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Comparative Analysis of the Advantages and Disadvantages of Utilizing Spirulina-Derived Pigment as a Bio-Based Colorant for Wood Impregnator

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Abstract: The aim of this work was to examine the advantages and disadvantages of using spirulina-derived pigment as a bio-based colorant for wood impregnators. It investigated the effects of three different quantities of spirulina granules on the aesthetic properties and durability of a water-based wood impregnator. The impact of this environmental friendly pigment on the overall appearance of the coatings was estimated through colorimetric measurements and observations using an optical microscope. The durability of the coatings with varying amounts of spirulina was assessed by subjecting the samples to UV-B radiation and cyclic thermal shocks and analyzing them using infrared spectroscopy and colorimetric inspections. Furthermore, the influence of additive concentration on the coating's barrier efficiency was examined through liquid resistance and water uptake tests. Finally, the scrub test was carried out to assess the effect of the spirulina pigment on the abrasion resistance properties of the protective layers. Ultimately, this study emphasized the remarkable coloration achieved through the use of the spirulina-based additive. However, the pigment derived from natural sources exhibited significant concerns associated with deterioration caused by UV-B radiation or the fading of the phycocyanin component found in spirulina. Thus, the work underscores the importance of implementing appropriate measures to safeguard the bio-based pigment from external factors such as temperature, solar radiation, and liquids.

Keywords: spirulina; wood impregnator; bio-based additive; natural pigment; protective coating

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1. Introduction

Throughout history, humans have extensively utilized wood as a valuable resource [1]. This is primarily due to its distinct physical and chemical properties [2], including a remarkable lightness in relation to its mechanical features [3] and ease of workability [4]. Additionally, wood is highly regarded thanks to abundant availability, along with its distinct visual characteristics [5,6]. Nevertheless, the inherent cellulosic nature of wood renders it susceptible to flammability [7], degradation caused by moisture [8], and sensitivity to solar radiation [9,10]. To address these practical challenges, organic coatings are often applied to wooden components. These coatings enhance the durability of the material by providing protection against solar light exposure [11,12], fluctuations in moisture levels [13], chemical attacks [14], physical damage [15], and also act as a deterrent to detrimental fungal microorganisms [16–18].

The utilization of hardwood in various exterior implementations has prompted both the academic and industrial sectors to explore innovative approaches for improving the functionalities of wood coatings [19,20]. One approach entails altering the ultraviolet (UV) absorption properties of wood coatings by incorporating diverse nanoscale particles, including TiO_2 [21], ZnO [22], SiO_2 [23], and CeO_2 [24]. Likewise, nanomaterials characterized by exceptional hardness, rigidity, and thermal stability, such as nanosilica [25], nanoalumina [26], nanoclay [27], and nanocellulose [28], have been used to enhance the mechanical properties and water resistance of wood coatings [29]. Additionally, the inclusion of nanomaterials such as copper nanopowders [30], nanotitanium [31], and silver [32–34] has been employed to augment the bactericidal and antifungal activities of wood finishes.

However, there is a growing market trend in protective wood coatings that involves the use of colored paint [35], which imparts specific aesthetic effects to wooden products [36]. This trend includes the incorporation of novel pigments [36] and is oriented to achieve distinct gloss values [37]. Recent research efforts have focused on investigating the durability of these pigments in wood coatings [38,39]. It is crucial to consider that the innovative pigments should offer unique aesthetic effects without compromising the protective properties of the organic coating. The synergy of hardwood finishes and various kinds of colorants can potentially give rise to significant challenges, since it has the potential to compromise the preserving efficiency of the organic films by creating gaps in the polymer framework or displaying inadequate inherent durability of the pigment [40,41].

Today, the wood finishing field is gradually shifting its attention to two key areas of interest: green feedstocks and the sustainable economy. There is an increasing focus on eco-conscious and versatile substitutes to conventional chemical additives [42,43], which are often produced without considering environmental sustainability factors [44]. Academia is now exploring the utilization of untreated additives in films [45,46]. In line with this objective, recent studies have examined the effects of incorporating various substances into wood coatings, including linseed oil [47], timber waste-derived colorants [48], microbial-assisted coloring [49], mycelium-based dyes [50], and biomass fibrous material [51].

In this context, spirulina derivatives could represent an interesting source of bio-based pigment for wood paints. Pigments derived from microalgae have gained significant scientific interest and are in high demand in the market [52] due to the growing need for acquiring natural pigments as environmentally-friendly alternatives. Spirulina (*Spirulina platensis*), a cyanobacteria, is widely acknowledged as a prominent microalgal resource for the commercial manufacturing of phycobiliproteins [53,54], that represent chromoproteins involved in light-harvesting processes. Apart from its noteworthy antioxidant and anti-inflammatory properties [55,56], spirulina also exhibits anticancer and antimicrobial characteristics [57]. Importantly, spirulina is rich in phycocyanin, an eco-friendly blue dye [58], making it a valuable source for pigment production in hardwood finishes. As much as 25% of its dehydrated material is composed of phycocyanin, highlighting its potential application in this context [59].

While the scientific community is increasingly focused on the extensive application of bio-based and renewable resources, the impact of green additives on coating performance has often been overlooked. A recent study examined the use of spirulina as a pigment source for wood varnishes in conjunction with a multifunctional filler composed of carnauba wax [60]. The research demonstrated the potential of spirulina as an alternative natural pigment but also identified certain potential issues regarding the durability of the pigment itself. Hence, the aim of this study was to assess the effectiveness of the spirulina-based pigment in wood stain for coloring purposes. This investigation analyzed the impact of the pigment on the protective performance of the coating layer and evaluated its chromatic durability through various accelerated degradation tests.

To assess the influence of pigment concentration on the specific properties of the coating, three different amounts of spirulina granules were incorporated into a commercial water-based wood impregnator. The effects of the additive on the coating's morphology and appearance were examined using scanning electron microscopy (SEM), optical stereomicroscope observations, and colorimetric analyses. These methods were employed to characterize the impact of the bio-based pigment on the structure and aesthetic qualities of the composite layers. Furthermore, the durability of the coatings in the presence of spirulina granules was assessed through two accelerated degradation tests. These tests involved subjecting the coatings to exposure in a climatic chamber and to UV-B radiation. The objective was to evaluate the barrier effect and the stability/protection of the coatings in terms of color change, respectively. In order to assess the potential chemical deterioration of the coatings under UV-B radiation exposure, Fourier-transform infrared spectroscopy (FTIR) measurements were conducted. Simultaneously, colorimetric analyses were performed to monitor any corresponding aesthetic alterations in the coatings. Furthermore, colorimetric tests were also employed to evaluate the susceptibility of the coatings to degradation within the climatic chamber when different amounts of pigment were added. The performance of the coatings was examined with an optical microscope. Moreover, the effectiveness of the coatings in terms of protection was assessed through different chemical tests. These evaluations aimed to analyze any potential color changes in the samples and determine whether the pigment influenced the barrier properties of the paint. Lastly, the abrasion resistance of the films and the impact of the sustainable fillers were assessed using the scrub test.

