed the presence of calcium carbonate ($CaCO_3$), predominantly in the aragonite form, which is characteristic of many marine shells [17, 18].

The Mussel shell powder (Figure 1) exhibits a purplish hue, although this coloration does not significantly alter the final appearance of the white coating. The powder displays an irregular particle size distribution, typically ranging from 5 µm to over 15 µm. This heterogeneity aligns with the natural structure of mussel shells, where fine and coarse granules coexist in a compact arrangement [19]. Both SEM and XRD analyses (Figures 1 and 2) confirmed that the filler primarily consists of calcite crystals, consistent with its expected mineralogical composition.

The Cuttlefish bone powder is primarily composed of aragonite, a biaxial crystal with an orthorhombic system, and calcite, a uniaxial crystal with a trigonal system, with aragonite being the predominant phase [20]. Figure 1 shows a wide particle size distribution, with particles mostly below 40 µm. X-ray diffraction (Figure 2) detected the presence of calcium-based compounds, including calcium oxide (CaO), calcite, and aragonite, suggesting a more chemically diverse composition compared to the other fillers.

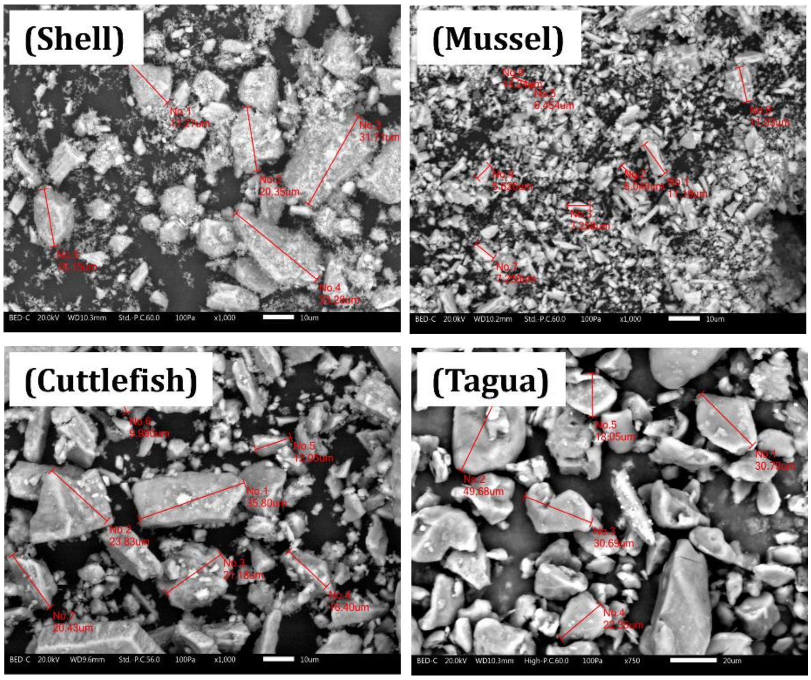


Figure 1. SEM images show the appearance and surface morphology of the powders.

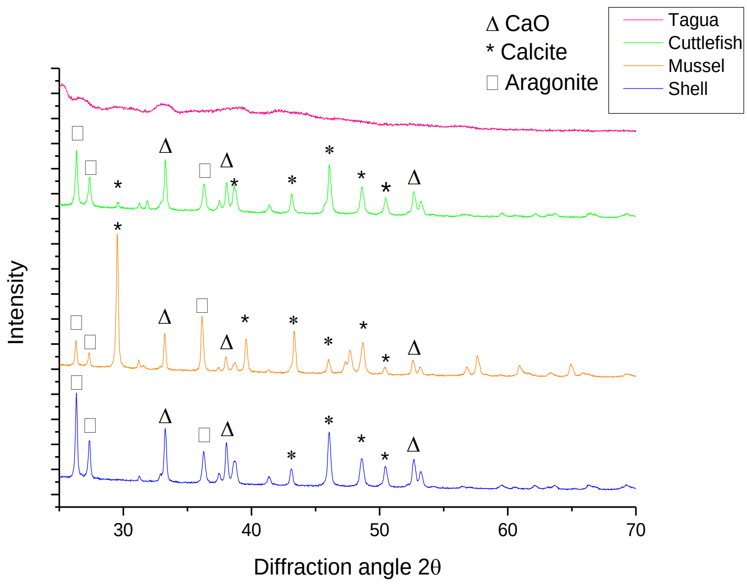


Figure 2. XRD analysis in 4 samples: Shell (1), Mussel (2), Cuttlefish bone (3), Tagua (4) for Calcite composition.

The composition and morphology of the Tagua powder (Figure 1 and Table 2) are consistent with findings reported in literature [21], made as amorphous wood compounds. Additionally, the absence of calcite in the Tagua powder and the amorphous structure are confirmed in Figure 2.

Regarding the coating surface characteristic, the gloss value varied depending on the type of material and coating thickness (see Table 3). The primer layer, common for all samples, present a thickness of 50 ± 10 µm The incorporation of Cuttlefish and Tagua powders led to a reduction in gloss, producing a matte effect. In contrast, Shell and Mussel powders contributed to higher gloss values, likely due to their bio-based filler composition. 95% of Shells are made from calcium carbonate [19]. Calcium carbonate is the primary component in Shells, Mussels, and

Cuttlefish, and it is shown in Figure 3, distributed as the filler in paints. However, the various crystalline forms of calcium carbonate in Figure 2 could influence the mechanical properties of the coating in different beneficial ways [19]. In general, as shown in the literature [22], the calcium carbonate content can enhance gloss in color coatings. Cuttlefish powder exhibited a slight increase of coating thickness and a matte appearance, attributed to its larger particle size. Conversely, the smaller particle size of Tagua powder contributed to a thinner coating layer. Overall, particle size played a critical role in determining coating thickness [21]. These bio-based fillers significantly influenced the coatings' surface morphology and texture, highlighting their potential for future research and development.

