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Review

An Overview of Natural Fiber Composites for Marine Applications

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Abstract: Environmental emergency awareness has been gaining momentum in recent years in the composite manufacturing industry, with a new generation of composite materials minimizing their harmful environmental impacts by employing more sustainable manufacturing processes and, where possible, replacing synthetic materials with more sustainable bio-based materials, thus more efficiently using energy and material resources. In this context, natural fiber composites are proposed as appealing candidates to replace or reduce the use of synthetic fibers for reinforcing polymers in several industrial fields, such as the marine sector, where composite usage has been extensively studied in recent years. This review aims to present a thorough overview of the usage of natural fiber composites for marine applications, discussing the most relevant criteria required for applications where water exposure is expected. For this purpose, the review outlines the natural fibers and matrices used, analyzes the resultant composites' mechanical properties, and presents the fiber treatments required before manufacturing, as well as the main manufacturing processes adopted for natural fiber composite production. The advantages and disadvantages of natural fibers compared to synthetic fibers are also presented, including economic and environmental credentials. Finally, a list of marine components with natural fiber reinforcements developed in recent years is reported.

Keywords: natural fibers; marine; composites; hemp; flax; ecofriendly materials; environmental materials; bio-based materials; sustainability; sustainable development

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1. Introduction

The fiber-reinforced polymer (FRP) composite market is a multi-billion-euro business with applications in the automotive, electronics, construction, marine, sporting goods, aerospace, and consumer product industries. FRP materials are attractive due to their unique ability to combine the properties of different materials to produce high-performance and easily tailored systems. Natural-fiber-reinforced polymer (NFRP) composites specifically have been researched more extensively in recent years for their potential applications in various fields [1].

The establishment of the FRP composite industry dates back to the early 1900s when fibers were first combined with phenolic resins, and they later reached commodity status during the 1940s with the development of glass-fiber-reinforced unsaturated polyester [2]. Since World War II, the market for composite materials has rapidly grown to meet the growing and variable demand coming from different industrial sectors, and up until recent years, only synthetic fibers were used for reinforcement [3]. However, in recent years, due to an increased awareness of environmental issues, sustainability has become a major concern for both industrial applications and academic research. Therefore, there is a great need for every industry sector to replace unsustainable products with more sustainable alternatives.

In the context of such considerations, it has been predicted that the global natural fiber composite market size will be valued at USD 10.89 billion by 2024 and is expected to grow at a compound annual growth rate (CAGR) of 11.8% [4]. Therefore, the replacement of synthetic fibers with natural fiber alternatives represents a very challenging topic, as testified by the high number of published papers researching natural fiber composites as compared to synthetic alternatives. NFRP composites specifically have been researched more extensively in recent years; since 2019, 10,346 papers with natural fiber composites in the title, in the abstract, or as a keyword have been published according to a Web of Science search undertaken by the authors, while 7799 articles were found on the Scopus portal using the same search criteria. In almost all instances, the number of papers, reviews, and book chapters increased incrementally year after year, demonstrating the surging interest in the topic.

Economic and environmental concerns, coupled with governmental initiatives, have encouraged research on the development and usage of biocomposites. A biocomposite can be defined as a composite material in which one or more component(s) is derived from a biological origin, such as natural fiber reinforcements or biopolymers, so biocomposites have different levels of environmental sustainability based on their constituent materials and their biodegradability [5–7]. The most common category of biocomposites used in industry is represented by those in which petroleum polymers are reinforced with natural fibers. Even though natural fibers can be sourced from plants, animals, and minerals, in this review, as generally occurs in all research about natural fiber composites for industrial applications, this term refers only to vegetable fibers sourced from plants. Among different types of natural fibers obtained from seeds, stems, or roots, flax, hemp, and jute attract the most interest because of their relatively high mechanical properties, such as specific stiffness and strength [8]. In line with the ecological transition in recent years, it is unsurprising that an industrial field that lends itself well to the replacement (total or partial) of synthetic fibers with vegetable fibers is the marine field, where composites are widely used [9].

Indeed, historically speaking, the marine industry, particularly the shipbuilding sector, has always relied on the use of huge quantities of natural materials for their main structural components. The oldest-known floating means of transportation, the Pesse canoe [10], discovered in the Netherlands and dated between 8040 BCE and 7510 BCE, is in fact made from a single Scots pine log; similarly, the Khufu ship, found in Egypt and dated around 2566 BCE, was made by planks made of Lebanon cedar joined by tenons made of Jerusalem thorn [11]. Wood, being buoyant and widely available and having the right combination of workability and mechanical properties, was the traditional material used for the construction of the main hull of boats and all other principal structural parts until the 19th century, with natural fibers such as flax, cotton, and hemp used for sails and coir, hemp, and manila (and, in some cases, sisal, although with lower performance) used for ropes. Metals were already present in boats in the Bronze Age and Late Iron Age; however their use was limited to braces and fastenings made of copper (2400 BCE) [12] and anchor claws made of lead, bronze, or iron [13]. It was not until 1816 that the first all-iron-hulled vessel (the Vulcan) was manufactured in Glasgow (Scotland) [14], but from that moment onward, metal structures started dominating the marine sector, first through a "composite" design (wrought iron frame and wood planking) and then, at the turn of the century, with steel starting to replace iron, with the HMS Iris (1870) and HMS Mercury (1878) being the first ships that used an all-steel design [15]. The first half of the 20th century also saw huge breakthroughs in the approach to shipbuilding: durable vessels capable of withstanding harsh environments while being relatively fast became a necessity during the Second World War, driving the massive use of steel that culminated with the construction of the 72,000-tonne Japanese battleship Yamato (1937) [16], while the rapid development of submarine vessels required new materials to withstand huge underwater pressures, leading to high-tensile-, high-yield-strength steel alloys, such as the HY-80 alloy used in the construction of the Permit-class submarines between 1960 and 1970 [17], and the titanium hull of the K-278 Komsomolets (1983) [18]. Although some combination of steel and wood was still in use for landing crafts until 1945 (the LCVP, also known as "Higgins boat" [19]), the next material revolution in shipbuilding happened with the development of composite materials, with the first fiberglass/polyester sailboat designed and manufactured in 1942 [20]. Load-bearing structures made with glass-fiber-reinforced polymer (GFRP) offered a good compromise between properties and lightness while, at the same time, guaranteeing the virtual elimination of the issue of seawater corrosion and interaction with marine organisms typical of metal vessels, hence reducing maintenance costs. Moreover, since the use of glass fibers resulted in a low magnetic signature, in 1970, the HMS Wilton was the first warship to be constructed entirely with GFRPs and used as a coastal minesweeper/minehunter [21]. In the marine civil sector, throughout the second half of the 20th century, composite materials experienced rapid growth and adoption, with more than 60% of the Japanese fishing boat fleet being made with glass fiber by 1984 [9] and the vast majority of small pleasure vessels and passenger transport nowadays being made with composite structures. As for carbon fibers, the development of tailorable manufacturing techniques and the reduction in raw materials have allowed their expansion from the aerospace and Formula 1 sectors to the marine sector at the beginning of the 21st century. Indeed, thanks to their exceptional specific properties, the replacement of steel and aluminum structures with CFRP guarantees a notable reduction in weight, an increase in strength of more than 40%, and an optimization of fuel efficiency of more than 50%, as demonstrated by the incredible performance obtained by luxury boats (such as the Say 42) and raceboats (such as the AMRO ONE). However, although the use of carbon fibers allows for manufacturing ultralight boats characterized by excellent mechanical properties, the excessive increase in carbon emissions involved in the production of synthetic fibers has shifted the research paradigm toward the development of alternative composite structures that can join the inherent advantages of ultralight-polymer-based materials with the good performance and low environmental impact of natural reinforcements. In other words, the philosophy behind this approach is to rediscover the original materials used in shipbuilding and update them to the 21st century by creating new synergetic structures that can overcome traditional synthetic solutions.