2. Materials and Methods

2.1. Materials

The spirulina granules, sourced from Garzanti Specialties (Milan, Italy), were utilized in their original form. The bio-based pigment has a particle size that is entirely retained on an 80-mesh sieve (<177 μm), with a bulk density ranging from 0.45 to 0.55 g/mL. Its composition primarily consists of ash (≤10%), moisture (≤8%), polypeptide (≥55%), crude phycocyanin (10%–15%), and chlorophyllic compound (11–14 mg/g). The additive can be characterized as a bio-based and environmentally friendly substance, as it exhibits a renewable carbon index exceeding 95%. Furthermore, it is readily soluble in water. The 150 × 150 × 2 mm^3 poplar wood plates were purchased from Cimadom Legnami (Lavis, Italy). The water-based wood impregnator G05 BIO based on linseed oil and natural waxes was provided by ICA Group (Civitanova Marche, Italy). It is formulated with raw materials from renewable sources. The commercial impregnator has a dry residue of 22.0 ± 2.0%, Ford Cup 2 viscosity of 55.0 ± 10.0 s, pH of 8.0 ± 0.5 and specific weight of 1.02 ± 0.05 g/mL. Sodium chloride (≥99.0%) and ethanol (99.8%) were acquired from Sigma-Aldrich (St. Louis, MO, USA) and used in their original state. The commercial detergent disinfectant product, Suma Bac D10 Cleaner and Sanitizer (Diversey, Fort Mill, SC, USA), which contains benzalkonium chloride (3.0–10.0 wt%), along with the cataphoretic red ink Catafor 502XC (Arsonsisi, Milan, Italy), were purchased and utilized for the liquid resistance tests.

2.2. Sample Production

To modify the formulation of the commercial impregnator, three different quantities of spirulina granules were added to achieve a final filler content of 0.2 wt%, 1.0 wt%, and 5.0 wt%. These amounts were selected by progressively increasing the concentration fivefold at each step until a wide range of colors was achieved. Prior to application, the three paint mixtures underwent mechanical mixing for 30 min, in order to completely dissolve the spirulina granules. The poplar wood panels were initially smoothed using 320 grit paper to achieve a uniform texture. Subsequently, the paints were sprayed onto the prepared hardwood surfaces and allowed to air dry for 24 h at room temperature. The impregnating agent was sprayed in accordance with the supplier's instructions, applying a pressure of 3 bar and a quantity of 60 g/m^2. This deposition and curing process was repeated twice. The study focused on evaluating the impact of varying amounts of the bio-based pigment in the coatings, as detailed in Table 1.

Table 1. Sample nomenclature with relative amount of spirulina pigment.

Sample Nomenclature	Spirulina Granules (wt%)
S0.0	0.0
S0.2	0.2
S1.0	1.0
S5.0	5.0

2.3. Characterization

The low vacuum scanning electron microscope (SEM) JEOL IT 300 (JEOL, Akishima, Tokyo, Japan) was utilized to examine the appearance of the bio-based additive and analyze the coatings' top and cross-sectional view. The objective was to investigate how the quantity of spirulina affects the compactness and structural morphology of the layers. The visual properties and aspect of the coatings were evaluated using the optical stereomicroscope Nikon SMZ25 (Nikon Instruments Europe, Amstelveen, The Netherlands) and employing color quantification conducted with a Konica Minolta CM-2600d spectrophotometer (Konica Minolta, Tokyo, Japan). The measurements were taken in SCI mode with a D65/10° illuminant/observer configuration.

In order to assess potential variations in the long-term resilience of the impregnator resulting from the incorporation of the sustainable additive, the samples underwent hastened decay experiments designed to mimic the application in harsh environmental conditions.

The samples were subjected to a UV-B chamber UV173 Box Co.Fo.Me.Gra (Co.Fo.Me.Gra, Milan, Italy), following the ASTM G154-16 standard [61] for a duration of 50 h. The experiment is particularly short due to its specific aggressiveness, which results in accelerated decay of the samples. This test aimed to evaluate the coatings' resistance to UV light. The accelerated degradation test employed Co.Fo.Me.Gra UV-B fluorescent lamps with a wavelength of 313 nm, an irradiance of 0.71 W/m^2, and a room temperature of 60 °C. To assess potential deterioration of the layers, FTIR infrared spectroscopy measurements and colorimetric analyses were conducted. Chemical modifications of the polymeric matrix were investigated using a Varian 4100 FTIR Excalibur spectrometer (Varian, Santa Clara, CA, USA).

To assess the impact of the amount of pigment on the coating's thermal resistance, the climatic chamber ACS DM340 (Angelantoni Test Technologies, Perugia, Italy) was employed to simulate drastic temperature variations. Following the UNI 9429 standard [62], the exposure test comprised 15 cycles, each consisting of the following:

- 4 h at +50 °C and relative humidity < 30%
- 4 h at −20 °C
- 16 h at room temperature.

To prevent moisture absorption by the underlying poplar wood substrate, the 5 uncoated surfaces of the $40 \times 40 \times 2$ mm^3 wood samples were sealed with silicone. Colorimetric analyses were conducted after every 3 iterations of exposure in the climatic chamber to track the changes in the appearance of the coatings throughout the experiment.

The influence of the amount of the bio-based pigment on the barrier properties of the polymer matrix was examined through chemical resistance tests following the GB/T 1733-93 standard [63]. Filter paper was immersed in solutions of 15% sodium chloride, 70% ethanol, detergent, and red ink. Next, the saturated filter paper was positioned on top of the coating surface and secured with a glass cover. Following a 24-h interval, the glass cover and filter paper were removed, removing any residual liquid on the coating. The resulting imprint and color change were assessed using colorimetric analysis techniques.