Table 2. Composition of Tagua powder (from EDS analysis)

Sample	Normalize mass (%)
C	51.04
O	42.28
F	0.04
Al	0.98
P	0.15
Cl	0.32
K	0.57
Ca	0.21
Cu	0.25
S	0.07
Mg	0.07
Si	0.03

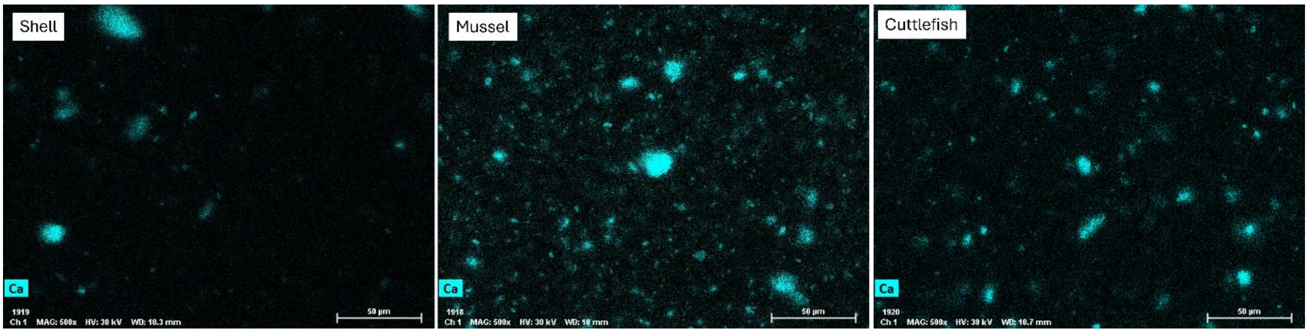


Figure 3. EDX map of the top-view colour coating shows calcium distribution for animal origin powders (Blue spot).

Table 3. Thickness and surface properties of the analyzed coating.

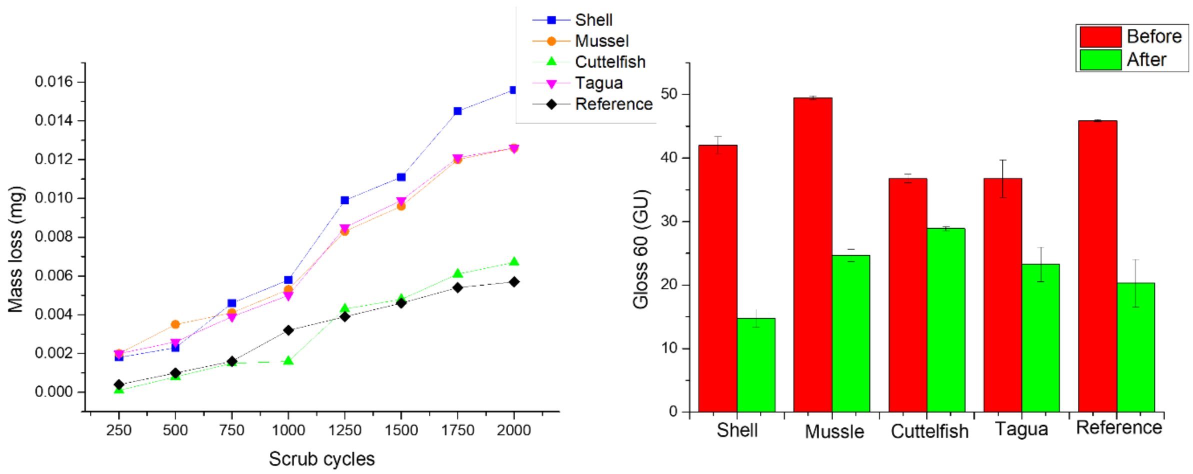
Sample	Thickness (μm)	Gloss 60° (GU)
Shell	160.3 ± 12.76	46.39 ± 0.2
Mussel	172.68 ± 21.36	46.85 ± 1.78
Cuttlefish	186.34 ± 13.3	38.61 ± 0.30
Tagua	114.38 ± 27.94	41.34 ± 1.18
Ref.	166.48 ± 9.35	44.85 ± 1.46

2. Abrasion resistance

The scrub test is a reliable method for characterizing the mechanical properties of organic-based compound coatings. It provides valuable insights into the reinforcing effects of pigments, as well as chemical and organic fillers, on the mechanical strength of coatings. Abrasion resistance was evaluated by subjecting the coated samples to repeated wear cycles using an abrasive pad. The weight loss of each sample was recorded every 250 cycles. To quantify this, the loss in coating mass per unit area (L) was calculated using Equation (1), where m_0 represents the initial weight of the sample, m_n is the weight after the nth abrasion cycle, and A is the area of the sample in contact with the pad during the test [23],

$$L = \frac{m_0 - m_n}{A} \qquad (1)$$

By observing the trend of mass loss per unit area (L) as a result of abrasion cycles in the graph shown in Figure 4a. The graph in Figure 4 illustrates the mass loss for each coating type as a function of the number of abrasion test cycles, along with the corresponding gloss reduction following the abrasion experiment. As the test progresses, mass loss steadily increases due to the continuous surface wear caused by the scrubbing sponge. Shell and Mussel coatings have different sizes of particles in the same area and exhibit significantly higher mass loss, likely due to the hardness of their bio-based particles. A notable reduction in gloss is also observed for Shell and Mussel after abrasion in Figure 4b. This can be attributed to the inherent shininess of these bio-based powders.



(a) (b)

Figure 4. Mass loss evolution during 2000 cycles of the abrasion test (a). Gloss reduction (b).

Once the surface particles are removed during abrasion, the gloss diminishes accordingly. Tagua powder exhibited a similar behaviour to Shell and Mussel, where particle concentration in localized areas and variation in particle size led to a significant reduction in both mass and gloss values after the abrasion test. In contrast, coatings with Cuttlefish powder demonstrated better performance in the abrasion test, maintaining lower mass loss and retaining higher gloss values, with a decrease of only 21% in comparison of 65% and 50% of the Shell and Mussel. The reference sample also shows a significant gloss reduction of 56%.