On the basis of this premise, this review aims to present a thorough overview of the use of natural fiber composites in marine applications, and it is organized into the following macro sections:

- Natural fiber selection criteria in marine application: This section provides an overview of the main natural fibers considered in industry, the chemical treatments required for composite manufacturing, and the mechanical properties and durability of natural fiber composites, also including consideration of their water absorption, hybridization approach, production costs, and environmental considerations.
- Matrix selection criteria for natural fiber composites in marine applications: This section reports the matrices suitable for natural fiber composites for marine applications, scrutinizing their advantages and disadvantages for natural fibers as well as their mechanical properties.
- Processing of natural fiber composites in marine applications: This section presents the common composite manufacturing methods for natural fiber composites used in the marine industry in both academic research and industry, also including a small summary of natural fibers' processing phases.
- Application of natural fibers in marine applications: In this section, numerous applications of natural fiber composites in the marine industry are illustrated, showing various diverse sea vessels and marine components, such as boat hulls and decks, using natural fiber reinforcement in recent years.

2. Natural Fiber Selection Criteria in Marine Applications

FRP composites are used in marine applications as lighter alternatives to metals. In addition, traditional materials are highly susceptible to chemical corrosion since hydroxide and chloride ions in underwater marine conditions react with metals such as steel or aluminum, degrading their properties and possibly leading to leaks and cracks when subjected to pressure underwater [9]. Repairing metal cracks in a marine environment is challenging, as metals are also difficult to weld underwater [22]. FRP composites are also desirable alternatives to wood, which degrades when exposed to biological agents, such as fungi, bacteria, and insects [23]. Based on this information, along with FRP composites' low density and good impact resistance to waves, it is not surprising that FRP composites have seen widespread usage in the marine sector, especially for those applications that require high-performing structures such as racing boats, yachts, and other lightweight marine applications.

Carbon-fiber-reinforced polymer (CFRP) composites are used in advanced FRP composite applications due to their excellent mechanical, thermal, and electrical properties [24]. GFRPs also possess good mechanical properties, are cheaper to manufacture than CFRPs, and have high corrosion and moisture resistance, making them desirable for marine applications [25]. However, there are economic and environmental concerns about the sustainability of CFRP and GFRP manufacturing, which will be discussed in detail in later sections, highlighting the favorability of NFRP composites in comparison. Furthermore, there are several instances of NFRP composites being used as alternatives to synthetic materials for both surface and immersed components using fabric as the reinforcement form; this will also be highlighted when discussing applications in Section 5.

Synthetic-carbon-fiber-reinforced composites have emerged as the preferred materials for high-performance lightweight marine applications, such as the Vestas Sailrocket 2, the current sailing speed record holder with an average speed of 65 knots in 2012 [26]. However, synthetic FRP composites such as CFRP composites have major disadvantages, such as very high production costs and an even higher carbon footprint, together with the huge recycling issue associated with the utilization of synthetic fibers and thermoset polymers; these issues have renewed interest in natural fibers as alternative composite reinforcements for marine applications [22]. Indeed, being intrinsically more sustainable (as they can be biodegradable) and, in most cases, characterized by a negative carbon dioxide (CO_2) footprint, natural fibers can provide a lightweight, cost-effective, more sustainable alternative to glass and carbon fibers, with an edge in certain properties, such as vibration damping and sound insulation, due to the fibers' complex, hierarchal microstructures [27]. The following sections present an analysis of the factors that define NFRP composites' utilization in marine applications, balancing their performance and selection criteria against established synthetic-glass- and carbon-fiber-reinforced composites in the process. The analysis aims to clarify the factors affecting NFRP composite manufacturing, properties, and performance in the marine industry to further discuss their possible applications and the current limits of their employment in the marine environment.

2.1. Mechanical Properties of Vegetable Fibers

This section contextualizes the most relevant comparisons between NFRP and synthetic composites in terms of mechanical properties and performance, the most important factors for material selection in manufacturing. The harsh marine environment especially requires materials that can withstand factors such as corrosion, UV exposure, high tides, wind, wave impacts, seawater immersion, fog, and humidity [28].

The primary point of discussion around the adoption of natural fibers for the replacement of synthetic fibers is the ability of NFRP composites to consistently replicate the mechanical properties of synthetic fiber reinforcements such as glass and carbon fibers. The variation in natural fibers' properties is due to the variation in fiber geometry, density, and chemical structure. The batch and variety of natural plant fibers and farming conditions such as temperature, humidity, and soil mineral content are thought to be highly influential on the mechanical properties of the resultant NFRP composite materials.

Recent advances in quantitative measurement methods could help to acquire more accurate data measurements for the mechanical properties of NFRP composites. For example, Griffith et al. recently proposed a high-throughput centrifugal method to measure the bulk mechanical strength of soft materials [29]. The proposed centrifugal method significantly reduces costs in comparison with other high-throughput measurement methods utilizing large-scale robotic systems. An alternative to the bulk technique is the single-molecule method using atomic force microscopy (AFM) and optical tweezers (OT) to measure mechanical properties, such as Young's modulus, fracture toughness, and energy dissipation [30]. The development of such measurement methods will contribute to large datasets of mechanical properties that machine learning can use to accelerate material discovery and optimization [31]. Computer simulations can also be combined with experiments and advanced measurement methods to develop NFRP composite materials via techniques such as adding nanoscale fillers while acquiring more accurate data about the mechanical properties of the materials [32].

Several plant-based natural fibers have good mechanical properties that present the potential for utilization as composite material reinforcement, especially as they have a lower density than glass fibers (1.5 g/cm^3 compared to 2.5 g/cm^3). Table 1 shows some relevant mechanical property values for common natural fibers (flax, hemp, and jute), along with those for glass fiber for comparison. The table was adapted from Pickering et al.'s table, which lists multiple sources to showcase the variability of natural fibers' mechanical properties compared to E-glass [33]. This variability is due to differences in the plant variety, growing conditions, soil quality, harvesting and processing conditions, the measurement method of tensile properties, and various other variables [34]. Flax particularly shows significant variability depending on the plant variety and growing conditions, with its tensile strength varying from 345 MPa to 1830 MPa, meaning that the tensile strength could increase by 430% depending on the plant variety and growing conditions, while hemp's tensile strength varies from 550 MPa to 1110 MPa, an approximately 200% increase. Both hemp and flax have much lower tensile strength than the lowest value of E-glass at 2000 MPa, but they can reach the tensile stiffness value of E-glass. When comparing specific tensile properties, flax may be able to reach, and perhaps even exceed, the tensile strength values of glass, and all three natural fibers listed in Table 1 can exceed the specific stiffness value of glass.

Table 1. Natural fiber and glass fiber mechanical properties and geometry values. Adapted from Pickering et al. [33].