Furthermore, the water permeability of the paints was assessed through the liquid water uptake test in accordance with the EN 927-5:2007 standard [64]. The five exposed surfaces of the poplar wood-panels, measuring $40 \times 40 \times 2$ mm^3, were fully sealed using silicone, following the identical approach used for the previous aggressive test, to prevent water absorption by the wood support. The specimens were pre-conditioned at 65% relative humidity and 20 °C before being placed in a vessel filled with water. The moisture absorption, measured in g/m^2, was calculated via tracking the mass increase of the samples before the test and at 6, 24, 48, 72, and 96 h thereafter.

Lastly, the abrasion resistance of the protective coatings was assessed using the scrub test to examine the impact of the pigment quantity. The scrub test was performed using an Elcometer 1720 Abrasion and Washability Tester (Elcometer, Manchester, UK), in accordance with the ISO 11998 standard [65]. The coatings' wear endurance was determined through quantifying the weight reduction of the specimens after every 250 cycles (at a rate of

37 cycles per minute) for a total of 1000 cycles. Unlike the conventional procedure, the test was carried out in a dry mode without the use of a cleaning solution. This modification was made to avoid the absorption of the test solution by the polymeric matrix and the wood substrate, as it would have compromised the accuracy of the results. Finally, colorimetric measurements were carried out to verify the color stability following the abrasion processes.

3. Results

3.1. Fillers and Coatings Morphology

SEM was employed to observe the granules obtained from spirulina, as depicted in Figure 1. These structures, with an average size exceeding 50 µm, possess an irregular shape. Nevertheless, this characteristic is inconsequential since they readily dissolve in water-based paints, as was emphasized in a prior study [60]. The analyses of the recent study using energy-dispersive X-ray spectroscopy (EDXS) emphasized that the spirulina granules are made of organic materials, displaying strong peaks corresponding to carbon, oxygen, and nitrogen. Furthermore, the granules contain small amounts of P, K, S, Mg, and Na [60].

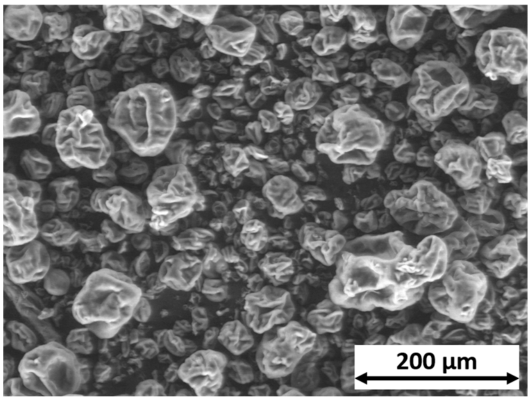
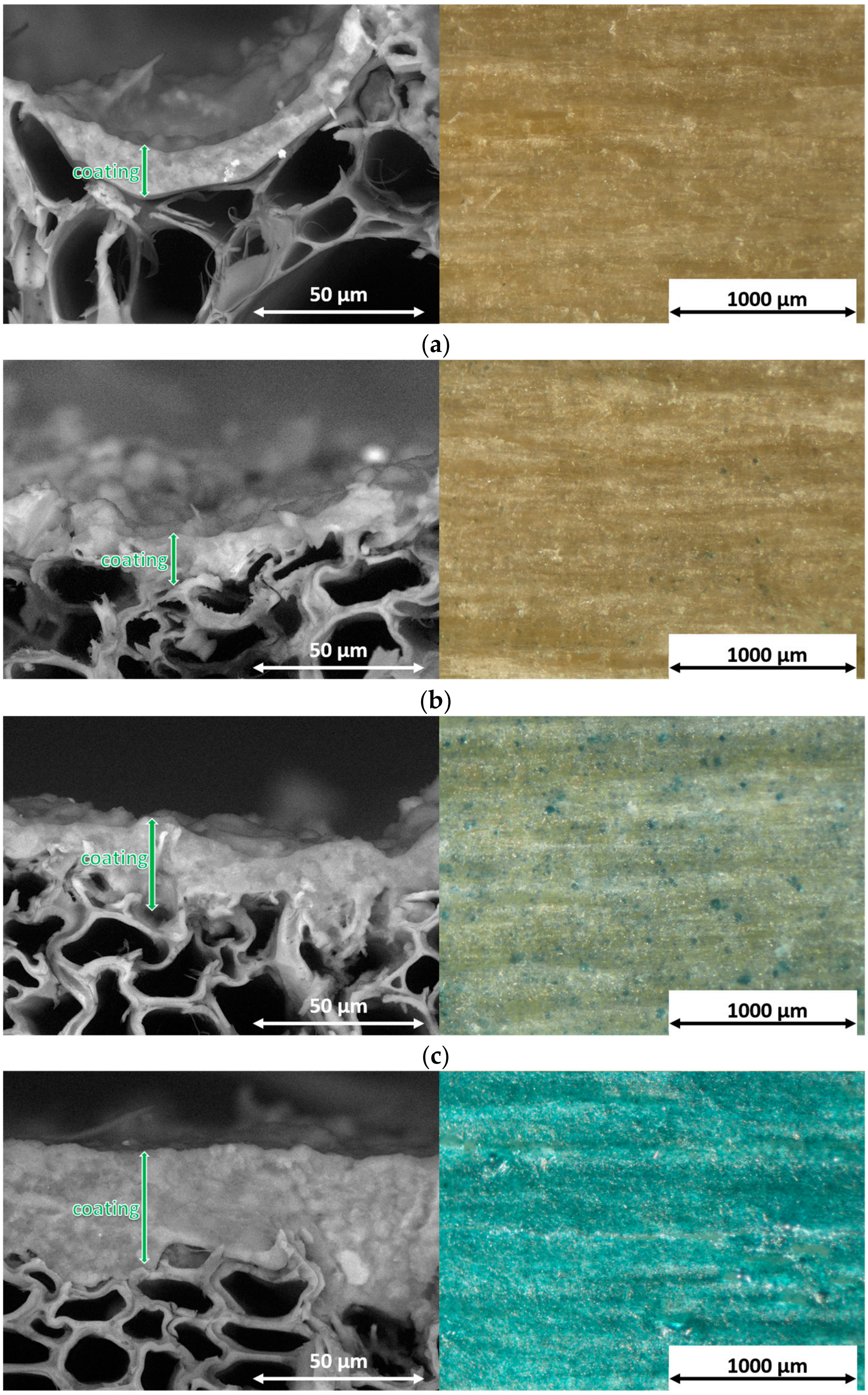


Figure 1. SEM micrographs of spirulina granules.

