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Epoxy Resin Biocomposites Reinforced with Flax and Hemp Fibers for Marine Applications

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Abstract: A broader application of biocomposites still faces many challenges regarding structural integrity, environmental resistance, and biodegradability. These issues are particularly important when their marine applications are considered. Therefore, this paper seeks to address the hygroscopicity, mechanical properties, and biofouling resistance of biocomposites made of epoxy resin with 28 m% bio-based carbon content reinforced with flax and hemp fibers. A series of experiments are performed to acquire water absorption rates, saturation limits, mass increase, tensile and flexural properties, interlaminar shear strength, impact resistance, and mass gain due to biofouling. All tests of mechanical properties are conducted before and after immersion in seawater. The acquired saturation limits of flax/epoxy and hemp/epoxy biocomposites amount to 7.5% and 9.8%, respectively. The water uptake causes the tensile and flexural properties to decrease by 26–74%, while interlaminar and impact strength increase for flax/epoxy and decrease for hemp/epoxy biocomposites. In addition, it is observed that in almost all cases, flax/epoxy has superior properties compared with hemp/epoxy biocomposites. It is expected that this research will motivate naval architects and classification societies to consider biocomposites as prospective hull materials that provide both structural integrity and environmental sustainability.

Keywords: biocomposites; ship hull material; flax; hemp; hygroscopicity; mechanical properties; biofouling; green shipbuilding; environmental sustainability

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1. Introduction

The ever-growing concerns about adverse impacts of human activities on ecosystems and the need to create environmetaly acceptable solutions greatly motivate current intensive research and development of new and environmentally friendly concepts across different scientific disciplines. This is especially valid in the case of technical disciplines concerning energy harvesting and its efficient consumption, product life-cycle management, and the development of new materials with a considerably lower environmental footprint. The embodied and processing energy are two main sources of the environmental burden associated with products and materials [1]. Therefore, the development of new materials, particularly composites, should consider not only their physical, chemical, and mechanical properties, but also a broader perspective including ecotoxicology, renewability of constituents' sources, renewable processing energy, as well as end-of-life challenges such as reuse, recycling, self-healing [2], self-growing [3], and on-demand functions [4]. This is where biocomposites step in as a remarkable opportunity to address not only mass reduction or improved damping and impact absorption but also short and long-term sustainability of the environment.

Biocomposites are a composition of two or more different constituents where at least one is derived from natural resources, yielding a new material of superior performance compared with the individual constituents [5]. The constituents are the matrix and reinforcing components (fibers, whiskers, particles, flakes), where the latter provides mechanical strength and the former ensures the integrity of the bulk material. Usually, the matrix is made of fabricated polymers (polyester, vinyl esters, epoxy), while in the case of biocomposites, various naturally based polymers, such as natural rubber, thermoplastic starch (TPS), polylactic acid (PLA), polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), or their blends can be used. These and many other polymers are also known for medical applications [6], including even nanomedical tissue engineering [7]. Similarly, conventional composites rely on the application of fabricated reinforcing components such as fiberglass, carbon fibers, or aramid fibers, while natural reinforcement originating from animals (silk, wool, hair) and vegetables (flax, hemp, jute, kenaf, sisal, banana, cotton, coir, coconut, bamboo, grass, rice, wheat, corn straws, etc.) can be used in the case of biocomposites [8]. In that way, different bioplastics and/or biofibers can be utilized to tackle issues such as the impact on human health, CO_2 emissions, oil-based production, and biodegradability [5]. However, many challenges are still ahead in the research and development of biocomposites, particularly in the case of the marine environment. Some of the most important issues that must be addressed thoroughly to enable the broader, especially marine, application of biocomposites are the economic aspects, mechanical properties in the marine environment, fouling resistance, hygroscopicity, biodegradability, and potential adverse impact on the marine life through eutrophication.

Traditionally, the vast majority of the nautical sector relies on various recreational or pleasure boats of different scales mostly constructed out of conventional composites [9]. In addition, for many years, the shipbuilding industry has been attempting a broader inclusion of composite materials in large merchant and passenger ships through the hybrid hull concepts. Some applications include the composite structure of the ship's bow and stern, a composite outer shell supported by a steel truss [10], simple integration of the composite load-carrying decks within the conventional steel ship structure [11], or even a complete ship hull constructed out of composite material [12]. Some of the most important benefits motivating the usage of composites instead of metal alternatives are lower structural mass, improved ship stability, corrosion immunity, hull resistance reduction, lower fuel consumption, lower maintenance costs, and improved life-cycle performance [13]. However, the associated impact of the fabrication process on human health as well as end-of-life issues (in the case of boats and ships exiting their service life after 30–40 years) represent serious medical and environmental problems. Therefore, a potential application of biocomposites in the marine environment is being considered for further development of conventional composite hull construction [14].

Given that, the main objective of this research is to present research on the potential application of biocomposites in the marine environment. Some potential applications of biocomposites include structural elements of ships and boats, offshore objects, or floating and underwater structures. Therefore, a series of experiments are performed to identify the physical and mechanical properties of selected biocomposites and to inspect the associated impact of the harsh marine environment through hygroscopicity, degradation, and fouling. From this, we expect to obtain fundamental data directing further research and development of biocomposites fostering their broader use by the naval architecture and ocean engineering communities. In addition, this is expected to bring the naval architecture community to new frontiers in urgent response to the tremendous problems of marine waste [15].

The research and development of biocomposites are addressed in several scientific areas and address aspects such as the economics of biocomposites, mechanical properties of different types of biocomposites in standard and marine environments, fouling resistance, as well as the effects of hygroscopicity, biodegradability, and eutrophication on the structural integrity and marine environment. Many references elaborating on these aspects to various degrees have been published recently in leading journals and popular editions. Therefore, here we provide only a brief review of the most relevant references while directing an interested reader to other available and more extensive reviews.