Property	E-Glass	Flax	Hemp	Jute
Density (g/cm^3)	2.5	1.5	1.5	1.3–1.5
Length (mm)	Continuous	5–900	5–55	1.5–120
Tensile strength (MPa)	2000–3000	345–1830	550–1110	393–800
Specific tensile strength (MPa/g·cm^{-3})	800–1400	230–1220	370–740	300–610
Tensile stiffness (GPa)	70	27–80	58–70	10–55
Specific tensile stiffness (GPa/g·cm^{-3})	29	18–53	39–47	7.1–39

Flax, hemp, and jute are all constituted by similar biopolymer components, albeit in different quantitative compositions. For example:

- Flax: 62–81% cellulose, 4–21% hemicellulose, 2–5% lignin, and 13–14% other components.
- Hemp: 67–81% cellulose, 6–22% hemicellulose, 3–13% lignin, and 12–13% other components.
- Jute: 56–72% cellulose, 12–35% hemicellulose, 9–14% lignin, and 14% other components [35].

Thus, all three natural fibers consist mainly of hydrophilic cellulose, then a lower percentage of hemicellulose, which acts as a matrix holding cellulose microfibrils together, and finally lignin, a hydrophobic component that is more abundant in jute, which has excellent hydrophobic properties, but it can also decrease the elastic modulus of the composite material [36–38]. It is also important to consider that the hemicellulose and lignin contents of the natural fiber structure are sometimes removed when undergoing the various chemical treatments recommended for improving mechanical properties [39], as will be discussed extensively in Section 2.4.

Flax and hemp in particular have seen significant interest from designers for their mechanical properties, with their composites showing higher specific stiffness in tension and plate bending compared to glass fibers [40]. It is also important to note that natural fiber selection for composite manufacturing is linked to the country of origin of the used natural fiber, with flax and hemp widely cultivated in Europe, for example [41]. Coir, jute, kenaf, and ramie are mainly cultivated in Southeast and East Asia and are used for a variety of textile applications, including reinforcement fabric manufacturing for composites [42–44]. Sisal, originally native to Mexica, is cultivated mainly in Brazil and in Africa in places such as Kenya, Tanzania, and Tunisia. Sisal fibers have been produced for millennia, reaching a peak of production in the 1960s, until the introduction of cheaper synthetic fibers cooled demand, but in the last two decades, the demand for sustainable materials has reignited interest in their production [45–48]. Flax and hemp in particular also have the advantage of requiring less space to farm in comparison to other plants. For example, flax has a yield of up to 2 tons of fiber yield per hectare [49], showing a significantly higher yield than other plants [50]. Cultivating natural fibers such as flax is appealing from an environmental point of view in comparison to producing synthetic fibers such as glass fibers and even other textiles such as cotton. Flax fibers require only 600–1000 L of water per kg for their production, depending on the climate and season [51,52], compared to 700–29,000 L per kg for cotton fibers. Flax and hemp also compare favorably with other natural fibers: for example, jute and bamboo are water- and energy-intensive natural fibers to produce, respectively. There are many environmental and health-promoting motives for flax cultivation that call for greater consideration in industrial agriculture [53].

Hemp was also demonstrated in a recent study to potentially produce similar amounts of fibers per hectare compared to flax, with 80% of the tensile properties. The industrial extraction of the fibers was shown to have reduced fiber yield and mechanical properties, with a possible explanation being the harsh processing parameters on an industrial scale, with the optimization of processing parameters potentially offering better yields and mechanical properties [54]. Hemp was also estimated to produce 1–5 tons per hectare in the United States per a study, compared to 0.80–0.93 tons per hectare for cotton [55], while European hemp has a yield average of 5.5 to 8 tons per hectare [56]. The European lands where hemp is cultivated increased by 70% between 2013 and 2018 and have increased by 614% since 1993 [57]. Hemp also has many benefits for its cultivation as an industrial crop, with applications in industries such as medicine, food, construction, and bioenergy [58]. The multi-purpose possibilities for different parts of the hemp plant create additional value for cultivation, decreasing the costs of the fibers as a result; further discussion on the economics of hemp and other natural fibers will be discussed in the cost section (Section 2.2) [59,60].

2.1.1. Mechanical Properties of NFRPs with Moisture Absorption

The environmental advantages of natural fibers such as flax and hemp over their synthetic glass and carbon fiber counterparts are widely cited, but what is also widely acknowledged is the very low moisture absorption rate of synthetic fibers, which is critical for mechanical properties and performance in a marine environment. The reduced durability of natural fibers is also a concern for long-term applications in harsh environments (such as seawater), as are relevant mechanical properties for structural integrity and longevity, such as tensile and flexural strength and stiffness and impact resistance [33,61].

The main issue affecting NFRP composites in a marine environment is their poor resistance to water absorption. Many natural fibers come from mainly cellulosic plants, such as flax and hemp. Such cellulosic natural fibers are hydrophilic; thus, they have a tendency to attract water and absorb moisture and humidity. The individual microscopic fibers' cell walls contain free hydroxyl (OH) groups, which encounter moisture (H_2O), making the cross-section of the fibers a medium for water absorption, increasing the diameter of individual fibers, and swelling the fibers within the matrix. This leads to issues such as the weakening of interfacial adhesion between the fiber and the matrix, voids, matrix cracks, and dimensional instability, all influencing the mechanical properties and performance of the composite [62]. Improving the fiber–matrix interfacial adhesion is a critical issue for the mechanical properties and durability of NFRP composites [63]. In a marine environment, matrix durability and damage by hydrolysis are also issues, as water diffusion through the polymeric matrix is a complex phenomenon that can also induce swelling and reduce fiber–matrix adhesion [64]. Cracks in the matrix also lead to further water absorption, as the cell wall expands with water absorption until a saturation point, after which the excess water propagates through the voids caused by fiber expansion [65]. The issue of the cell wall's absorption of water heavily determines the mechanical properties of the natural fibers and the performance of the resulting NFRP composites, especially in the marine environment, where moisture absorption is expected to be constant. Therefore, reducing the moisture absorption from NFRP composites is critical for marine environment applications [66].

Several authors have tested the mechanical properties of hemp-reinforced composites for the marine environment. Dhakal et al. [67] conducted tensile and flexural tests on hemp-fiber-reinforced unsaturated polyester composites, with various fiber volume fractions and water immersion conditions. The composite laminates were prepared by hand layup and compression molding with methyl ethyl ketone peroxide (MEKP) as a catalyst. The moisture absorption percentage was found to increase proportionally with the fiber volume fraction, as the hydrophilic, cellulose-based natural fibers absorb more water. The moisture absorption rate was shown to be higher at an elevated temperature of 100 °C, showing unpredictable non-Fickian diffusion behavior, unlike the uniform Fickian diffusion behavior normally seen in natural fibers at room temperature, resulting in a 23% higher moisture absorption rate at an elevated temperature. The tensile and flexural measurements of stress and strain, respectively, were shown to increase with the fiber volume fraction. Interestingly, samples with different volume fractions exhibited different reactions to water immersion, with the highest volume fraction sample (26%) showing a 22% increase in tensile strength after 888 h of immersion to reach the water saturation point, while most other samples showed a decrease in tensile strength. The tensile strain was also shown to increase with moisture content, with the flexural strain doubling in value for the 26% volume fraction samples after water immersion. However, the flexural strength decreased with water immersion for almost all samples; this could be explained by the decrease in fiber–matrix adhesion with increased water content. The increase in tensile properties with water absorption was explained by the fibers swelling with excessive water, filling gaps between the fiber and matrix; such a phenomenon in NFRP composites causes water to act as a plasticizer. Although the increase in the tensile stiffness and strength of NFRP is positive, the variability of mechanical properties is dangerous for structural components. The significant increase in water content also increases the weight of the NFRP component, which is undesirable for a structural application.