One of the factors influencing abrasion resistance is the hardness of the coating. However, the data show that for Shell-based coatings, the addition of fillers does not significantly improve abrasion resistance or gloss retention compared to the reference sample. In contrast, Cuttlebone and Tagua powders demonstrated better performance in gloss retention after the abrasion test. This aligns with literature findings, which highlight the challenge of improving paint hardness using bio-based fillers [24, 25] unless the fillers are derived from extremely hard materials, such as olive pits [26] or macadamia shells [27].

The appearance of the samples is further detailed through microscopic analysis shown in Figure 5, which presents top-view images of the coatings captured using an optical microscope. Under the testing conditions, the addition of organic particles across all granulometries and concentrations resulted in increased mass loss throughout the abrasion cycles, compared to the control coating without filler. This trend is visually supported by comparing the abraded areas of all samples in Figure 5. The surface of the reference sample appears significantly smoother than those containing organic fillers, suggesting that the abrasive pad exerted less mechanical action. Additionally, no visible material detachment was observed in the reference coating, unlike in the samples with bio-based additives.

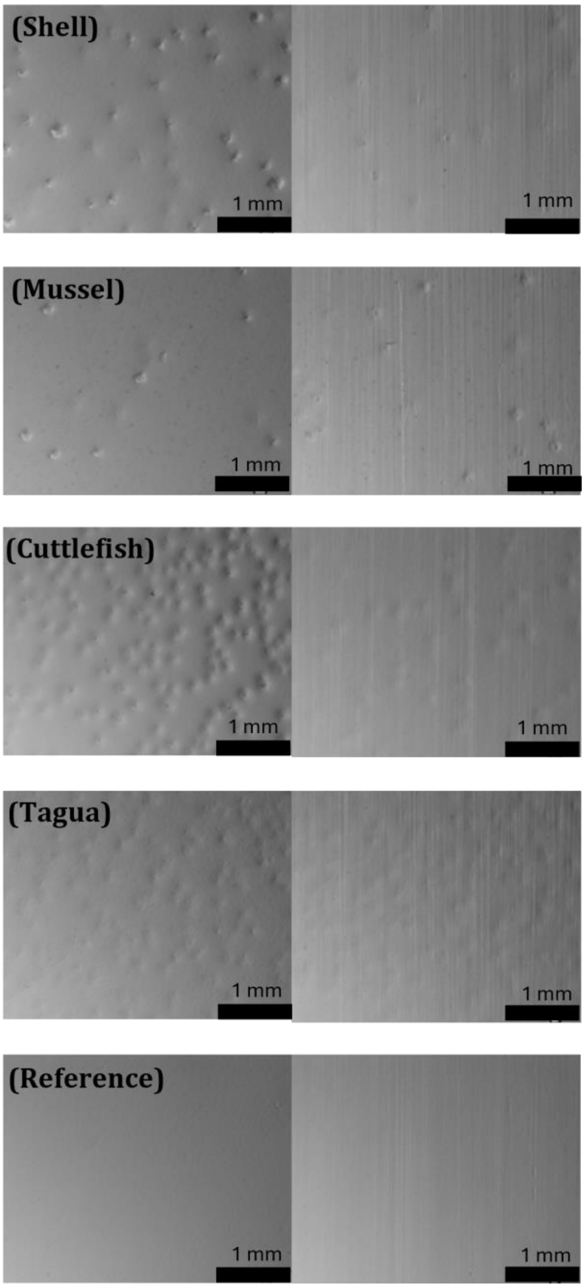


Figure 5. Optical micrographs of the top-view depicting the appearance and surface morphology after the scrub test before (on the left) and after (on the right).

3. Impact of additive on the coating´s durability in Aggressive Environments

3.1 Salt spray chamber exposure

Strong wet adhesion is a key factor for improving the ability of a coating to act as a protective barrier, because through it the coating can repel water and the corrosive environment. This function can be achieved by changing the composition [28], structure [29], or morphology [24] of the coating system. Samples were exposed to a salt fog chamber for 500 hours, with observations recorded every 100 hours. Within the first 24 hours, all samples exhibited blister formation around the scratch and all over the panel, attributed to water uptake, which was visually inspected during each monitoring session, as shown in Figure 6. The incorporation of bio-based fillers did not enhance the protective properties of the coatings; instead, it appeared to negatively affect performance by promoting moisture absorption due to their hygroscopic nature. In waterborne coatings, water penetration to the metal substrate is critical and remains a significant limitation, particularly at the coating/metal interface, as observed in this study. The loss of adhesion in coatings containing organic fillers continues to challenge long-term stability in practical engineering applications [24]. Tagua is composed of lignocellulose and is characterized by a hygroscopic behaviour, which is already highlighted in several works [21, 25].

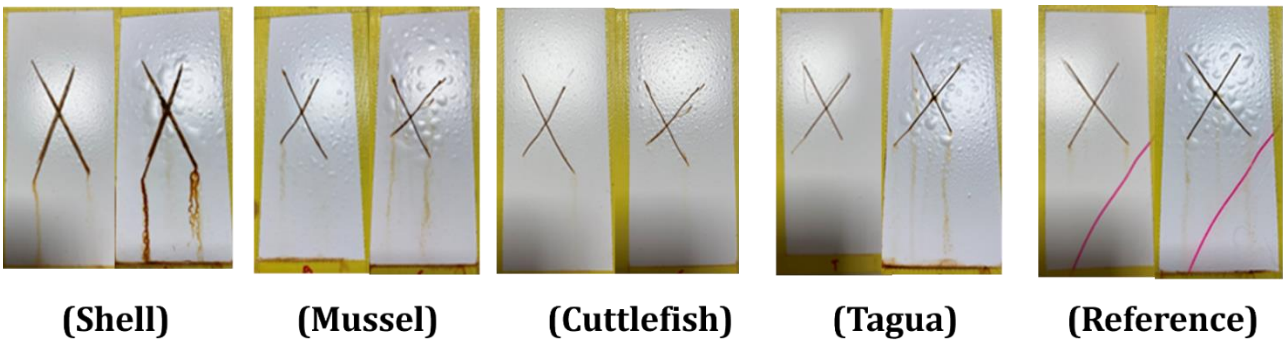


Figure 6. Coated samples at 24 hours (on the left), at 168 hours/7 days (on the right).