The major concern of the economic aspects of biocomposites is related to the implementation and commercialization of concepts such as material synthesis and sustainable production, which are still at a rather early stage of development [16], especially when the possibilities for plastic recycling [17] or biowaste exploitation [18] are considered. Nevertheless, an annual growth in biocomposite demand of about 11% is predicted until the end of the present decade [19–21]. The main drivers for the growth of the biocomposite industry are the detachment of the material cost from the fluctuating price of oil and energy as well as the circular economy philosophy [22,23]. In addition, positive effects on agriculture can be expected in the case of the broader application of biocomposites [15].

The mechanical properties of biocomposites are traditionally the focus of the majority of papers. One of the first works related to the physical and mechanical properties of polymer-based composites reinforced with natural fibers was presented in [24] where reinforcement of epoxy and polyester matrices with wood, jute, and cotton fibers was considered. This work was followed by a study focused on the mechanical properties of polylactic acid (PLA) reinforced with natural flax fibers [25], which yielded encouraging conclusions, particularly as the considered biocomposites proved to be competitive with their conventional counterparts. However, certain mechanical and thermal properties of biocomposites are sensitive to moisture uptake that results in the diffusion of water molecules, capillary water suction at interfaces between fibers and matrix, and fiber swelling inducing material cracking and delamination. Therefore, a study on the water absorption impact on the mechanical properties of the hemp fiber-reinforced composites was presented in [26], proving a significant reduction in tensile and flexural properties due to fiber-matrix interface degradation. The importance of the moisture absorption properties of composite materials was also stressed by the American Society for Testing and Materials [27], especially when fluids other than water are considered. In addition, the influence of long-term immersion in natural seawater on the physical and mechanical properties of a biocomposite reinforced with 20 m% (where m% stands for mass share) flax was researched experimentally in [28]. It was proven that biocomposites suffer from relatively high moisture absorption, linearly reducing the associated mechanical properties and causing a mass gain of about 12%. Finally, a potential application of commercial bio-based epoxies in fiber-reinforced composites was considered recently in [29]. The mechanical properties of different bio-based resins were experimentally determined and some proved to be promising options with mechanical properties comparable to those of conventional petroleum-derived epoxies.

Along with mechanical properties, the structural integrity of biocomposites has been addressed in different studies in light of biodegradability and environmental resistance. The durability of biocomposites in the marine environment was addressed in [30] where issues such as the hydrophilic nature of natural fibers and microbiological attacks were highlighted as potential sources of structural integrity loss. In addition, the surprisingly good fouling resistance of the poly(L-lactic acid) (PLLA) matrix was attributed to the slow release of the low molecular mass PLLA in natural seawater [31]. Similarly, the environmental degradation in biocomposites was presented in [32] where it was attributed to the inherent characteristics and chemical composition of bio-fibers constituted of cellulose, hemicellulose, lignin, and pectins. Three different types of environmental degradation were considered, namely, temperature and moisture, weathering, and biological attack. A more extensive review of the current achievements concerning the environmental resistance of biocomposites was presented recently in [33], which reports on the degradation and fouling resistance of two different biocomposites exposed to the tropical marine environment for six months.

The presented literature review demonstrates that many issues related to the potential application of biocomposites in demanding marine applications are still at a rather low level of maturity. Consequently, further research and development are necessary, particularly as the leading classification societies do not recognize biocomposites as a potential hull structure material, nor do they provide any guidelines for this application. Therefore, the main purpose of the present paper is to consider the potential application of flax/hemp-reinforced biocomposites in the marine environment. For this purpose, a series of experiments were performed to investigate the mechanical properties, hygroscopicity, biodegradability, and fouling resistance of bio-based epoxies reinforced with flax and hemp fibers in different proportions. These experiments will contribute to fostering a broader application of biocomposites within the naval architecture and ocean engineering communities, thereby boosting further implementation of the lifecycle and sustainability principles in ship structural design, ship production aspects, and environmentally friendly shipping.

2. Materials and Methods

2.1. Materials and Specimen Preparation

The marine application of two different types of biocomposites was considered, one being reinforced with flax fibers and the other with hemp fibers. The flax and hemp fabrics with 181 g/m^2 and 189 g/m^2, respectively, were purchased from Exoglasgrad d.o.o., Croatia, Zagreb. Without any chemical treatment, the fibers were integrated into the matrix at 0/90° concerning the testing axis using a hand lay-up procedure. For the matrix, a biosourced, general-purpose epoxy resin with the commercial name ONE and the appropriate fast hardener ONF were purchased from Wessex Resins Inc., Romsay, Hampshire, UK. The components were mixed in the mass ratio of 2:1. The fast-curing resin (F type) has 18 min of pot life. According to the producer's datasheet, the matrix material has 28 m% of bio-based carbon content. Literature values of the mechanical properties of the components are summarized in Table 1, as reported in [34].

Table 1. Mechanical properties of flax, hemp, and biobased epoxy [34–36].

	Density, ρ, (g/cm^3)	Young Modulus, E, (GPa)	Tensile Strength, σ_m, (MPa)
Biobased epoxy	1.09	3.2	67.6
Flax (typical value)	1.29–1.50 (1.48)	27.6–160 (30)	345–1100 (750)
Hemp (typical value)	1.0–1.45 (1.45)	30–60 (70)	310–750 (600)

The fiber content of the flax and hemp in the resulting biocomposites was 39.5 and 38.3 m%, respectively. Table 2 outlines the number of layers of each biocomposite and the fiber mass fraction.

Table 2. The number of layers and fiber mass fraction obtained in the case of flax and hemp reinforcement.

Biocomposite	Number of Layers	Fiber Mass, (g)	Total Plate Mass, (g)	Fibers Fracture, (%)
Flax/epoxy	10	290	733	39.5
Hemp/epoxy	7	212	553	38.3

Three composite plates were prepared for each reinforcement type. One plate of each biocomposite type was used for mechanical testing, both dry and wet, and an additional two plates were employed for the biofouling resistance testing. Before lamination, each mold was covered with a transparent release film. Upon applying the resin to the fabrics, each layer was left briefly to absorb it and a gentle squeeze rolling was applied to release the trapped air bubbles. Each composite plate was cured for seven days at the ambient temperature of 25 °C. Specimens were cut out using a circular saw. Dimensions for mechanical tests were determined according to relevant standards: for tensile testing, ISO 527-4:1997; for flexural testing, ISO 14125:2005; for interlaminar shear strength, ISO 14130:2005; and for Charpy impact testing, ISO 179-1:2000 [37–42].