Chethan et al. [68] investigated the mechanical properties of hemp/epoxy in a marine environment. The hemp/epoxy composite laminates were manufactured by compression molding. The composite samples were immersed in natural seawater for 150 days at room temperature. Tensile properties, flexural properties, and moisture content were analyzed. Dry samples showed tensile strength and stiffness of approximately 36.5 MPa and 0.855 GPa, respectively, and after 150 days of seawater immersion, the tensile strength and stiffness decreased by 13.7% and 10.5%, respectively. Dry samples also had a flexural strength of around 84 MPa, which was reduced by 17% after seawater immersion.

For flax-reinforced NFRP composites, recent work by Lekube and Burgstaller [69] compared the tensile properties and porosity of NFRP and GFRP commingled composites, with polylactic acid (PLA) and polypropylene (PP) binder fibers acting as the matrix; maleic anhydride-grafted polypropylene (MAPP) was added to PP to improve interfacial adhesion. Commingled composites use thermoplastic fibers as a matrix to bind fiber reinforcements [70]. The fibers were mixed and processed into fleeces using a carding machine, and the fleeces were subsequently compression-molded to manufacture the composite laminate. Composite samples were tensile-tested, and porosity was calculated based on density measurements. The flax/PLA composite's tensile strength and stiffness were found to be significantly higher than those of flax/PP composites, even with the MAPP additive. The higher stiffness value of flax/PLA was explained by the higher modulus of the PLA fibers, which were not fully melted in the compression molding process. The highest Young's modulus value for flax/PLA was 11.3 GPa at around a 40% fiber volume fraction, while for flax/PP, it was 7.1 GPa at around a 33% fiber volume fraction. In comparison with glass fibers, for similar fiber volume fractions, flax/PLA composites have slightly higher tensile strength and stiffness in comparison with glass/PLA. In contrast, glass/PP composites had a 30–50% increase in mechanical properties compared to flax/PP, but it should be noted that this was largely because the glass fibers used were sized for compatibility with PP [71]. The porosity of the composite laminates was found to decrease with increasing stacked layers, but no clear correlation was found between the porosity and mechanical properties of flax samples, unlike the glass-reinforced ones; this could be explained by the sizing of glass fibers for compatibility in the PP matrix, as well as the inherent porosity of the flax fibers' cellulose structure. De Kergariou et al. [72] optimized a method to measure the porosity of flax/PLA composites, which could be modified for the porosity measurement of other NFRP composites. Increasing the porosity of the composite could increase acoustic properties such as sound absorption at the expense of mechanical properties, such as tensile strength and stiffness, although significantly increasing porosity volume does lead to less brittle behavior [73]. Berges et al. [74] found moisture uptake to increase the damping ratio by 50% for flax/epoxy composites subjected to hygrothermal conditions at 70 °C and 85% RH (relative humidity), where water mass uptake at saturation was 3.3%. A decrease of 20% in the longitudinal elastic modulus was measured at the expense of improving the damping ratio. Figure 1 shows a diagram illustrating porosities in the NFRP composite structure.

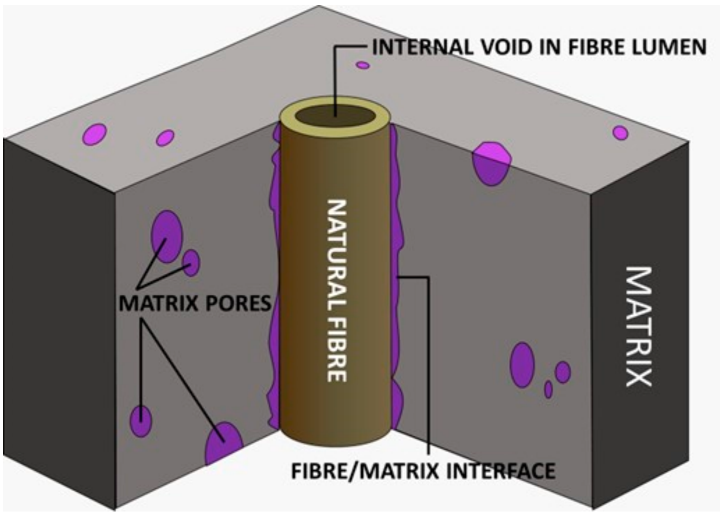
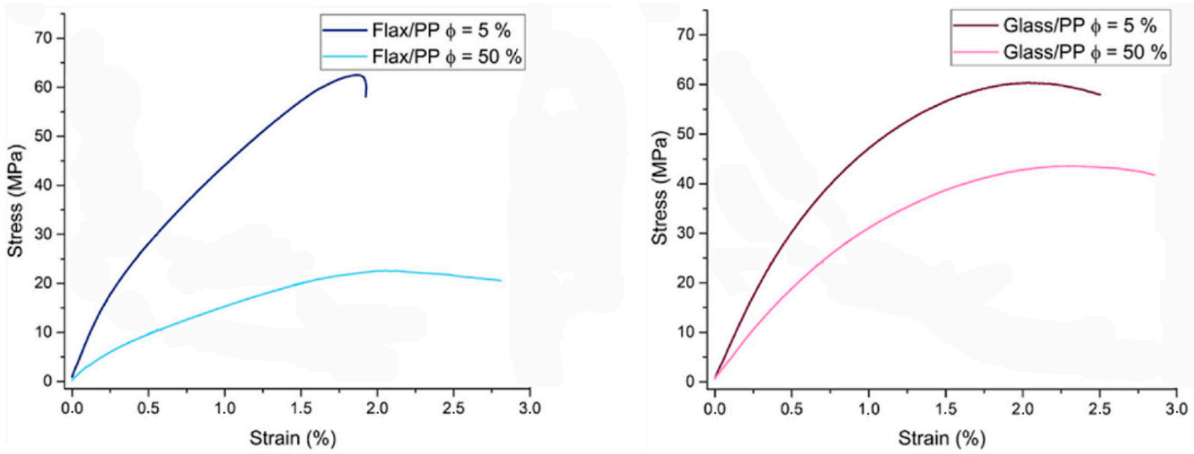


Figure 1. Porosities present in NFRP composites.

Gager et al. [75] also investigated the porosity of nonwoven flax/PP commingled composites, finding that the porosity could be controlled by increasing the compression molding rate, thus reducing the geometry and quantity of voids in the composite. Flax/PP samples at 5%, 30%, and 50% porosity were compared with their glass/PP counterparts. Different humidity levels were used to test for water absorption and hygroscopic expansion behavior, finding similar tensile properties for flax and glass samples at 5% porosity, with glass showing less deterioration in mechanical properties with increasing porosity. These findings are demonstrated in the stress–strain curves shown in Figure 2. Thus, reducing the porosity of the NFRP composite by optimizing the compression molding process could improve mechanical properties, but hygroscopic expansion is another issue affecting mechanical properties, and it is not clearly influenced by composite porosity.



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

Figure 2. Tensile properties of (**a**) flax/PP and (**b**) glass/PP nonwoven composites at 5% and 50% porosity contents [75].

It is noted that the stress–strain curves in Figure 2 show a noticeable difference between the linearity of the glass/PP curves due to their uniform structure, while the flax/PP curves show non-linear behavior due to the nature of the flax fibers, particularly their poor individualization, with the homogeneity dependent on the fiber microstructure and harsh fiber processing parameters also limiting homogeneity between the flax fibers [76,77]. Consequently, poor individualization leads to breakage in the fibers and matrix and fiber/matrix debonding at high strains, followed by friction between the fibers and matrix after debonding and slippage between individual flax fibers in the matrix.