3.2 Filiform

Considering the filiform corrosion experiment, Figure 7 illustrates the number and length of filiforms, while Figure 8 depicts the delamination around the scratch after 14 days (336 hours). Coating adhesion plays a critical role in corrosion protection, as poor adhesion facilitates the movement of water, oxygen, and ions, thereby accelerating corrosion processes. In contrast, strong adhesion can inhibit delamination even under high moisture conditions. Although Shell, Mussel, Cuttlefish bone, and Tagua fillers were expected to serve as barrier materials, they did not demonstrate the anticipated corrosion-inhibiting effects. The presence of blisters around the panels in every sample, along with filiform corrosion, suggests that the organic fillers may create preferential pathways for moisture under high humidity. In many cases, filiform corrosion filaments developed and expanded as blisters, further indicating compromised coating integrity [11]. In conclusion, while the inclusion of bio-based fillers enhances gloss, it adversely affects the corrosion resistance of the coatings. The barrier properties of the composite layers are compromised due to the introduction of these powders, which can form interfacial gaps with the polymer matrix, allowing moisture and aggressive ions to infiltrate. Similar behaviour has been reported in prior studies [11, 26, 27], where lignocellulosic fillers promoted water uptake by creating percolation pathways that facilitate capillary water transport [21]. To quantitatively evaluate the impact of the four bio-based additives on the protective performance of the coatings, electrochemical impedance spectroscopy (EIS) was carried out.

3.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique used to evaluate the protective performance of paints, including their adhesion, barrier properties, and potential defects. EIS is non-destructive, as it involves applying a small polarization to the coated surface. One key parameter used in the analysis is the impedance modulus at low frequency (typically 0.01 Hz), denoted as $|Z|_{(0.01)}$. This value, derived from the Bode plot, can approximate the overall protective capability of a coating.

Although $|Z|_{(0.01)}$ is widely accepted as a benchmark, it can sometimes lead to misinterpretation, especially in the case of coatings with inherently high barrier properties [30]. However, in the present study, the waterborne nature of the paints and the increased permeability introduced by the addition of organic powders created appropriate conditions for the reliable use of this parameter as an indicator of protective performance.

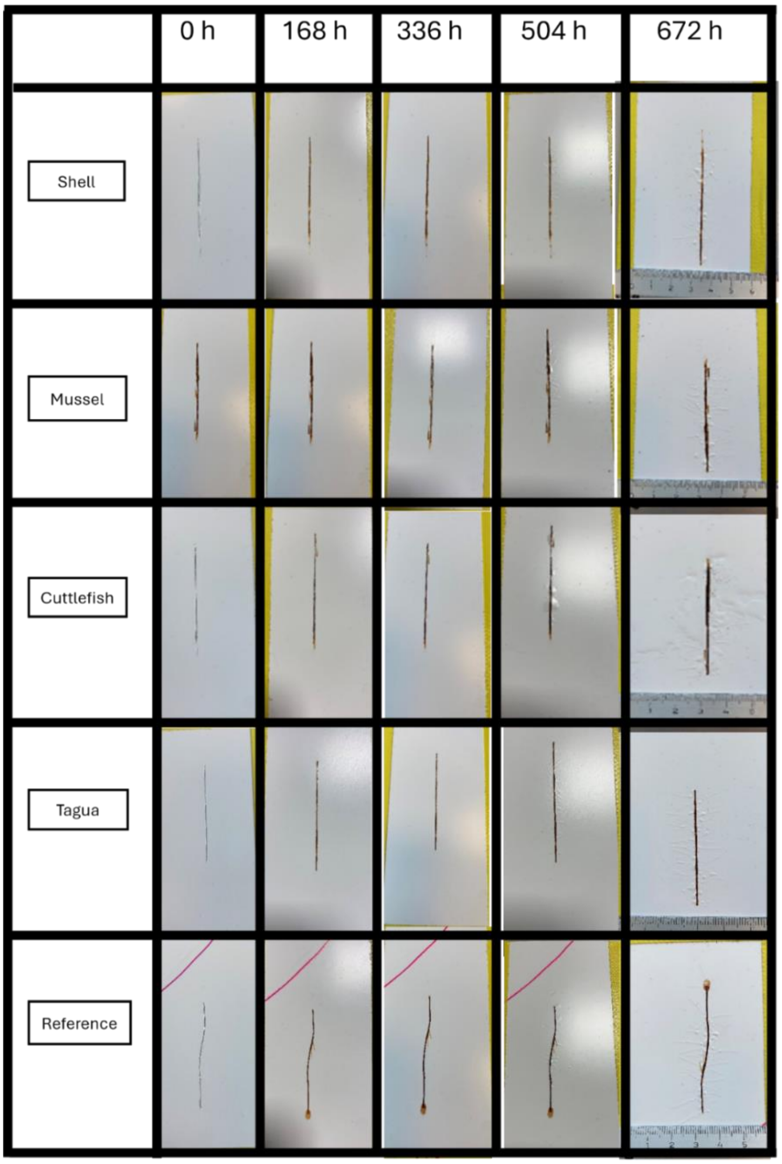


Figure 7. Changed in appearance samples from 0 h to 672 h during exposure time in the filiform experiment.