Consequently, the spirulina granules were incorporated into the commercial wood impregnator in accordance with the specified quantities presented in Table 1. This process resulted in the production of four series of samples for the purpose of this study, namely S0.0, S0.2, S1.0, and S5.0. To examine the impact of varying quantities of spirulina on the morphological anatomy of the hybrid films, the brittle fracture process was employed under liquid nitrogen conditions. The SEM images displayed on the left-hand side of Figure 2 focus on the cross-section of the samples, whereas the images on the right-hand side provide a top-view perspective of the coatings as observed through an optical microscope. The purpose of the former images is to emphasize the influence of spirulina on the paint deposition process, thereby resulting in modifications to the morphology of the final coating. In general, the coatings tend to have thicknesses of restricted dimensions, which is typically expected when using a wood impregnator. Nevertheless, the presence of spirulina seems to affect the size of the protective layer. Indeed, through its impact on the rheology of the organic matter, spirulina also influences the deposition process. This effect can be observed in the varying thickness of the layers, ranging from approximately 15 µm in the sample without filler (S0.0) to around 45 µm in the coating with a high concentration of spirulina (S5.0). The increase in coating thickness does not seem to result in the formation of defects within the layer's structure. Instead, the layer appears compact, indicating a positive synergy between the filler (spirulina) and the polymeric matrix of the paint.



(**a**)

(**b**)

(**c**)

(**d**)

Figure 2. SEM micrographs of the cross-section (on the left) and top-view optical microscope micrographs (on the right) of (**a**) sample S0.0, (**b**) sample S0.2, (**c**) sample S1.0, and (**d**) sample S5.0.

Concurrently, spirulina exerts a substantial influence on the visual appearance of the coating, as demonstrated by the top-view optical images. The filler imparts its characteristic green-blue hue to the sample, with the color becoming progressively stronger and more vibrant as the amount of spirulina increases. This suggests an effective coloring effect achieved by the filler. Figure 3 illustrates the overall color variation, denoted as ΔE, of the coatings in comparison to the reference sample S0.0, which does not contain spirulina. The calculation of ΔE was performed following the guidelines outlined in the ASTM E308-18 standard [66]:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}, \quad (1)$$

where the colorimetric coordinates L*, a*, and b* represent different aspects of color. L* denotes the lightness, with 0 representing black and 100 representing white objects. The coordinate a* indicates the presence of red (positive values) or green (negative values), while the coordinate b* reflects the presence of yellow (positive values) or blue (negative values) tones. In a recent study, the role of spirulina as a bio-based pigment in water-based paints was emphasized, showcasing its coloring capabilities [60]. However, this particular research unveils the potential chromatic changes that can be achieved by altering the quantity of spirulina in the impregnant formulation. The accompanying graph demonstrates a notable variation in ΔE (color difference), which amplifies as the concentration of the bio-based pigment increases. Considering that the literature establishes a threshold of $\Delta E \geq 1$ as the minimum perceptible difference to the human eye [67,68], Figure 3 suggests a remarkable aesthetic change in the coating. This observation aligns with the earlier findings demonstrated by the optical images presented in Figure 2. A concentration of 0.2 wt% of spirulina is adequate to induce a color alteration of approximately 4 units, almost imperceptible under the microscope (Figure 2b). This change exhibits a linear increase, reaching approximately 20 units when the pigment concentration is quintupled (sample S1.0). These findings align with the previous literature research [60]. Subsequently, the values of ΔE do not demonstrate a linear progression but stabilize at around 50 units in sample S5.0. Nevertheless, these ΔE values are exceptionally high and challenging to achieve with other pigments at such low concentrations [34,69].

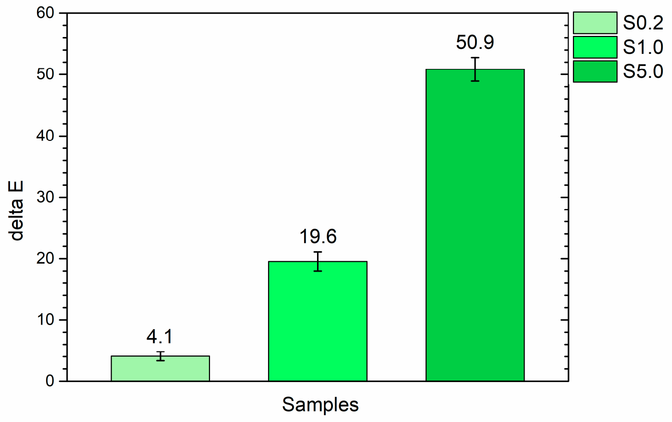


Figure 3. Color variation compared to sample S0.0.

Hence, this study reaffirms the significance of spirulina as a valuable bio-based resource for incorporating distinctive pigmentation in wood paints. The natural pigment exhibits minimal adverse effects on the protective layer, allowing for its application in specific quantities to achieve desired green hues. The analyses reveal the opportunity to enhance the aesthetic characteristics of wooden products with minimal environmental impact.

3.2. Endurance of the Samples in Severe Surroundings

Spirulina plays a distinct contribution in modifying the visual characteristics of wood coatings, particularly from a color and tone perspective. However, it is crucial to assess the consequence of this renewable additive on the paint's durability. To address this issue, the samples underwent accelerated degradation tests, including exposure to UV-B radiation and significant temperature fluctuations, aiming to evaluate the influence of spirulina on the paint's resilience.

3.2.1. UV-B Exposure

Figure 4 illustrates the outcomes of the FTIR analyses, carried out before and after the exposure of the samples to 50 h of UV-B radiation. The wood panel displays consistent peaks in the two spectra. The region between 3400 and 3300 cm^{-1} corresponds to the stretching vibration of the –OH group [70], while the stretching region between 3000 and 2800 cm^{-1} refers to the –CH group found in cellulose, hemicellulose, and lignin [71]. The peak at 1728 cm^{-1} represents the stretching vibrations of the unconjugated C=O group and specific polymeric chain moieties, such as esters, present in the wood [72]. The bands at 1592 cm^{-1} and 1461 cm^{-1} indicate the C=C benzene ring vibration of lignin and C–H deformation vibration, respectively [73]. Additionally, the peaks at 1233 cm^{-1} and 1028 cm^{-1} correspond to the C–O stretching and typical C–O–C stretching vibrations of cellulose [74]. Following exposure to UV-B radiation, the intensity of the peak at 1728 cm^{-1} increases, while the signal of the peak at 1233 cm^{-1} decreases. These observations indicate that the wood panel undergoes degradation and experiences changes in the molecular arrangement of cellulose [51].