Gager et al. [75] also found that hygroscopic expansion in the flax/PP composite only occurs out of plane due to the random dispersion of the nonwoven fabric, unlike unidirectional flax composites, which have a rate of hygroscopic expansion of up to 3.3% in the longitudinal fiber direction, as previously measured by Le Duigiou et al. [78]. Réquilé et al. [79] also found unidirectional hemp/epoxy composites to have similar hygroscopic behavior at different humidity levels and with continuous water movement, as expected in a marine environment. The orthotropic hygroscopic expansion in unidirectional natural fibers is explained by their geometric in-plane anisotropy. Interestingly, Réquilé et al. found 3% moisture content at 75% relative humidity (RH) to be an optimal point for the mechanical properties of the hemp/epoxy composite, as also confirmed by Péron et al. [80]. Lu et al. [81] studied the moisture absorption and hygroscopic expansion of flax/polyester and flax/epoxy composites, deducing that elementary flax fibers (single fibers) have a lower rate of hygroscopic expansion and a lower radial hygroscopic expansion coefficient (β_r) compared to technical flax fibers (fiber bundles). The hygroscopic expansion for flax/polyester and flax/epoxy was found to be similar, with the epoxy samples experiencing slightly less moisture absorption, which clearly indicates that flax has a dominating influence on the hygroscopic behavior of the composite. The values of the hygroscopic expansion coefficient are highly relevant, as hygroscopic expansion is a highly influential variable for analyzing the natural fiber/matrix interface, key to the composite's mechanical properties [82], as shown in Figure 3. Lu et al. also observed that the flexural properties of samples significantly deteriorated after 54% RH, possibly due to the moisture absorption inducing damage such as fiber pull-out from the matrix and the splitting of individual fibers.

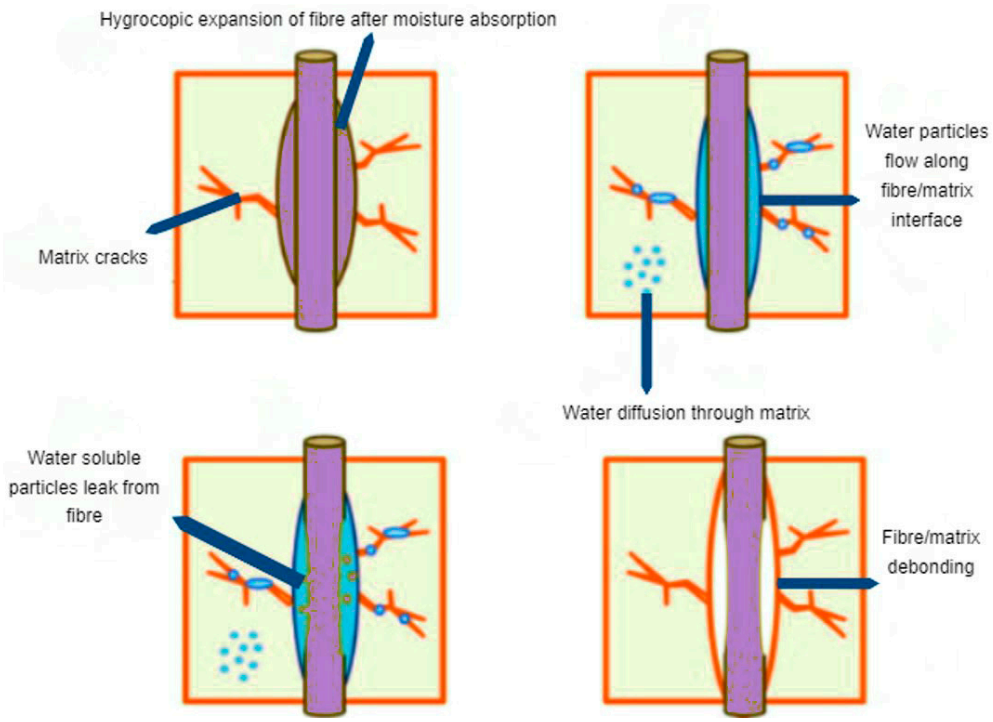


Figure 3. Hygroscopic expansion effect on the fibers [83].

The degradation of NFRP composites' mechanical properties with increasing moisture content is difficult to predict, as multiple studies have found moisture absorption to degrade mechanical properties in a non-linear fashion when going beyond a certain point of absorption [79,81,84]; however, several authors have attempted to develop models and strategies to better predict mechanical properties in proportion to moisture content. Réquilé et al. [79] theorized that the increase in moisture content leads to a monotonic reduction in the tangent modulus according to an exponential decay function; this was based on hemp/epoxy composites tested in a marine environment at room temperature, continuous air flow, and a range of humidity conditions from 9% to 98% RH. Han et al. [85] used numerical modeling to calculate the fiber hygroscopic expansion force and simulate the radial expansion of the fibers and, consequently, the hygroscopic expansion ratio for hemp fibers. The resulting calculations for hemp/PP hygroscopic expansion were in good agreement with empirical experiments, showing values of 3.7% and 3.5%, respectively. It is important to underline that the authors used short hemp fibers and injection molding for the experiment; therefore, the results would be different for continuous unidirectional fabrics. Nevertheless, Han et al.'s results and model are promising for predicting long-term hygroscopic behavior and laminate architecture. Similarly, Abida et al. [86] experimented with quasi-unidirectional flax/epoxy composites to measure the rate of hygroscopic expansion in the three directions of the laminate, as well as the radial direction of the fibers. The authors found a flax radial hygroscopic expansion coefficient β_r =1.06, compared to relatively low composite hygroscopic expansion in the transverse weft direction ($\beta_T = 0.13$), higher expansion in the out-of-plane z-direction along the laminate layers ($\beta_z = 0.85$), and negligible expansion in the longitudinal direction along the fiber length ($\beta_L = -0.02$). Abida et al. also confirmed the linear relationship between tensile properties and moisture content up to a certain point, 4.9% in this instance.

The literature shows that there are possible routes to limit moisture absorption in NFRP composite laminates, such as using nonwoven fabrics and asymmetric laminates. It is also possible to estimate the effect on the mechanical properties, thus limiting the variability and unpredictability of NFRP composites that are detrimental to its usage for applications where moisture uptake is expected such as in the marine environment. Le Duigou et al. [87] developed a bioinspired hygromorphic (materials that change shape according to environmental humidity) flax/MAPP composite, along with analytical and simulation models that could estimate the composite curvature between 50% and 90% RH, but not under 50% RH, also interestingly finding the composite aspect ratio to not influence the moisture content rate, which could be a promising factor for multiple designers in the marine industry [84]. Péron et al. [80] also developed a model for flax/MAPP composites, investigating hygroscopic stresses that occur due to water uptake. They found the layup sequence to be highly influential on moisture content and, consequently, mechanical properties; an asymmetric layup of [0_1, 90_5] was used based on Le Duigou et al.'s work on hygromorphic natural fiber actuators [78]. Furthermore, recent research has shown the ability to effectively tailor the NFRP composite's properties for highly advanced, specialized applications, such as 4D-printed continuous flax-reinforced hygromorphic biocomposites [88] and 4D-printed cellulose filament hydromorphic mesoscale structures [89]. The development of such advanced NFRP composite materials is interesting for possible functional applications and designs for the marine environment.

2.1.2. Durability and Fatigue of NFRP Composites

After analyzing the mechanical properties of NFRP composites in the marine environment, the next step is to analyze the long-term durability of NFRP composites in a marine environment. Novel NFRP composite materials especially should be analyzed for durability, strength, failure behavior, and fatigue to achieve marine composite certification [90]. Besides the prominent effect of moisture absorption on mechanical properties in both the short and long term, other factors will affect the composite's performance and structural integrity in the long term, such as UV radiation, marine fouling, waves' cyclic loading, and hydrostatic pressures in underwater applications [91].