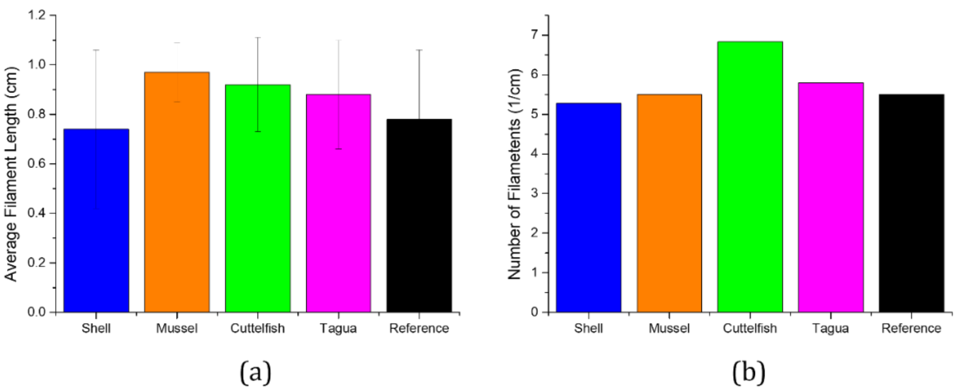


Figure 8. Filiform degradation parameters. (a) report the mean filament length, while (b) display the specific number of nucleated threads per unit length.

According to established literature [11, 21, 31, 32], coating is generally considered protective if its total resistance remains above 10^6 Ω·cm². Values below this threshold are indicative of degradation or failure in protective function. In this study, the evolution of $|Z|_{(0.01)}$ over 300 hours of exposure to saline solution was monitored (Figure 9). Initially, all samples displayed high impedance values between 10^8 and 10^9 Ω·cm², indicating effective initial protection. However, after the first 8 hours, impedance dropped significantly to the range of 10^6–10^7 Ω·cm², attributed to water uptake, which is typical in waterborne coatings [33]. These coatings contain hydrophilic additives, such as wetting and dispersing agents, stabilizers, and thickeners, which enhance their susceptibility to moisture absorption. Despite this early decline, after 24 hours of immersion, impedance values stabilized across all samples, and $|Z|_{(0.01)}$ remained relatively constant for the rest of the test duration, suggesting a steady-state equilibrium had been reached. The reference sample demonstrated the most stable behaviour, with a consistent increase in impedance modulus over time. After 336 hours, it maintained the highest $|Z|_{(0.01)}$ value, confirming superior long-term barrier protection. Among the coatings containing bio-based fillers, Cuttlefish bone showed the most favourable performance. It initially exhibited the highest impedance value and, although it dropped after 8 hours, it stabilized at a high level, approaching that of the reference. This suggests that the filler used in Cuttlefish has minimal impact on the coating's barrier properties and performs well in maintaining protection against corrosion. Shell sample displayed moderate recovery and stability, performing better than Mussel samples and Tagua one, but still below Cuttlefish and the reference. In contrast, Mussel and Tagua showed the lowest impedance values throughout the test. These two samples exhibited limited recovery. However, it is still accepted as a protective threshold since it remains above 10^6 Ω·cm², but it might indicate poor long-term protection. These results suggest that the nature of the bio-based filler strongly influences the permeability and protective performance of the coating. Specifically, Cuttlefish shows promise for use in protective coatings, while Mussel and Tagua may require reformulation to mitigate water ingress pathways. Shell and Mussel behaviour is likely due to the formation of preferential paths at the particle/coating interface, allowing water to pass through these paths rather than the polymeric matrix [34]. The consistently high impedance values in the reference samples suggest that the poor performance of the seashell samples is not due to water uptake [11, 35]. The organic fillers negatively affect the interface between the particles and the resin, creating interfacial gaps that facilitate the penetration of electrolytes and allow them to reach the substrate [21]. The presence of Tagua particles in the paints, due to their hydrophilic characteristic, leads to a general decrease in the impedance modulus at the end of the test, compared with other samples [21].

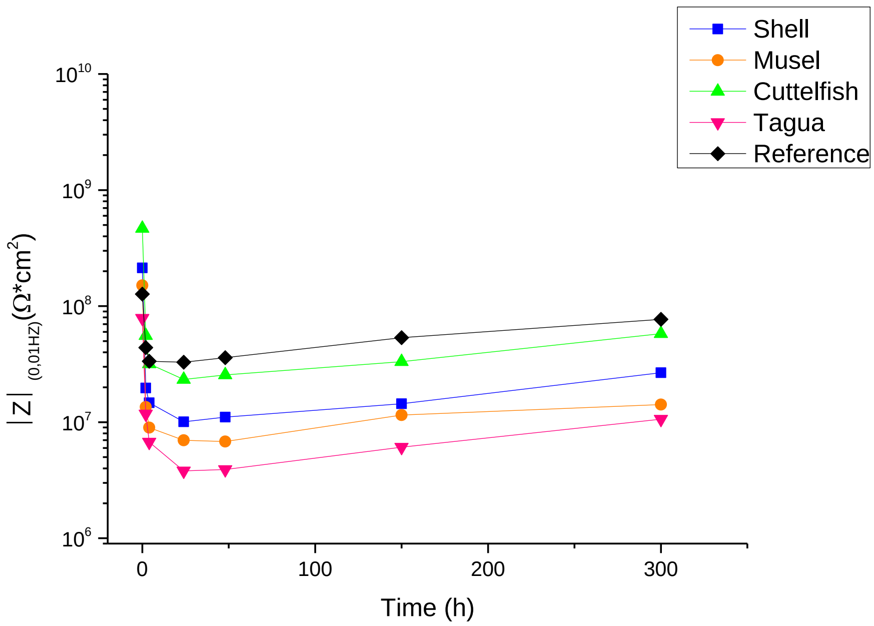


Figure 9. Bode impedance modulus $|Z|_{(0.01)}$ evolution with time.

3.3 Xenon test

A common issue with using chemical and organic fillers in color coatings is their tendency to undergo physical and chemical deterioration when exposed to sunlight [36, 37]. To assess this, the samples were exposed in a Xenon light to evaluate any potential aesthetic changes in the coatings.