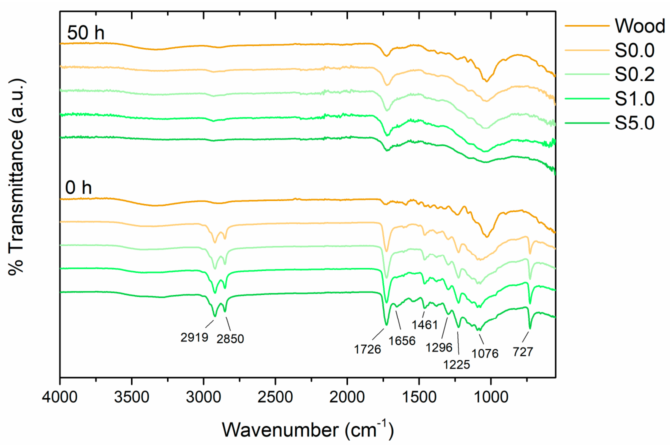


Figure 4. Evolution of the FTIR spectra of the samples before and after exposure to UV-B radiation.

In contrast, the FTIR spectra of the four coatings exhibit a high degree of similarity, with the peaks of the wooden substrate being completely masked by the impregnator signal. Likewise, the presence of spirulina in the coatings cannot be discerned through FTIR analyses, as the spectrum of the paint, based on linseed oil, effectively conceals its distinctive signals. The two peaks at 2919 and 2850 cm^{-1} correspond to asymmetric and symmetric C–H stretching, respectively, while the intense peak at 1726 cm^{-1} refers to the stretching of C=O. The signal at 1656 cm^{-1} can be attributed to the C=C stretching vibration from unsaturated acids and the peak at 1461 cm^{-1} is associated to the scissoring bending mode of CH_2 [75]. Moreover, the different peaks at 1296, 1225, and 1076 cm^{-1} are representative of C–O stretching vibrations. Finally, the signal at 727 cm^{-1} corresponds to the CH_2 rocking vibration [76]. Similarly in this instance, exposure to UV-B radiation induces noticeable decay of the paint, resulting in a significant reduction in intensity, and in some cases, complete disappearance, of specific peaks. Indeed, other studies in the literature have emphasized the limited UV-B resistance of paints based on linseed oil [77].

While the presence of spirulina may not be evident in the FTIR analyses, the impact of UV-B radiation on the samples' aesthetics is significant, as depicted in Figure 5. The image showcases the change in their aspect as a consequence of UV-B exposure. The poplar wood, primarily composed of cellulose and lignin, experiences significant decay. The outcome of this degradation is clearly manifested in the noticeable yellowing of the wooden panel. Sample S0.0 also exhibits similar yellowing effects, which can be attributed to the degradation of the transparent polymeric layer and subsequent decay of the underlying wood. The ultimate outcome of UV-B radiation exposure is consistent across samples S0.2 and S1.0, wherein the colored component derived from spirulina completely disappears.

This occurrence is attributed to the deterioration of the organic pigment at a physical and chemical level, resulting from changes in the chromoprotein compounds [78] and the deterioration of phycocyanins [79], which are its primary constituents. Moreover, several studies have examined the impact of temperature on the degradation of phycocyanin, which exhibits a specific degradation rate between 47 and 69 °C [80,81] (temperatures similar to those of the UV chamber). Sample S5.0 exhibits residual remnants of spirulina, which are visible as isolated colored spots that have not yet undergone complete degradation.

Figure 5. Alteration in the visual appearance of the coated samples and the wooden reference panel following exposure to UV-B radiation.

The final result of the test manifests as notable chromatic variations across the samples, which are effectively illustrated in the graph presented in Figure 6. The color change of sample S0.0 is slightly lower than that exhibited by the wooden panel, as the linseed oil-based layer already gives a slightly yellow tone to the sample. Consequently, the decay of the sample is chromatically less evident than that of the pure wood substrate. Given the small amount of spirulina in sample S0.2, a comparable outcome is observed. However, as the concentration of the bio-based pigment increases, the color change becomes more significant due to the combined degradation of the polymeric matrix and spirulina. The intensity of the green-blue color increases with higher concentrations of spirulina, but this hue diminishes almost entirely with the deterioration of the pigment following exposure to UV-B radiation. Consequently, sample S5.0 exceeds 40 units of ΔE, affirming the drastically altered appearance depicted in the images of Figure 5. Indeed, a preceding study [60] had cautioned against employing spirulina as a pigment in outdoor paints and emphasized the necessity of applying supplementary top layers. These additional coatings should serve the purpose of safeguarding the bio-based pigment against the inevitable physical and chemical degradation.

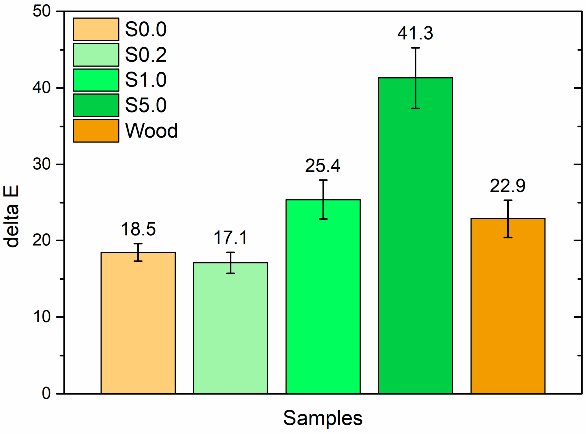


Figure 6. Changes in color during UV-B exposure.

In conclusion, the spirulina granule is an organic substance that is notably susceptible to degradation when exposed to UV-B radiation, even if incorporated in a polymeric matrix. This degradation results in the loss of its aesthetic qualities and color. While spirulina extract serves as an intriguing colorant material for organic coatings, it is crucial to prevent unfiltered sunlight exposure in order to guarantee its long-term resilience and color-retention capabilities.