Fatigue life simulations and testing are important considerations for composite materials used for marine applications, especially for highly functional and structural applications, such as offshore oil and gas drilling, marine propellers, and composite risers [92–94]. Several methods have been described to reduce the fatigue degradation of NFRP composites, including using coupling agents, nanoscale fillers, and epoxy elastomer blends and decreasing the variance of elastic properties between laminate ply interfaces [95–97]. The addition of nanoscale fillers is particularly regarded as one of the best solutions for improving mechanical properties such as fatigue [98,99].

Shah et al. [100] investigated the fatigue performance of various NFRP composites in comparison to GFRP composite alternatives. The effects of the fiber quality, percentage, orientation, and stress ratio on fatigue performance were investigated. Jute, hemp, and flax fiber fabrics were used to manufacture composite samples via a vacuum infusion process with polyester as the matrix. Static tensile tests found high-quality flax-reinforced composites to have the highest ultimate tensile strength (UTS) value of 236.3 $\pm$ 12 MPa at an approximately 27% fiber volume fraction, compared to hemp having a UTS value of 171.3 $\pm$ 6.5 MPa at an approximately 36% volume fraction and jute having a UTS value of 224.7 $\pm$ 26.5 MPa at an approximately 38% volume fraction. Despite the variation in UTS, the NFRP composites had similar fatigue strength coefficients (b), ranging from -0.0739 to -0.0623. Meanwhile, the values of b were around -0.074 for GFRP composites, meaning that the fatigue strength degradation of NFRP composites is equal to or slower than that of GFRP composites. The different FRP samples were subjected to tension–tension (R = 0.1) fatigue tests at different stress levels (% of respective UTS). Figure 4 shows the fatigue S-N curves, with b values also highlighted. The fatigue failure mechanism in all tested NFRP composites was found to be similar, possibly due to the similar fiber structural architectures and chemical compositions of the natural fibers. These factors influence micro-crack formations at the fiber–matrix interface and within the fibers themselves. It was noted that the similarity in the fatigue behavior of NFRP composites could mean using their UTS as an indication of fatigue performance.

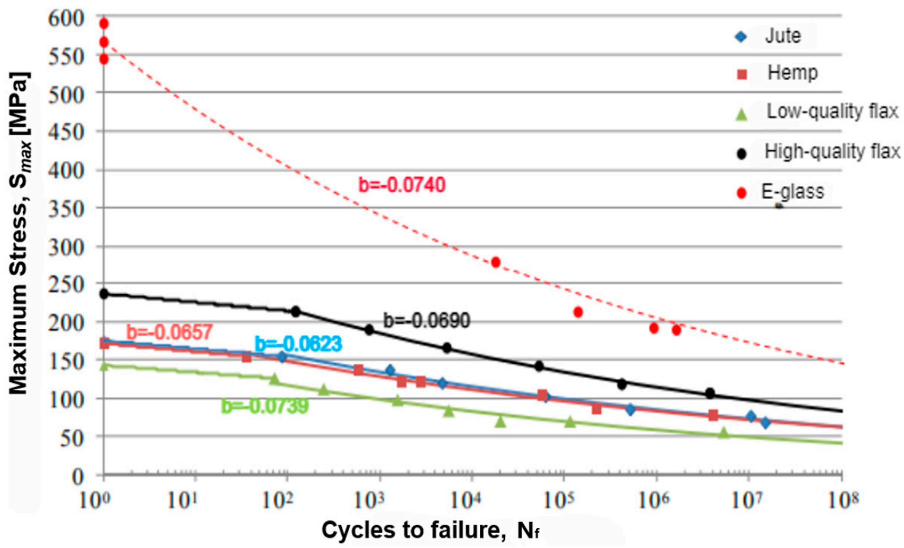


Figure 4. Lifetime fatigue S-N curves for polyester composites reinforced with natural fibers and glass fibers for comparison [100].

Liang et al. [101] compared the fatigue behavior of flax and glass fibers using an epoxy matrix with $[0/90]_{3S}$ and $[\pm 45]_{3S}$ stacking sequences. For the $[0/90]_{3S}$ laminates, glass samples lost around 7–25% of their stiffness depending on the loading level, while for the similar flax-reinforced laminate, a 2% increase in stiffness was observed. The increase in stiffness is explained by the realignment of the cellulose microfibrils relative to the fiber axis; in effect, the microfibrils are straightened when the fibers are axially loaded, increasing the stiffness of the composite. The stiffening phenomenon was described by Baley for flax fibers [102], showing that the straightening of cellulose microfibrils can cause a significant increase of up to 60–80% in fiber stiffness. An increase in cellulose fiber stiffness with cyclic loading was also observed by Placet and de Andrade Silva et al. [103,104].

Fotouh et al. [105] analyzed the fatigue behavior of hemp-reinforced high-density polyethylene (HDPE) composites, using different fiber volume fractions and fatigue stress ratios. The fatigue strength was also analyzed considering moisture absorption after immersing composite samples in water for 35 days, with the water decreasing fatigue strength due to the hydrophilic hemp fibers. However, a new modified stress model was developed using the values of the immersed samples, thus predicting the fatigue behavior of NFRP composites at different volume fractions, stress ratios, and moisture contents. The developed fatigue model is promising for fatigue strength predictions of NFRP composites after a long cycle of operation in a marine environment.

Davies et al. [106] investigated the aging of flax-fiber-reinforced acrylic composites manufactured by infusion in boatyard conditions, using quasi-directional flax fabrics in different stacking sequences and an acrylic thermoplastic matrix (Elium™). The samples were immersed in seawater tanks at different temperatures to examine the hygrothermal aging effect, resulting in greater moisture absorption at elevated temperatures. Davies et al. calculated the reduction in quasi-static mechanical properties after aging and then subjected samples to cyclic four-point bending flexural tests. The tests found significant reductions in stiffness reaching over 50%, while strength reductions were kept under 30%. Davies et al. also proposed a seawater exposure testing setup that tests samples on a single face, more suitable for marine applications such as boat hulls. Haggui et al. [107] also analyzed the fatigue performance of a flax-fiber-reinforced acrylic matrix composite under static and cyclic loading. The tests found fiber orientation to be highly influential on the damage extent and mechanism under static and cyclic loading. The unidirectional flax-fiber-reinforced laminates were found to have significantly improved cyclic performance. The static tensile testing of the unidirectional laminate found the tensile stiffness and strength to be 23 GPa and 210 MPa, respectively. The cyclic tension load testing showed samples' UTS to decrease to 50% after about 10^6 cycles N_r.

Graupner et al. [108] compared the static and fatigue performance of different flax, glass, and flax/glass-reinforced composites using an epoxy matrix manufactured by resin transfer molding (RTM). The results showed that at high loading cycles, from about 7^3 to 8^3, high-quality flax samples had higher fatigue strength than glass samples, showing the potential durability of flax composites with processing optimization. Finite element analysis (FEA) simulation also found flax composites to have better fatigue performance than glass composites. It was also found that hybrid composites can have a better fatigue performance than glass composites after 2×10^5 load cycles. Further discussion on the advantages of hybrid composite materials is found in Section 2.5.