Figure 10a illustrates the gloss trends. The reference sample shows a nearly constant gloss level with minimal variation, indicating that the waterborne paint is not significantly affected by physical-chemical degradation. Similarly, the four composite coatings exhibit some variation in gloss, suggesting minor degradation of the bio-based fillers due to Xenon light exposure. However, the gloss values remain relatively stable after the first 24 hours. The reduction in gloss after 24 hours may be explained by gloss retention, which is defined as the percentage change in a specimen's gloss during weathering relative to its initial value. During accelerated weathering, gloss changes are strongly correlated with the level of surface coating degradation, which may primarily affect either the pigment or the resin component of the coating [38].

Figure 10b presents the results color change measurements analyzed during the accelerated degradation test under 500 hours. This stability is further supported by the color variation data. The composite samples present a total color change (ΔE) of less than 1 unit, which is generally considered negligible. These results are comparable to the performance of other polymeric bio-based fillers, such as polyamide 11 powders [11, 39], and are significantly more stable than lignocellulosic fillers, which are prone to photo-oxidation under the Xenon test [21, 27]. Most samples showed little or no significant color change. Detailed analysis of the color coordinates L*, a*, and b* (Figure 10b) reveals that Shell, Cuttlefish, Tagua, and reference showed the color variation is darkening (decrease in L*) and a shift toward green and blue tones (decrease in a* and b*). Mussel fillers, in contrast, tended to shift slightly toward blue and exhibited less pronounced darkening (decrease in b* and L*), indicating better results in solar radiation exposure.

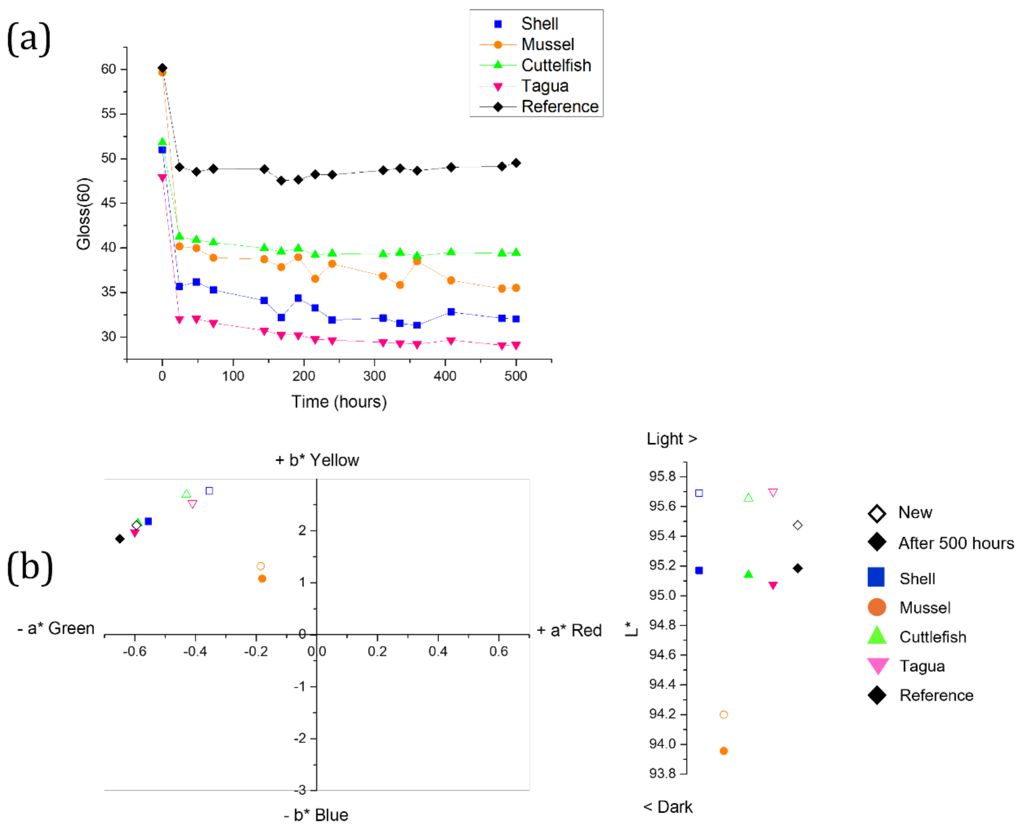


Figure 10. Changes in (a) gloss, (b) a*,b* coordinate, L* coordinate during the Xenon exposure test.

The Xenon chamber exposure test confirms the strong aesthetic durability of bio-based fillers derived from Mussel, attributed to the calcite's inherent resistance to solar radiation, which is one of the most important minerals known to increase the mechanical and physicochemical properties of coating [40]. If only for the Xenon test, Mussel powders make such fillers promising candidates for outdoor applications exposed to sunlight. However, this performance contrasts with results from salt spray chamber tests, where prolonged contact with aqueous environments compromises the coating's integrity and protective function.

DISCUSSION

This study evaluated the effects of four bio-based fillers—Seashell, Mussel, Cuttlefish bone, and Tagua—on the performance of waterborne acrylic coatings applied to steel substrates. The incorporation of these natural fillers influenced multiple functional properties, particularly gloss, abrasion resistance, and durability under environmental stress.

Gloss and surface analyses revealed that Shell- and Mussel-based coatings initially offered higher gloss values due to their particle structure but suffered significant reduction after abrasion. In contrast, Cuttlefish bone and Tagua powders, with their distinct particle morphologies, demonstrated greater gloss retention and mechanical integrity under abrasion conditions. Microscopic observations confirmed that bio-based particles, particularly when unevenly distributed, promote localized weaknesses leading to higher mass loss.

In aggressive environments, such as salt spray and filiform corrosion tests, all bio-based additives showed susceptibility to water uptake and adhesion loss. This was especially evident in samples containing hydrophilic fillers like Tagua. These coatings exhibited blister formation and early degradation, highlighting the challenge of maintaining adhesion at the coating–substrate interface. The structural properties of shell-based fillers, such as their plate-like morphology, appear to facilitate moisture ingress, forming preferential pathways for water diffusion. Unfortunately, the addition did not lead to improvements in the corrosion behavior of waterborne paints as hoped.