2.2. Water Absorption Tests

The hygroscopicity is of great significance for almost all composite materials, particularly as some polymers have a natural tendency to absorb water. This is especially pronounced in the case of cellulose propionate, polyamide, and ethylene vinyl alcohol with maximum absorption values reaching 10% of the total mass. A more detailed list of the water absorption values of different plastics is available in [42]. The adverse impact of absorbed water is reflected in the reduction of the composite material's mechanical properties, extraction of soluble components, degradation of material structure, and changes in dimensional and mass properties. Therefore, the property of hygroscopicity is of great importance if harsh marine conditions are considered, particularly as it could significantly affect the ship's structural integrity, as well as alter its hydrostatics and seaworthiness.

To detect potential degradation of the polymer structure it is necessary to conduct mechanical testing of a material previously exposed to seawater. The water absorption tests were performed according to ISO 62:2008. All wet specimens were dried in an oven with forced-air convection for at least 24 h at 50 °C. The specimens were immersed in natural seawater at the Adriatic coast with a salinity of approximately 3.7 PSU. During the seawater absorption test, all the specimens were taken out every 24 h, wiped with a dry cloth, and weighed immediately. The saturation was considered substantial if the average mass increase shown by three consecutive measurements was less than 1% or 5 mg, whichever was greater. The mass increase μ was then calculated concerning the initial specimen mass as:

$$\mu = \frac{m_w - m_d}{m_d} \cdot 100\% \quad (1)$$

where m_w is the wet specimen mass and m_d its initial (dry) mass.

2.3. Mechanical Testing

Tensile testing, flexural testing, interlaminar shear strength testing, and Charpy impact testing were conducted according to the relevant ISO standards named in Section 2.1. The mechanical tests were performed for each composite type before and after immersion in seawater for 14 days. For each material and property, six samples were prepared. The standard procedure of tensile, flexural, and interlaminar shear strength testing was performed using a 50 kN universal testing machine, produced by Shimadzu, while impact testing was conducted on a conventional Charpy pendulum impact tester, produced by Zwick.

2.4. Biofouling Resistance Tests

Two flax/epoxy and two hemp/epoxy were used for biofouling testing. One of each type was coated with a standard copper-based antifouling paint in two layers, and the remaining two plates were kept in their original state. Following the procedure outlined in [33,43], all the plates were kept immersed in the seawater at Stupin Bay, in the city of Rogoznica on the Adriatic Sea, at a depth of 2 m, starting in July 2021 and ending in December 2021. The plates were inspected each month to check for an increase in biofouling properties and the associated mass.

3. Results and Discussion

3.1. Seawater Absorption

The mass increase due to the seawater absorption was measured every 24 h, and its portion was determined using Equation (1). The results are represented graphically in Figure 1. The absorption rates of flax/epoxy and hemp/epoxy calculated from the slope of the linear section of the graphs were 0.20 %/h and 0.22 %/h, respectively. It is obvious that the kinetics of seawater absorption during the first 24 h of immersion were comparable regardless of the reinforcement type. The saturation of flax/epoxy and hemp/epoxy was reached after approximately 144 and 240 h, respectively. Since the maximum mass increase of flax/epoxy was 7.5% and that of the hemp/epoxy was about 9.8%, the seawater absorption capacity of hemp/epoxy was 30% higher.

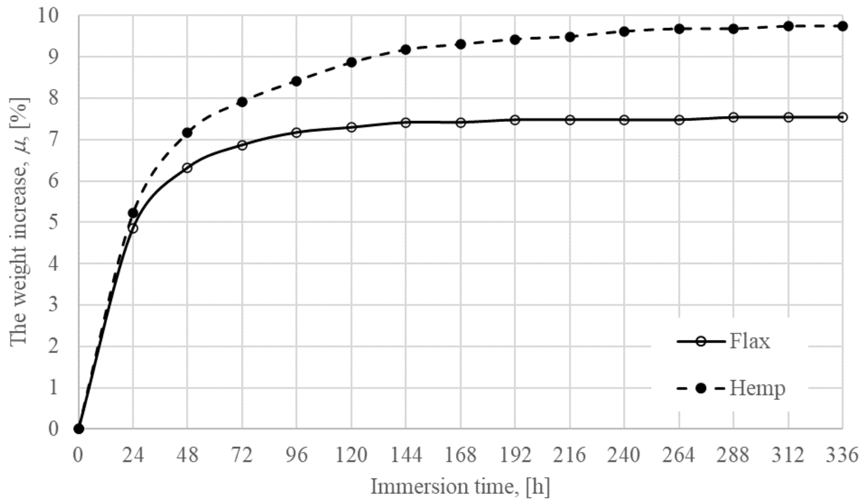


Figure 1. The seawater uptake of flax/epoxy and hemp/epoxy.

A similar saturation level of 9.57 m% was reported in [44] for epoxy reinforced with approximately 50 m% flax fibers. However, the earliest and the most interesting period of seawater absorption kinetics was omitted from that research as the weight increase was measured at time intervals of two months. Additionally, the results obtained are similar to those presented in [26,28]. In the former reference, the freshwater absorption capacity of unsaturated polyester (UP) reinforced with hemp fibers at room temperature was 10.97 m% after immersion of 888 h, whereas in the latter, the mass gain due to a long-term (two-year) seawater exposure of polylactic acid (PLA) matrix reinforced with only 20 m% flax fibers was about 3.3 m%. A detailed analysis of seawater absorption of flax, PLA, and a flax/PLA composite was provided in [28]. Although PLA is only moderately stable in seawater at temperatures between 8 and 19 °C, absorbing 0.77 m% of seawater, the estimated seawater uptake of fibers was 20 times higher. This suggests that the fibers are the most sensitive component of the biocomposites when hygroscopicity is considered and that it can be considered as almost proportional to the mass fraction of the reinforcement. This is in agreement with the fact that a majority of polymers have a hydrophobic nature (e.g., UP and epoxy) or at least a moderate hydrophilic nature (e.g., PLA); hence, their contribution to the water uptake is negligible or very low at a reasonable fiber content.