3.2.2. Climatic Chamber Exposure

The behavior of the specimens in the accelerated degradation test was assessed based on their alteration in aspect and the occurrence of cracks (defects), in accordance with the guidelines outlined in the UNI 9429 standard [62]. The specific details regarding these evaluations are summarized in Table 2.

Table 2. Classification of whitening and crack development resulting from the climatic chamber exposure.

Class	Fractures	Fading
0	Free of defects	No whitening
1	Cracks discernible with 4× optical setup	Light fading
2	Evident and easily observable fractures	High whitening

Typically, organic coatings are vulnerable to abrupt temperature changes because of their delicate characteristics under low temperatures and vulnerability to moisture penetration through their inherent porosity. Consequently, these factors contribute to the formation of cracks [34], which have the potential to undermine the protective properties of the polymeric layer. Therefore, the presence of cracks is a crucial factor to consider when assessing the performance of samples under thermal stress. In this regard, all the specimens exhibited positive outcomes, as their films did not exhibit any visible defects. According to the standard, all the layers belong to class 0, indicating the absence of defects as observed under a 4× magnification optical microscope.

Likewise, in the category of "appearance consistency," all four samples demonstrated favorable performance, despite many studies having pointed out the poor stability of phycocyanin at temperatures above 45 °C [82,83]. The progression of the overall color change of the samples, ΔE, throughout the duration of the climatic chamber exposure, is illustrated in Figure 7. The inclusion of spirulina in the paint imparts a green hue, which experiences minimal alteration due to thermal degradation during the testing. The samples exhibit a comparable final color change, ranging from 4 to 5 points. Nevertheless, due to the bio-based attributes of the pigment, the overall color change ΔE is nearly insignificant. No significant whitening is observed in the samples, as evidenced by the minimal increase in the L* coordinate (approximately 1 point), along with slight variations in the a* and b* coordinates. Given the similar performance of the four coatings, it can be concluded that the presence of spirulina has minimal impact on the durability characteristics of the linseed oil-based paint subjected to thermal shock and the color change of the coatings can be associated to the behavior of the sole polymeric matrix.

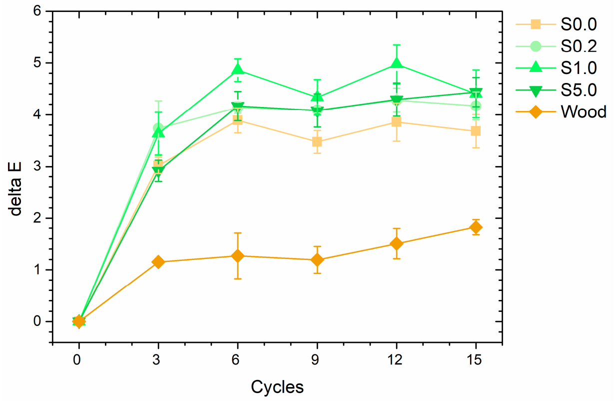


Figure 7. Changes in color observed in the samples during the climatic chamber exposure.

In conclusion, all the samples exhibit favorable durability characteristics when subjected to temperature variations, as there is minimal occurrence of whitening and fractures in the coatings. The addition of the bio-based pigment does not affect the protective properties of the impregnator, demonstrating its stability in response to thermal stresses. Therefore, this type of additive holds potential for use in outdoor coatings exposed to significant temperature fluctuations. However, to ensure the long-lasting color effectiveness of the spirulina-derived pigment, it is recommended to prevent straightforward solar irradiation of the hybrid films, as it can induce photodegradation of the renewable pigment, leading to the deterioration of aesthetic properties in the paint.

3.3. *Coating Liquid Resistance*

The liquid resistance test is valuable for understanding the barrier qualities of wood coatings and how pigments [36,48] and additives [51,84] in the polymeric matrix can potentially affect them. To evaluate the test outcomes, the amount of color alteration resulting from the interaction between the coating and the test solutions is assessed, with reference to the sources provided in Table 3 [85].

Table 3. Values indicating the extent of color change associated with the degree of discoloration.

Level	Extent of Color Fading	ΔE
0	no alteration in color	≤1.5
1	extremely minimal discoloration	1.6–3.0
2	minor change in color	3.1–6.0
3	noticeable discoloration	6.1–9.0
4	significant change in color	9.1–12.0
5	total discoloration	>12.0

Figure 8 illustrates the appearance of the samples after the test, emphasizing the discoloration outcomes of the coatings. The image clearly demonstrates that the spirulina-based pigment is notably susceptible to aqueous solutions (NaCl) and especially ethanol, resulting in the complete disappearance of the green color in the coating. In the literature, there are frequent warnings regarding the heightened sensitivity of phycocyanin to environmental conditions and its limited resistance to external factors [86], suggesting the need to prevent contact with solutions outside the pH range of 5.5–6.0 [87] through suitable protective measures for the pigment [86,88]. Indeed, the intensity of discoloration phenomenon becomes more pronounced as the initial concentration of spirulina increases, leading to the gradual fading of its vibrant color. Conversely, the neutral pH cleaning solution results in less evident aesthetic changes, while the impact of the red ink seems to decrease with increase of the concentration of bio-based pigment, as spirulina introduces darker shades in the coating.

For a more precise assessment of the test results, Figure 9 presents the exact magnitude of color shift prompted by the test solutions in each of the films. The graph prominently illustrates the degradation of the spirulina-based pigment by associating the corresponding degree of discoloration with each sample. The linseed oil-based impregnator demonstrates satisfactory resistance when exposed to NaCl solution, ethanol, and detergent, whereas spirulina does not exhibit equally favorable durability. As observed earlier in Figure 8, an increased concentration of spirulina in the coating leads to significant color changes when the coating comes into prolonged contact with the test solutions. In fact, when the bio-based filler quantity reaches 1 wt% or more, the sample consistently exhibits a minimum discoloration level of grade 4 across all the four experiments conducted with different solutions. In contrast, when exposed to red ink, all four series of samples display similar behavior, resulting in a discoloration level of 5. This outcome was anticipated, considering the characteristic properties of red ink, known for its intense coloring efficiency and ability to penetrate easily within the paint's polymer structure [51].