EIS analysis confirmed that while all coatings began with high impedance values, those containing Cuttlefish bone retained performance closest to the control sample over time. Mussel and Tagua samples, while above the protective threshold, showed signs of poor long-term stability. The variation in impedance responses among samples highlights the importance of filler type, morphology, and compatibility with the coating matrix.

Xenon light exposure revealed that, despite limitations in aqueous environments, some bio-fillers (notably Mussel) exhibited excellent aesthetic stability, with minimal gloss and color changes. Mussel powder contains a high content of calcite compound that could enhance Xenon test results compared to other fillers. These findings suggest that Mussel-derived fillers could be suited for outdoor applications.

This organic filler may be suitable for use as a topcoat in multi-layer coating systems, as it shows promising results in terms of color stability. However, it performs poorly in terms of adhesion. Therefore, combining it with a strong adhesive primer and applying it as a topcoat could be a viable approach for future industrial applications.

CONCLUSIONS

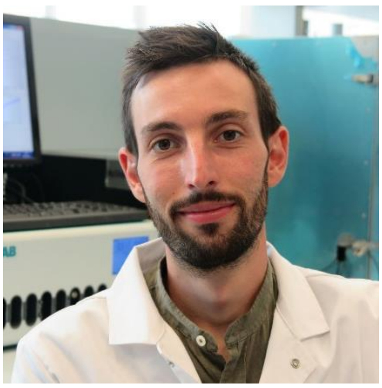
This study demonstrates that while bio-based fillers offer sustainable alternatives for waterborne coatings, their impact on performance is highly dependent on their composition, structure, and interaction with the polymer matrix. Among the tested additives, **Cuttlefish bone** showed the best balance between durability and barrier performance, whereas **Mussel filler** stood out for its excellent solar radiation stability. However, **Tagua** and **Shell** powders introduced challenges in maintaining corrosion resistance due to their hydrophilic or porous structures. These findings highlight the need for careful filler selection and formulation optimization in developing eco-friendly coatings for industrial use.

REFERENCES

1. Local Authorities, Environmental Protection Act 1990, in Environmental Protection in England, no. No.472, London: TSO, 1990, Chapter 43.
2. Galliano F. and Landolt D., Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel, Progress in Organic Coatings 44(3), (2002), 217-225.
3. Almeida E., Santos D., and Uruchurtu J., Corrosion performance of waterborne coatings for structural steel, Progress in Organic Coatings 37(3-4), (1999), 131-140.
4. Leidheiser H., Musit S., and Mcintyre J. F., The improved corrosion resistance of steel in water after abrasive blasting with alumina, Corrosion Science 24(23), (1984), 197-208.
5. Thometzek P., Ludwig A. , Karbach A., and Köhler K., Effects of morphology and surface treatment of inorganic pigments on waterborne coating properties, Progress in Organic Coatings 36(4), (1999), 201-209.
6. Huttmanová E., Chovancová J., Petruška I. and Sallaku K., Circular Economy in Action: Examining the Decoupling of Economic Growth and Material Use across EU Countries, European Journal of Sustainable Development 13(4), (2024), 13-22
7. Calovi M. and Rossi S., Synergistic contribution of bio-based additives in wood paint: The combined effect of pigment deriving from spirulina and multifunctional filler based on carnauba wax, Progress in Organic Coatings 182, (2023), 107713.
8. Calovi M. and Rossi S., Functional Olive Pit Powders: The Role of the Bio-Based Filler in Reducing the Water Uptake Phenomena of the Waterborne Paint, Coatings 13(2), (2023), 442.
9. Karakaş F. and Çelik MS., Effect of quantity and size distribution of calcite filler on the quality of water borne paints, Progress in Organic Coatings 74(3), (2012), 555-563.
10. Toro P., Quijada R., Yazdani-Pedram M. and Arias JL., Eggshell, a new bio-filler for polypropylene composites, Materials Letters 61(22), (2007), 4347-4350.
11. Rodríguez-Gómez FJ., Calovi M. and Rossi S., Micronized Shell-Bioaggregates as Mechanical Reinforcement in Organic Coatings, Materials 17(16), (2024), 4134.
12. Nadal ME., Early EA. and Thompson EA., Specular Gloss, NIST Special Publication SP250-70, (2006), 72.
13. ASTM D4213-24, Test Method for Scrub Resistance of Paints by Abrasion Weight Loss.
14. ASTM B0117-19, Standard Practice for Operating Salt Spray (Fog) Apparatus.
15. ASTM D2803-09R20, Standard Guide for Testing Filiform Corrosion Resistance of Organic Coatings on Metal.
16. Yu Y., Jiang M., Wang S., Guo Y., Jiang T., Zeng W. and Zhuang Y., Impact of particle size on performance of selective laser sintering walnut shell/co-pes powder, Materials 14(2), (2021), 448.
17. Srichanachaichok W. and Pissuwan D., Micro/Nano Structural Investigation and Characterization of Mussel Shell Waste in Thailand as a Feasible Bioresource of CaO, Materials 16(2), (2023), 805.
18. Hart A. and Onyeaka H., Eggshell and Seashells Biomaterials Sorbent for Carbon Dioxide Capture, (In) Carbon Capture, IntechOpen, 2021.
19. Gigante V., Cinelli P., Righetti M., Sandroni M., Tognotti L., Seggiani M. and Lazzeri A., Evaluation of mussel shells powder as reinforcement for PLA-based biocomposites, International Journal of Molecular Sciences 21(15), (2020), 5364.
20. Kong L., Zhu E., Yang A., Li X., Zhong L. and Jiang H., From marine debris to a valuable medical resource: A review on biology, chemistry, ethnopharmacology, bioactivity and application in biomedical materials of cuttlebone, Journal of Ethnopharmacology 341, (2025), 119333.
21. Cristoforetti A., Donati L. and Rossi S., Tagua Powder as a Bio-Based Filler for Waterborne Acrylic Coatings: Enhancing Performances and Sustainability, Coatings 8(1), (2025), 20.
22. Kumar N., Bhardwaj NK. and Chakrabarti SK., Influence of pigment blends of different shapes and size distributions on coated paper properties, Journal of Coatings Technology and Research 8(5), (2011), 605-611.
23. Calovi M, Rossi S., Deflorian F., Dirè S., Ceccato R., Guo X. And Frankel G., Effects of graphene-based fillers on cathodic delamination and abrasion resistance of cataphoretic organic coatings, Coatings 10(6), (2020), 602.
24. Wan H., Song D, Li X., Zhang D., Gao J., and Du C., A new understanding of the failure of waterborne acrylic coatings, RCS Advances 7(61), (2017), 38135-38148.
25. Najafi SK., Tajvidi M. and Chaharmahli M., Long-term water uptake behavior of lignocellulosic-high density polyethylene composites, Journal of Applied Polymer Science 102(4), (2006), 3907-3911.