3.2. Mechanical Properties

Dry and wet flax/epoxy and hemp/epoxy were compared based on typical mechanical properties required when considering composites for marine applications, namely, strength and modulus under tensile and flexural load, and apparent interlaminar shear strength. The resulting stress–strain diagrams of tensile and flexural tests are represented in Figures 2 and 3. Additionally, impact strength was tested.

At first glance, it is obvious that the exposure of both composites to seawater strongly reduces modulus and strength, whereas it increases the elongation at break, regardless of the load type. Under the tensile load, the elongation at break of flax/epoxy and hemp/epoxy increased from 4% to 8% and from 2.5% to 3.5%, respectively (Figure 2). Hence, after the seawater treatment, the elongation at break of flax/epoxy doubled, and that of hemp/epoxy increased by 40%. Nearly the same increase is visible for the flexural load, though the data are more heterogeneous (Figure 3), which can also be observed in the standard deviations presented in Table 3. A graphical comparison of tensile and flexural moduli and strengths of the dry and wet composites is provided in Figures 4 and 5.

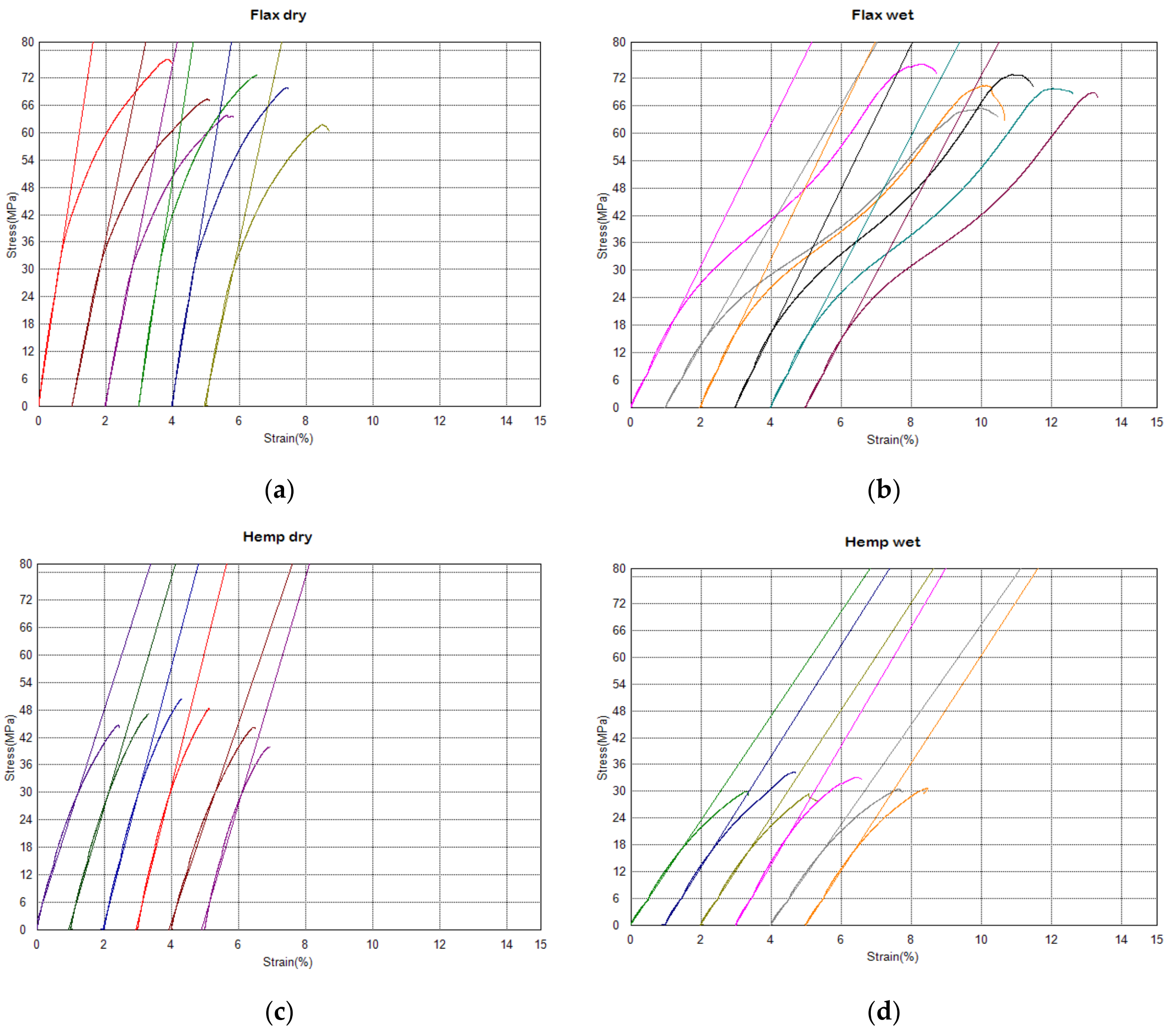


Figure 2. Stress–strain test results for 6 samples under tensile load: (**a**) flax/epoxy dry, (**b**) flax/epoxy wet, (**c**) hemp/epoxy dry, and (**d**) hemp/epoxy wet. (The 1% shift along the x-axis is intentional and allows better clarity of the results. Each sample is presented using different colour).