Scida et al. [109] studied the aging effects of hygrothermal conditions and UV radiation on NFRP composites. Samples were manufactured by compression molding nonwoven flax and kenaf fibers, with PP as the matrix. A UV protection film was used to successfully reduce the aging effect on the composites. The UV protection film slightly reduced mechanical properties prior to aging, but after 4 weeks of aging, the film managed to successfully reduce the degradation of the tensile properties of strength and stiffness; reduce the discoloration of the composite, especially for kenaf fibers; and halve the acoustic emission events associated with interface debonding and fiber pull-out. The statistical model used to calculate such damage is described by Saidane et al. [110].

So far in this section, it has been observed that there is a possibility to alleviate some concerns over the unpredictability of homogeneous NFRP composites' mechanical properties in the short and long term for marine applications. Various methods were discussed to improve the mechanical properties and performance of NFRP composites for marine applications. Such improvement aims to increase the competitiveness of such sustainable composites with less sustainable synthetic GFRP and CFRP composites, but along with the performance and sustainability, the industry and manufacturers are of course interested in the economics of manufacturing NFRP composites; this is discussed in the next section.

2.2. Costs

The costs of manufacturing NFRP composites for marine applications are usually related to the origin country of the fibers. The energy consumption costs during manufacturing can widely vary between different composite materials depending on the energy efficiency of the production method used [111] and also the cost of the chemical treatment, as will be discussed further in Section 2.4. There is also variation cited in the literature surrounding the costs of each fiber reinforcement production process based on the differing costs of the cultivation and transportation of natural fibers based on the country of origin. For this purpose, it is desirable to make use of Life Cycle Costing (LCC) tools when comparing costs of different fiber reinforcements for manufacturing composites, as LCC includes all the costs from cradle to grave, thus offering a more complete picture for manufacturers [112,113].

For fibers such as jute, ramie, and particularly kenaf, it seems that the ratio between their elastic moduli and price would make them ideal candidates, as shown in Figure 5, which compares Young's modulus against the price for different fiber reinforcements. However, it is important to consider where natural fibers are cultivated and the costs and environmental impacts associated with their transportation overseas, which, in this case, strongly influences the material selection process [114]. For example, a study in Italy in 2016 compared the production costs of 1 m^2 of material for boat hull construction using natural fibers and traditional synthetic materials [115]. The cost analysis found the manufacturing of the boat using flax and cork to be 168 EUR/m^2 (201 EUR/m^2 adjusted for inflation in 2023), 28% cheaper than using the traditional carbon fiber (CF) and polyvinyl chloride (PVC) foam materials, costing 232 EUR/m^2 (278 EUR/m^2 adjusted to inflation). This is in consideration of the Italian composite manufacturing market in 2016. The study considered material costs for a specific manufacturing method, a hand layup and vacuum infusion process, for the composite laminate. The same manufacturing method was applied to manufacture both composite materials, although this might not always be the case, with different treatments potentially required for natural fibers.

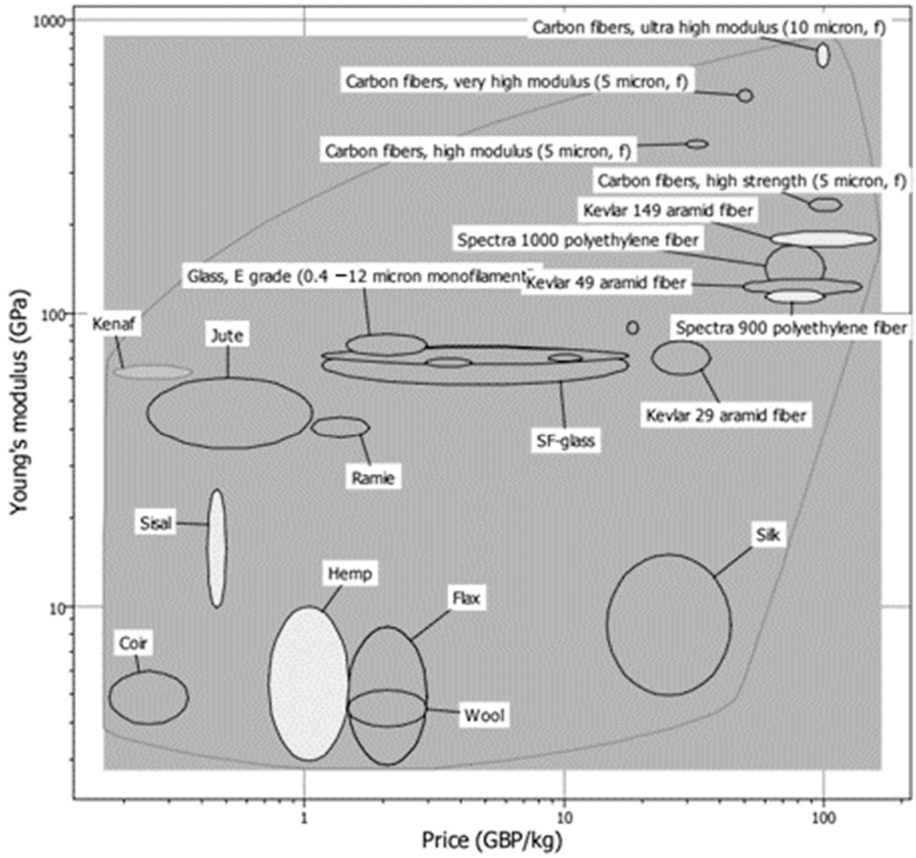


Figure 5. Young's moduli of different fiber reinforcements versus price in (GBP/kg) [116].

The costs of raw materials for the manufacturing process usually vary depending on several factors, such as purchase quantity, delivery costs (the associated emissions and carbon footprint are also discussed in Section 2.3), and commercial factors such as the negotiating power of the purchaser and the market environment, including the competitiveness of suppliers [117]. There are some cost factors that apply specifically to the case of natural fibers, such as the scale of production and the technology and facility requirements associated with it. NFRP composites are in fact currently being manufactured on a relatively small scale compared to CFRP and GFRP composites, but the scale-up of production for NFRP composites will lead to a gradual decline in production costs. The usage of natural fiber reinforcement in the composite industry is expected to become more prevalent, with the utilization of natural fibers such as flax and hemp now considered a market reality for European manufacturers, and with advancements in research increasing the competitiveness of their mechanical properties in comparison to synthetic fibers and highlighting their edge in environmental value and specific properties, such as vibration damping [118–120].

As more research is being undertaken into the development of NF fabrics for structural composite applications, the costs of reinforcement fabrics are being reduced. The industrial extraction of flax fibers from the plant occurs by a mechanical process called scutching to produce long technical fibers, followed by a hackling process that produces flax tow. The scutching/hackling mechanical process has been performed using industrialized machines in recent years [54,121,122]. Scutched flax fibers are long, uniform, pure fibers that are usually used for composite reinforcement for their mechanical properties, while flax tows are a non-uniform, impure, cheaper by-product of flax and not usually used for composite applications [123]. Graupner et al. [124] investigated the preparation of cheaper flax fiber reinforcements. Cheaper fiber yarns were made from flax tow to compare with higher-quality, commercially available unidirectional long flax yarns. The composite materials using flax tow were cheaper to produce, with around 86–92% of the mechanical properties. The price of the flax fabric was thus reduced from EUR 4.45–5.00 per m^2 to EUR 4.03–4.20 per m^2, and this price reduction is proportional to the raw material, as the price of high-quality scutched flax is estimated at 4.40 EUR/kg compared to 1–1.5 EUR/kg if flax tow is used. Another study by the same authors developed hemp yarns from the total fiber line with no preferred fiber orientation, processing more fibers from the plant's stem, which reduced the cost of raw natural reinforcement to less than 1 EUR/kg, even cheaper than using flax tow at 1–1.5 EUR/kg, as disordered hemp processing is the most common processing method in Europe with various production lines [125]. The downside of using this recently developed cost-effective hemp manufacturing process was a 40–50% reduction in impact properties compared to flax, while in terms of planar properties (tensile and flexural), the new material was able to retain around 80% [126]. For hemp, the cost could be significantly decreased by multiple factors, such as relaxed regulations on the plants driving the seed cost down and field retting decreasing the cost of fertilization [55].