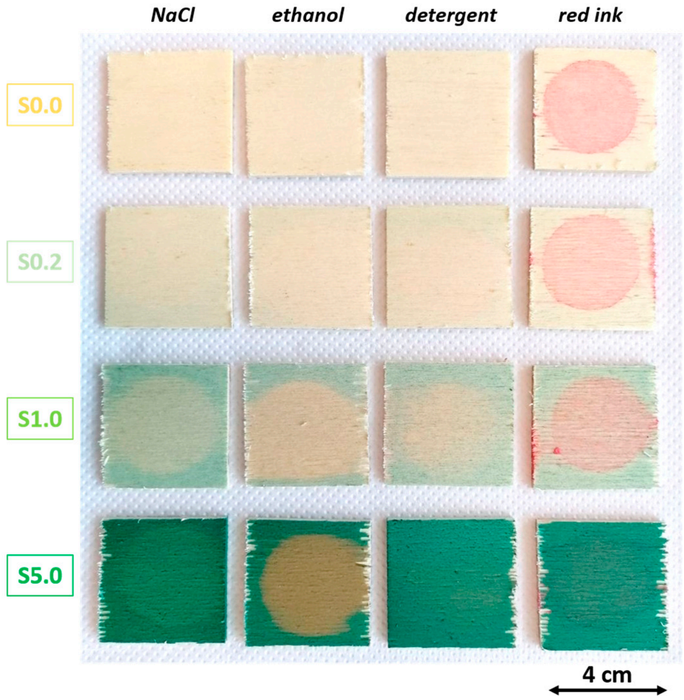


Figure 8. Appearance of the sample after the liquid resistance test.

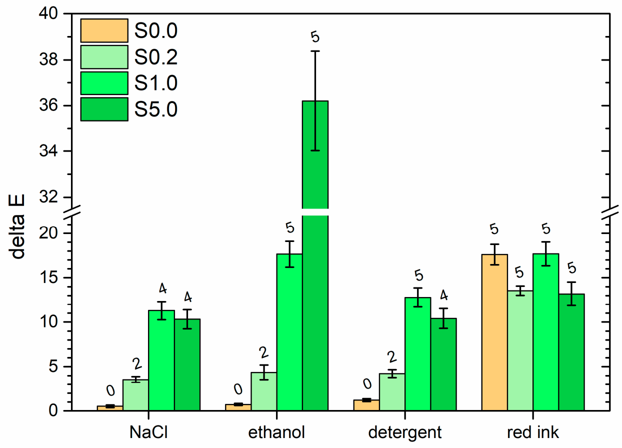


Figure 9. Color alterations in the coatings following exposure to liquids. The numerical values above the columns correspond to the reported levels of color fading indicated in Table 3.

The test results emphasize the significant propensity of the bio-based additive to degrade when exposed to various types of solutions. Nevertheless, it is crucial to emphasize that the liquid resistance test offers solely qualitative outcomes, linked to chromatic alterations of the films. Therefore, to evaluate the precise tangible effect of the pigment derived from spirulina on the barrier properties of the coatings, the samples underwent further analysis using the liquid water uptake test. The results of the water uptake test, depicted in Figure 10, demonstrate the progression of the water absorption phenomenon observed throughout the test. The figure also incorporates a curve that represents the performance of the wooden substrate, serving as a reference to emphasize the insulation capabilities of the coatings. Notably, the plots of the painted samples from all four series perfectly overlap throughout the whole test timeframe. Accordingly, it can be inferred that the presence of the spirulina pigment does not contribute to water absorption processes in the coatings. Indeed, when compared to other literature studies that report water uptake values as high as 2000 g/m^2 [89], the absolute water uptake values of the four coatings remain very low even after 100 h of testing.

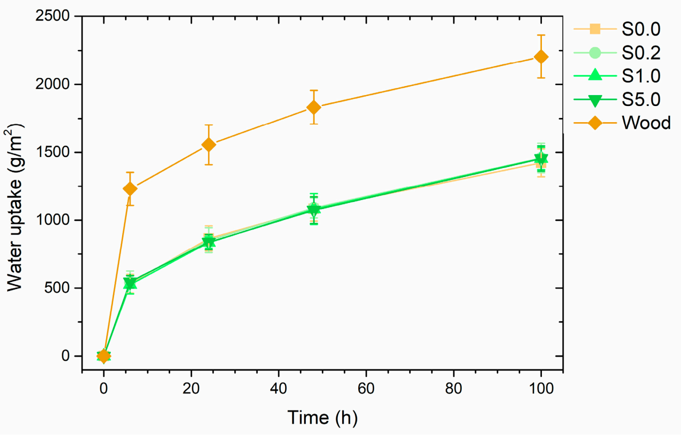


Figure 10. Progression of water absorption during the test.

However, as mentioned earlier, the pigment is susceptible to contact with various solutions. Therefore, colorimetric measurements were conducted on the samples at the conclusion of the water uptake test to examine whether the coatings experienced any loss in aesthetic qualities. Figure 11 illustrates a significant color change in the samples. Even the coating of sample S0.0, which does not contain spirulina, undergoes a noticeable alteration in color, indicating non-optimal barrier performance of the initial impregnating agent. However, this phenomenon is further intensified in samples S1.0 and S5.0, which contain a high concentration of the pigment and consequently undergo physicochemical deterioration processes, reaffirming the earlier findings.

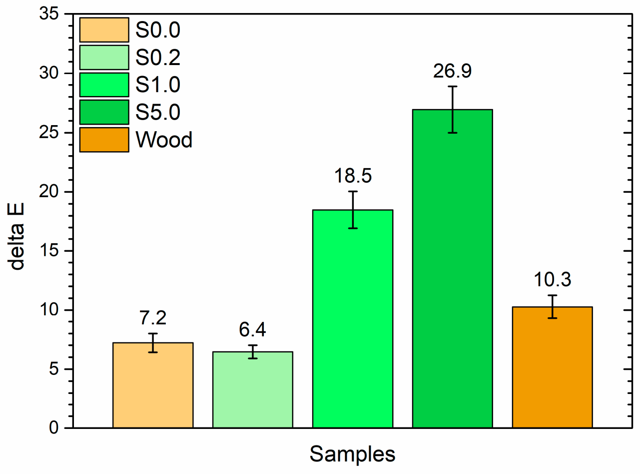


Figure 11. Samples color change due to the water uptake test.