The tensile strength of the dry flax/epoxy was 50% higher than that of the dry hemp/epoxy, whereas the flexural strength of the hemp/epoxy was 10% higher. During the flexural load, the samples in the upper surface were under compression load and those in the lower were under tensile load. Although the compression strength was not tested, the lower tensile strength and the higher flexural strength of the hemp/epoxy led to the conclusion that hemp/epoxy has a better compression strength.

Before the seawater exposure, the tensile modulus of flax/epoxy was 60% higher than that of the hemp/epoxy, whereas the flexural modulus of the hemp/epoxy was 40% higher. This is analogous to the effects observed for the corresponding strengths of dry biocomposites. For the same reason related to the stress distribution as described in the previous paragraph, the flax/epoxy has better mechanical properties when exposed to the tensile load and worse properties under the compression load.

In general, the tensile and flexural properties decreased when the composites were treated with seawater, with two exceptions for flax/epoxy, namely, the tensile strength with only a slight improvement of 2.6% and the interlaminar shear strength that was doubled. The increase in these properties was not expected, and further investigation is needed. The flexural strength of flax/epoxy decreased by 47%. The tensile and flexural strength of hemp/epoxy were reduced by 32% and 26%, respectively, whereas the apparent interlaminar shear strength decreased by 35%.

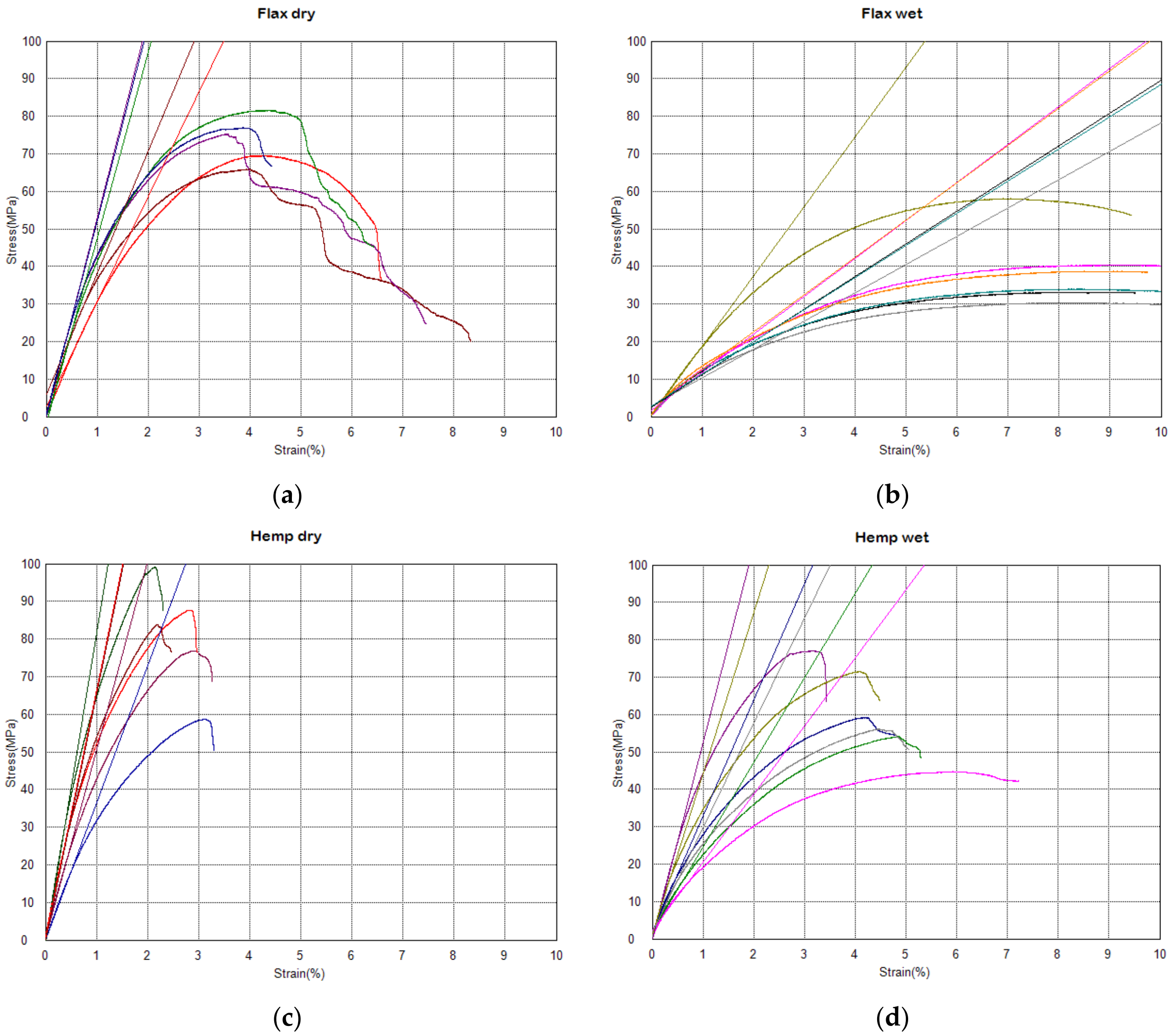


Figure 3. Stress–strain test results for 6 samples under flexural load: (**a**) flax/epoxy dry (**b**) flax/epoxy wet, (**c**) hemp/epoxy dry, and (**d**) hemp/epoxy wet. (Each sample is presented using different colour).

Table 3. Mechanical properties of the flax/epoxy and hemp/epoxy in dry and wet conditions.