26. Momber AW., Irmer M. and Marquardt T., Effects of polymer hardness on the abrasive wear resistance of thick organic offshore coatings, Progress in Organic Coatings 146, (2020), 105720.
27. Calovi M. and Rossi S., Olive pit powder as multifunctional pigment for waterborne paint: influence of the bio-based filler on the aesthetics, durability and mechanical features of the polymer matrix, Industrial Crops and Products 194, (2023), 116326.
28. Jafarzadeh S., Claesson PM., Pan J. and Thormann E., Direct measurement of colloidal interactions between polyaniline surfaces in a uv-curable coating formulation: The effect of surface hydrophilicity/ hydrophobicity and resin composition, Langmuir 30(4), (2014), 1045–1054.
29. Van Zoelen W., Buss H., Ellebracht N., Lynd N., Fischer D., Finlay J., Hill S., Callow M., Callow J., Kramer E., Zuckermann R., Segalman R., ACS Macro Letters 3(4), (2014), 364-368.
30. Cristoforetti A., Rossi S, Deflorian F. and Fedel M., On the Limits of the EIS Low-Frequency Impedance Modulus as a Tool to Describe the Protection Properties of Organic Coatings Exposed to Accelerated Aging Tests, Coatings 13(3), (2023), 598.
31. Amirudin A. and Thierry D., Application of electrochemical impedance spectroscopy to study the degradation of polymer-coated metals, Progress in organic coatings 26, (1995), 1-28.
32. Rossi S., Deflorian F., Fontanari L., Cambruzzi A. and Bonora PL., Electrochemical measurements to evaluate the damage due to abrasion on organic protective system, Progress in Organic Coatings 52(4), (2005), 288–297.
33. Hochmańska-Kaniewska P., Janiszewska D. and Oleszek T., Enhancement of the properties of acrylic wood coatings with the use of biopolymers, Progress in Organic Coatings 162, (2022), 106522.
34. Meng F., Liu L., Tian W., Wu H., Li Y., Zhang T. and Wang F., The influence of the chemically bonded interface between fillers and binder on the failure behaviour of an epoxy coating under marine alternating hydrostatic pressure, Corrosion Science 101, (2015), 139-154.
35. Miszczyk A. and Darowicki K., Water uptake in protective organic coatings and its reflection in measured coating impedance, Progress in Organic Coatings 124, (2018), 296-302.
36. Plota-Pietrzak A. and Masek A., Influence of organic and inorganic fillers on the photoaging behavior of polyolefins, Polymer Degradation and Stability 219, (2024), 110598.
37. Groeneveld I., Kanelli K., Ariese F. and van Bommel MR., Parameters that affect the photodegradation of dyes and pigments in solution and on substrate – An overview, Dyes and Pigments 210, (2023), 110999.
38. Vlad Cristea M., Riedl B. and Blanchet P., Enhancing the performance of exterior waterborne coatings for wood by inorganic nanosized UV absorbers, Progress in Organic Coatings 69(4), (2010), 432-441.
39. Calovi M. and Rossi S., Exploring polyamide 11 as a novel renewable resource-based filler in wood paint: Investigating aesthetic aspects and durability impact of the composite coating, Progress in Organic Coatings 188, (2024), 108262.
40. Kabacińska Z., Yate L., Wencka M., Krzyminiewski R., Tadyszak K, and Coy E., Nanoscale Effects of Radiation (UV, X-ray, and γ) on Calcite Surfaces: Implications for its Mechanical and Physico-Chemical Properties, Journal of Physical Chemistry C 121(24), (2017), 13357–13369.

AUTHOR DETAILS

	S. Rossi, Full professor at the University of Trento, teaching "Protection of Materials and Structures," "Product Design," and "Materials Science and Technologies." He leads the Coatings and Industrial Anticorrosion Lab in the Department of Industrial Engineering. His research focuses on corrosion protection using organic, metallic, enamel, and ceramic coatings, including smart and innovative solutions. He employs electrochemical techniques and accelerated tests. Author of over 235 international publications with an h-index of 41.
	N. Khongsay is a food and biotechnology researcher with a multidisciplinary background, including experience in chemistry, agriculture, and medical equipment. In 2024, she began a new research journey in the Corrosion Laboratory at the University of Trento, marking the start of her position in this field.
	L. Benedetti is a dedicated laboratory technician who has held his position at the University of Trento since 1991. He is responsible for all laboratory activities and equipment within the corrosion laboratory. He also provides guidance and troubleshooting support for experimental procedures.
	A. Cristoforetti is a postdoctoral researcher at the University of Trento, a position he has held since 2024. He is responsible for research activities on corrosion-resistant coatings and surface treatments within the MAKO project, focusing on biomimetic aluminium surfaces for aerospace applications. His work includes electrochemical testing, materials characterization, and the development of protective oxide layers, contributing to innovation in sustainable and high-performance materials.

N. Mattei is a passionate postgraduate researcher at the University of Trento. With a background in biotechnology, specifically in microbes and infections, he broadened his research interests by joining the S. Rossi Coating and Corrosion Laboratory as a research fellow at the beginning of 2025.