Hence, the limited absorption of the solution observed in Figure 10 does not exclude a significant color change in the coating when the spirulina-based pigment comes into contact with water. It can be concluded that spirulina does not have a detrimental impact on the barrier performance of the linseed oil-based impregnator. The bio-based pigment, even when applied in high quantities, does not cause significant disruptions in the polymeric matrix, thereby impeding the additional liquid absorption phenomenon. However, due to the heightened sensitivity of phycocyanin, strong discoloration occurs in spirulina, necessitating adequate protection to avoid direct contact with various liquids. The findings of the study emphasize the importance of implementing appropriate measures to shield the bio-based pigment from external factors such as temperature, solar radiation, and liquids. Consequently, unless the component is adequately safeguarded with additional clear-coats, the use of spirulina in impregnating agents for outdoor applications is not recommended.

3.4. Coating Abrasion Resistance

Figure 12 depicts the progression of mass loss in the samples throughout the scrub test. The samples show comparable behavior, with a linear mass loss trend. After all, spirulina was not introduced in order to enhance the wear resilience characteristics of the films. In this perspective, in fact, the bio-based pigment has already amply demonstrated that it does not exert particular protective roles [60]. At the same time, however, spirulina does not seem to induce significant irregularities in the matrix of the barrier films, whose performances are guaranteed.

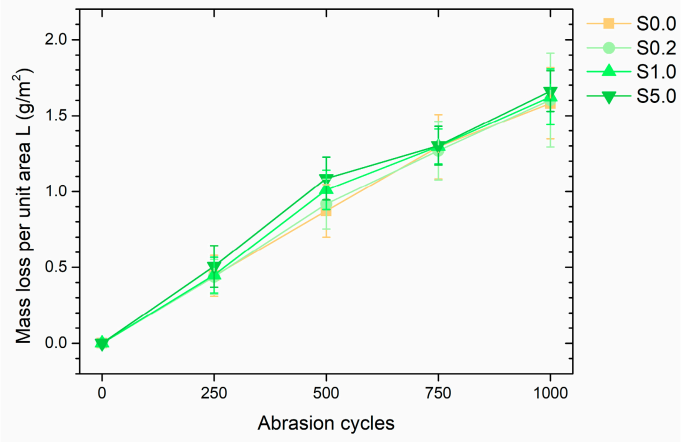


Figure 12. Evolution of the samples' mass loss per unit area, plotted against the number of scrub abrasion cycles.

However, to assess the pigment's chromatic efficacy even after undergoing physical degradation of the coating, colorimetric measurements were conducted on the samples during the scrub test. Figure 13 illustrates the results of these measurements, demonstrating a similar outcome for all four samples. The physical degradation caused by the abrasive sponge of the equipment results in a minor color change in the coatings, which is almost negligible (ΔE less than 3 points). Interestingly, the presence of higher amounts of spirulina seems to result in a slight reduction in ΔE over time. This observation is attributed to the thicker coating layers, as evidenced by the cross-section images in Figure 2. Indeed, the abrasive processes involved in removing material can lead to the exposure of the wooden substrate. Nevertheless, thicker coatings provide greater protection to the underlying wood, for the same amount of material removed. Additionally, the minimal color change observed indicates that spirulina effectively maintains its role in delivering vibrant color even after undergoing the abrasive test.

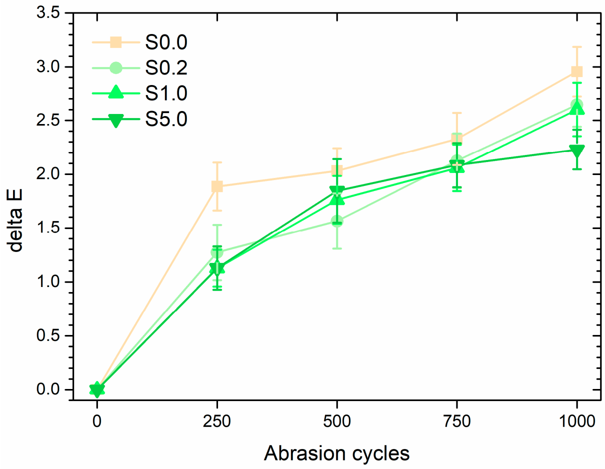


Figure 13. Changes in color observed in the samples during the scrub test.

Ultimately, the spirulina granules do not undermine the preserving efficacy and resilience of the impregnator, ensuring a vivid and durable color even after undergoing abrasion processes. The phycocyanin nature of the pigment makes it susceptible to physicochemical degradation when exposed to various external agents. However, it is not prone to functional decay caused by aggressive mechanical factors.

4. Conclusions

This study presents the advantages and disadvantages of using spirulina granules as a bio-based resource for wood stain pigments. The natural pigment reveals minimal negative effects on the structure of the protective layer, enabling its application in specific quantities to achieve desired green tones. The analyses conducted indicate the potential to enhance the aesthetic qualities of wooden products with minimal impact on the environment.

Nevertheless, it should be noted that spirulina granule is an organic substance that is notably vulnerable to degradation when exposed to UV-B radiation, resulting in the fading of its aesthetic qualities and color. On the other hand, the inclusion of the bio-based pigment does not compromise the protective properties of the impregnator, indicating its stability when subjected to thermal stresses. Hence, this particular additive is a viable option for utilization in outdoor coatings that are subjected to considerable temperature fluctuations. However, to ensure the long-lasting color effectiveness of the pigment derived from spirulina, it is recommended to prevent placing the coating in direct contact with sunlight, as it can initiate photodegradation of the renewable pigment, resulting in the degradation of the aesthetic qualities in the paint.

The liquid resistance tests conducted on the coatings revealed that even when applied in significant quantities, the bio-based pigment does not cause significant disruptions in the polymeric matrix, thereby preventing excessive liquid absorption. However, it is important to note that due to the high sensitivity of phycocyanin, the spirulina-derived pigment undergoes pronounced discoloration, necessitating appropriate protection to prevent direct contact with various liquids.

Lastly, pigment derived from spirulina does not jeopardize the protective effectiveness and longevity of the organic layer, ensuring a vibrant and long-lasting color even after undergoing abrasive processes.

To conclude, the findings of the study demonstrate the impressive coloration achieved with the spirulina-based additive. However, they also emphasize the necessity of implementing suitable precautions to protect the bio-based pigment from external elements such as temperature, solar radiation, and liquids. Therefore, unless the component is adequately shielded with additional clear-coats, the utilization of spirulina in impregnating agents for outdoor applications is not advised. In order to overcome the disadvantages revealed in this study, the spirulina-containing impregnator could be added with additional UV-shielding fillers, or overpainted with transparent and protective top-coats, with the aim to isolate the bio-based pigment from external agents.

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