Mechanical Property		Flax—Dry	Flax—Wet	Hemp—Dry	Hemp—Wet
Tensile test	Strength (MPa)	68.6	70.4	45.7	31.3
	Standard deviation	5.4	3.3	3.7	2.0
	Modulus (MPa)	4258	1496	2648	1214
	Standard deviation	563	103	293	73
Flexural test	Strength (MPa)	73.8	39.1	81.2	60.4
	Standard deviation	6.2	10.0	14.9	11.9
	Modulus (MPa)	4302	1116	6010	3263
	Standard deviation	1184	376	1744	1300
Interlaminar	Apparent interlaminar shear strength (MPa)	10.4	20.7	9.27	6.0
	Standard deviation	0.3	3.16	1.6	0.6
Impact strength (J)		1.72	3.73	0.76	0.77

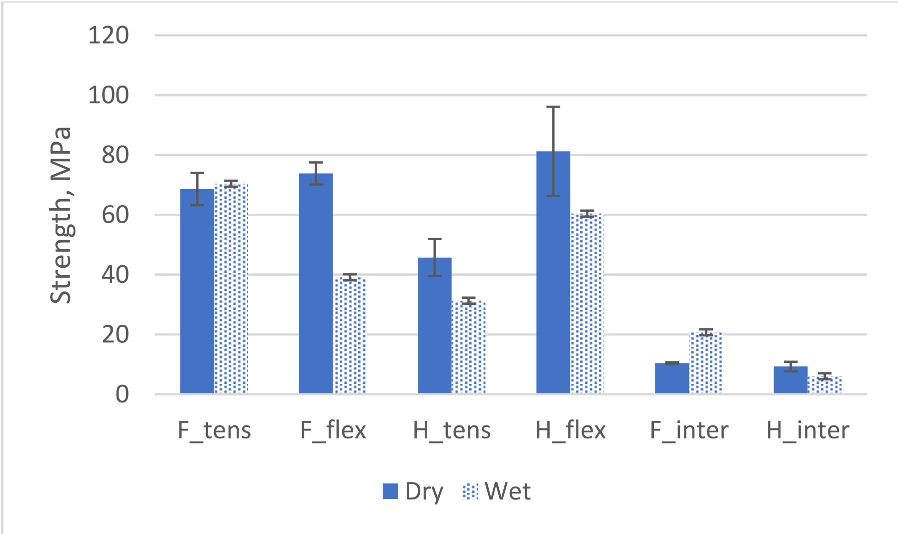


Figure 4. Effect of seawater treatment on tensile (tens), flexural (flex), and apparent interlaminar shear strength (inter) of flax/epoxy (F) and hemp/epoxy (H).

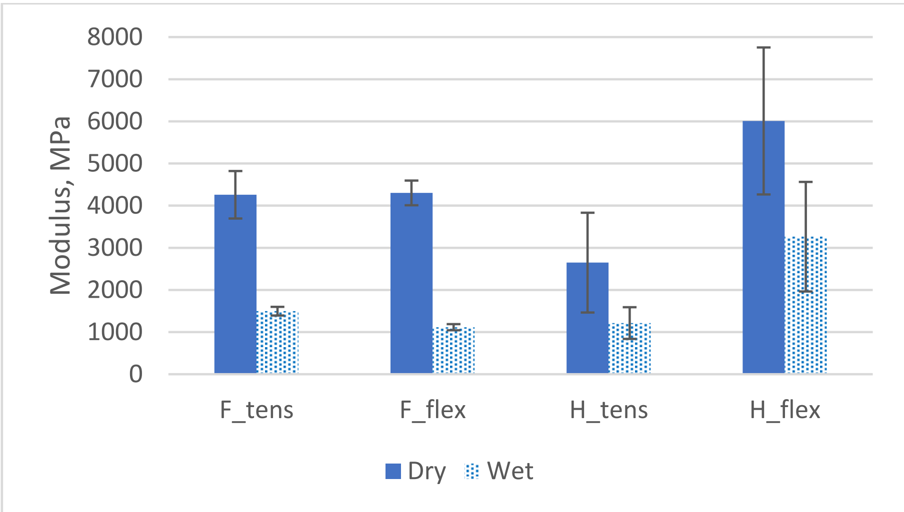


Figure 5. Effect of seawater treatment on tensile (tens) and flexural (flex) modulus of flax/epoxy (F) and hemp/epoxy (H).

The exposure of the biocomposites to seawater reduces stiffness, which is represented through the moduli (Figure 4). Both the tensile and flexural moduli of flax/epoxy were more affected than those of the hemp/epoxy. The tensile modulus of flax/epoxy was reduced by 65% and the flexural modulus by 74%. The tensile and flexural moduli of hemp/epoxy were reduced by 54% and 45%, respectively.

After immersion, the impact strength of flax/epoxy increased by 117% and that of hemp/epoxy by only 1%. This is also in agreement with the stress–strain curves, where the elongation at the break of the flax/epoxy biocomposite increased much more than that of the hemp/epoxy.

An overview of the tensile and flexural strengths and moduli is provided in Table 3 together with the apparent interlaminar shear strength and impact strength of all the biocomposites in dry and wet conditions.

Similar conclusions related to tensile and flexural testing of flax/epoxy and hemp/epoxy in dry and wet conditions may be found in the literature. However, many available results are conditioned to the specific manufacturing procedure and fiber fractions that are different from those considered here. Nevertheless, their comparison is noteworthy as it may indicate factors other than fiber type directly influencing mechanical properties. Hence, we compare the measured mechanical properties separately, i.e., flax/epoxy with the results presented in [44], and hemp/epoxy with those presented in [26].

In [44], Yan and Chouw prepared an epoxy-based composite with 55 vol% of flax fibers by hand lay-up. The fiber fracture was approximately 8% higher and had approximately 40% higher values of mechanical properties compared with the composite tested in this study. One year of exposure to seawater with lower salinity than that of the Adriatic Sea resulted in a mass gain of 9.8 %, but the saturation level was not clear since the first data were taken after 2 months. In this study, saturation was reached after only 6 days (Figure 1), reaching 7.5%. In the same study, tensile modulus and strength reached 72.9% and 71.7% of the control unexposed samples, respectively, whereas in this study, the tensile strength slightly increased, and the modulus retention was 35%. Flexural modulus and strength in [44] reached 76.5% and 81.7%, respectively, whereas in this study, the retention of the same properties was 26% and 53%, respectively. Additionally, the composites studied here had values for the elongation at the break before and after the immersion twice as large as in [44]; hence, the materials that were prepared in this study are obviously more deformable. The obvious reasons were that the composites tested in this study had a lower fiber content and that the salinity was higher. Apart from that, the reasons were probably the consequence of the properties of the components and weaker bonds established at the interface between the matrix and the reinforcement. The fibers were not chemically treated to improve the adhesion before the lamination. Additionally, the lower adhesion might be also affected by the relatively short pot life of the resin, which results in a short manipulation time.

In general, biocomposites reinforced with hemp fibers are less studied than those with flax fibers. Therefore, here the composites are compared to a similar system, with a UP matrix instead of epoxy. Tensile testing of hemp fibers/UP composite with different fiber fractures [26] resulted in a ±25% change in the tensile strength of wet specimens compared with the original (dry) specimen condition, including a strain increase of about 1.5%. In addition, the flexural test demonstrated an approximately 20% drop in the flexural strength of wet specimens accompanied by an increase in strain. Similar effects on the mechanical properties of hemp/epoxy are presented in Table 3 where an approximate drop of 25% in tensile and flexural strength is evident. Additionally, an increase in strain may be noted in both cases in Figures 2 and 3.

Among all composites, glass fiber-reinforced polymers (GFRP) are the most common materials in marine applications. The reasons are their acceptable properties, low price, and availability on the market. The Croatian Register of Shipping (CRS) has published their Rules for the classification of ships. In Part 24—Non-metallic materials [45], there are minimal values of mechanical properties for GFRP. However, there is a lack of standards for all other composites. The minimum values for tensile strength and modulus are 85 MPa and 6500 MPa, respectively, for flexural strength and modulus the minimum values are 150 MPa and 5500 MPa, respectively, and for apparent interlaminar shear strength, the required value is 17 MPa. From Table 3 it is obvious that the composites prepared in this work by a hand lay-up procedure did not meet the requirements for GFRP. However, our other studies show that the properties of composites prepared by vacuum bagging with a carefully selected flax/epoxy pair were very close to the CRS requirementss [46]. In [46], the average values of tensile strength and modulus were 123 MPa and 7328 MPa, respectively, flexural strength and modulus were 147 MPa and 9782 MPa, respectively, and apparent interlaminar shear strength was 16.3 MPa. Further studies on such hybrids are being performed to improve flexural strength and interlaminar shear strength.

3.3. Biofouling Resistance

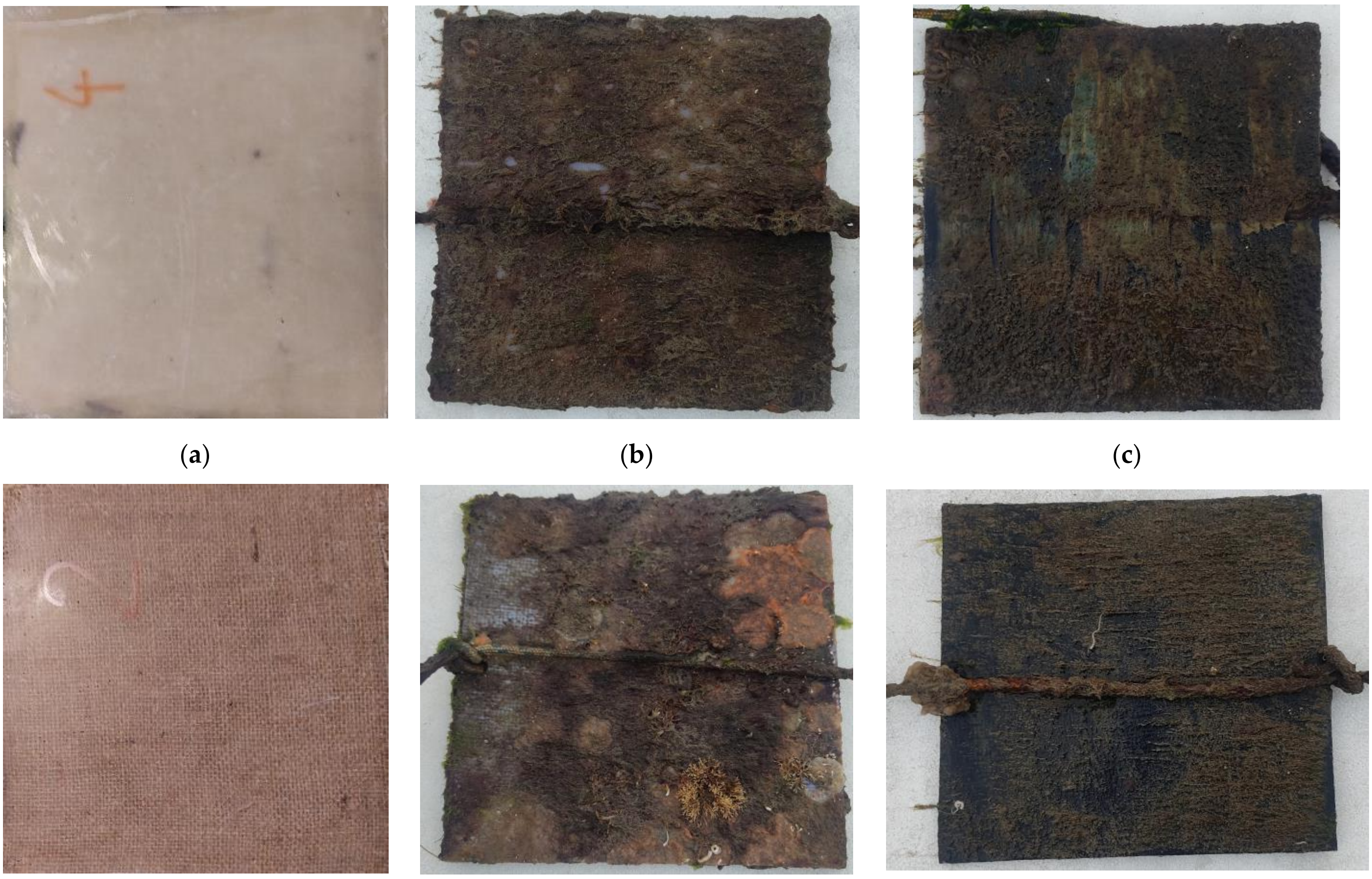
After their underwater deployment, the biocomposite plates were carefully taken out from the sea each month for inspection of the surface condition. The surface condition results for protected and unprotected flax/epoxy and hemp/epoxy plates that were monitored monthly are summarized in Table 4. The range of representative surface conditions was determined according to the Naval Ships' Technical Manual, which includes a descriptive definition of biofouling development [47]. The surface conditions of the hemp-reinforced biocomposite after six months of immersion are presented in Figure 6 as the worst case. From Table 4 and Figure 6, it is obvious that the surface has massively changed, regardless of the biocomposite type. However, the intensity of the change is less pronounced in the case of plates protected by the antifouling coating. The typical organisms forming the attached biofouling community were predominantly green algae, including several tubeworms and barnacles, which are usual for the Adriatic Sea environment [43]. The extensive presence of green algae could be attributed to the effects of epoxy-originated nitrogen dissolution in the seawater stimulating the effects of local eutrophication. Additionally, based on the biofouling-induced mass gain, it can be noted that the hemp/epoxy plate without antifouling coating is the most prone to the settlement of seawater organisms. Conversely, when protected, it demonstrated quite a resistance to biofouling effects. Similarly, the effect of the antifouling coating significantly reduced the biofouling dynamics and the total mass gain in the case of the flax/epoxy plate.

Table 4. The surface conditions of the biocomposite plates as determined at the end of each month of immersion and the total mass gain after 6 months.

Plate	Month						Total Mass Gain after 6 Months, (g)
	July 2021	August 2021	September 2021	October 2021	November 2021	December 2021	
Flax/epoxy, unprotected	Light slime	Heavy slime	Heavy slime	Small calcareous fouling or weed	Small calcareous fouling or weed	Medium calcareous fouling	82.74
Flax/epoxy, protected	Typical as applied AF * coating	Light slime	Light slime	Light slime	Heavy slime	Small calcareous fouling or weed	42.27
Hemp/epoxy, unprotected	Light slime	Heavy slime	Heavy slime	Small calcareous fouling or weed	Small calcareous fouling or weed	Medium calcareous fouling	115.17
Hemp/epoxy, protected	Typical as applied AF * coating	Light slime	Light slime	Light slime	Heavy slime	Heavy slime	6.59

* AF—Antifouling.

A very interesting report on the biofouling of lecithin/wax/polyurethane (LWPU) and polydimethylsiloxane (PDMS) biocomposites was presented in [33]. The biocomposite samples were deployed for six months within a coral reef environment, and their surface condition was inspected after that period. Approximately 30 different species were identified settling on the surface of biocomposites, mainly including benthic organisms. It was also pointed out that the PDMS biocomposite was more prone to the biofouling effect due to the presence of nitrogen and ammonium as important nutrients supporting their growth. Unfortunately, no application of antifouling coating was reported. Although this research considered a completely different marine environment, the biofouling resistance of unprotected flax/epoxy and hemp/epoxy reported in Table 4 indicates similar trends in the settlement of marine organisms on the surface of specimen plates, including extensive development of benthic organisms and green algae.



(**a**) (**b**) (**c**)

(**d**) (**e**) (**f**)

Figure 6. Photographs of biofouling samples: (**a**) flax/epoxy plate without antifouling protection before immersion, (**b**) flax/epoxy plate without antifouling protection after six months of immersion, (**c**) flax/epoxy plate with antifouling protection after six months of immersion, (**d**) hemp/epoxy plate without antifouling protection before immersion, (**e**) hemp/epoxy plate without antifouling protection after six months of immersion, (**f**) hemp/epoxy plate with antifouling protection after six months of immersion.

4. Conclusions

Biocomposites have the potential to become one of the leading materials for various products in the future. It is expected that their broad application will strongly impact environmental and economic issues such as the renewability of material sources, life-cycle sustainability, end-of-life issues, human and animal health, and others. However, many challenges still prevent their broader inclusion in the global manufacturing systems due to their relatively low level of maturity. This is especially the case when considering the application of biocomposites in marine environments. Therefore, this paper addressed issues such as hygroscopicity, mechanical properties, and biofouling resistance of flax/epoxy and hemp/epoxy with the aim of motivating naval architects and classification societies to consider the application of biocomposites as a ship hull material.

A series of experiments were performed on epoxy resin with 28 m% of bio-based carbon content reinforced with flax and hemp in dry and wet conditions. First, the hygroscopicity of each biocomposite was investigated through measurements of absorption rates and saturation points, where hemp/epoxy proved to be more prone to water absorption than flax/epoxy. Then, the associated mechanical properties were acquired through measurements of tensile, flexural, interlaminar, and impact properties of flax/epoxy and hemp/epoxy in both dry and wet conditions. Again, flax/epoxy demonstrated superior mechanical properties over hemp/epoxy in almost all cases. Finally, the biofouling resistance was investigated by deploying protected and unprotected flax/epoxy and hemp/epoxy plates in the Adriatic Sea and by regular inspections of their surface conditions. The acquired data showed that the unprotected hemp/epoxy was the most prone to the settlement of marine organisms while the surface of its protected counterpart remained in an almost intact state after six months of deployment.

Finally, many research questions and challenges remain open concerning flax/epoxy and hemp/epoxy that need to be answered before their application as structural materials. These include aspects of in-service biodegradability, chemical stability, thermal stability and conductivity, vibration and noise damping, fatigue, crack propagation, and others. In addition, different arrangements of flax and/or hemp fibers as well as other resins could be tested for their influence on the hygroscopic, mechanical, and biofouling properties of biocomposites. Hence, only a thorough approach to the problem including different aspects of ship structural properties may lead to the final application of biocomposites as a ship hull material.

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