The progression is clear in developing NF from cheaper raw materials, with higher efficiency in production and improved mechanical properties. Such developments will reduce the cost of manufacturing NFRP composite components for the marine industry in comparison with the traditional FRPs used, such as CFRP and GFRP. The argument for decreasing costs can also be raised in terms of financial and operational commitments, such as decreasing consumable costs and production waste [127], but there are also savings in energy consumption and the carbon footprint when using natural fibers as an alternative to synthetic fibers. The environmental and energy cost savings will be discussed in the next section, which will also analyze the various factors of sustainability when comparing NFs to GFs and CFs.

2.3. Environmental Impact

The environmental impact of NFRP composites could be significantly lower than that of GFRP and CFRP composites by optimizing the manufacturing process and chemical treatments to increase mechanical properties [128]. The following section highlights the environmental edge that NFRP composites have over synthetic-fiber-reinforced composites, with three subsections highlighting different factors of FRP components' sustainability.

2.3.1. Energy Consumption

Natural fibers undergo multiple mechanical and chemical treatments from harvesting, through extraction, all the way to composite laminate preparation, as demonstrated in Figure 6, all to improve the final composite product's mechanical properties [129]; such treatment processes will be discussed at length later in Section 2.4. The production of natural fibers with the mentioned processes consumes energy and resources. Nevertheless, natural fibers are still currently considered to be much more efficiently produced from an energy standpoint when compared with their glass fiber counterparts. For example, the energy used to produce 1 kg of scutched flax fibers has been estimated to be 4.4 MJ, 10 times less than is used for glass fibers at 45 MJ [50]. For hemp, the production of 1 kg of yarn was estimated to consume as little as 3.4 MJ [130], and 26 MJ in more conservative estimates [131], still significantly less than is consumed for synthetic glass fibers.

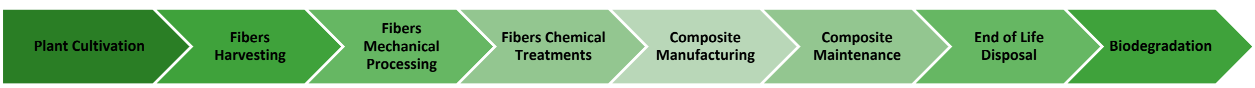


Figure 6. Natural fibers' cradle-to-grave life cycle processes.

Tchana Toffe et al. [132] estimated the energy consumption for producing flax/PLA tape at 0.25 MJ/kg, 31% of the 0.8 MJ/kg for glass fiber fabric. Shah et al. [133] compared the energy consumption of natural fiber production compared to synthetic glass and carbon fiber reinforcement, drawing upon several sources. NFs' energy consumption was estimated to range between 4 and 15 MJ/kg of fiber produced, compared to GF at 30–50 MJ/kg fiber, and CFs' production consumes very high levels of energy at 130 MJ/kg fiber. It was also highlighted that NFs are biodegradable, recyclable, non-abrasive to machines, and non-toxic, unlike synthetic GFs and CFs. Table 2 shows an estimation of the non-renewable energy consumption for the production of fiber reinforcement mats made out of glass and flax at 54.7 and 9.55 MJ per kg fiber, respectively [134].

Table 2. Non-renewable energy used in the production of different fibers (MJ/kg). Adapted from Testoni [134].

Non-Renewable Energy Requirements (MJ/kg)			
Glass Fiber Mat		**Flax Fiber Mat**	
Raw materials	1.7	Seed production	0.05
Mixture	1.0	Fertilizers	1.0
Transport	1.6	Transport	0.9
Melting	21.5	Cultivation	2.0
Spinning	5.9	Fiber separation	2.7
Mat production	23.0	Mat production	2.9
Total	**54.7**	**Total**	**9.55**

The mechanical treatment of natural fibers constitutes a significant percentage of non-renewable energy consumption during the manufacturing process. For example, up to 35% of non-renewable energy consumption in flax fiber production is due to mechanical treatment. The mechanical harvesting process of scutching flax consumes 4.4 MJ/kg of fiber, while for hackling flax, 11.6 MJ/kg of fiber is consumed [135]. The energy consumption of flax is still considered lower than other widespread harvested plants, with cotton consuming 33.1 MJ/kg of yarn [136]. For jute and kenaf fibers, the carding process consumes 0.13 kWh and 0.20 kWh per kg fiber, respectively [137,138]. However, the ongoing development of a more efficient yarn production phase for natural fibers could thus significantly reduce the environmental impact of natural fiber production [139]; indeed, the harmful environmental damage of producing synthetic fibers is significantly higher than for natural fibers. Le Duigou et al. [140] compared the harmful environmental effects of glass fiber production in comparison to flax fibers, finding a reduction of 90% in abiotic depletion (depletion of fossil fuels, minerals, and water [141]), 98% in human toxicity, and 88% in photochemical oxidation when using flax fibers, although a 17% increase in eutrophication was noted due to flax production needing fertilizers or pesticides at times. Eutrophication occurs when a water environment is suddenly enriched with nutrients, causing algal growth, a decrease in biodiversity, and changes in water chemistry [142]. A solution to minimize the phenomenon of eutrophication is the cultivation of flax in quality soils, reducing the need for fertilizers. Crop rotation could also be used to reduce the usage of pesticides [143,144].

In comparison, hemp has the added environmental benefit of not requiring any pesticides [145] due to its fast growth and high seeding rates. Hemp can also purify soil contaminated with heavy metals, chemicals, and pollutants, showing its environmental potential as a rotation crop [58,146]. Shahzad [130] compared the harmful chemicals emitted by producing 1 kg of hemp and glass fibers, with glass emitting 8.8 g and 2.9 g of sulfur oxides (SO_x) and nitrogen oxides (NO_x), respectively, compared to only 1.2 g and 0.95 g for hemp. Hemp is also able to grow with high variability in precipitation; after the first six weeks of growth, the plant is not affected by the variability in water, thus not needing a constant water supply and increasing its environmental sustainability [55].

2.3.2. Life Cycle Analysis

A life cycle analysis (LCA) is an important tool to measure the environmental impact of a product over its life cycle, from cradle to grave [147]. Summerscales considered a quantitative LCA to be an essential metric of the sustainable assessment of performance in the marine environment before the mass production of composite parts [63], through all processes from cradle to grave, as shown in Figure 6. LCAs are increasingly being incorporated into NFRP composites' design and manufacturing processes as a method of measuring such sustainable composites' true environmental impact in comparison with synthetic fiber composites [148]. An LCA can factor in the variables expected to affect the composites' performance in the marine environment, such as aging, moisture, temperature, biodegradation, ultraviolet exposure, and durability considerations [149].

Tchana Toffe et al. [132] compared the cradle-to-grave LCAs of flax/PLA tape and glass fiber (GF) triaxial fabric. The flax/PLA tape's carbon footprint was 0.036 kg CO_2, 33% of the glass fiber fabric's 0.11 kg CO_2, although this was a general calculation of the energy and carbon footprints associated with the flax and glass tapes' manufacturing processes. Boland, De Kleine, et al. [150] studied the LCA of GFRP composites and NFRP composites for a specific application, automotive components, finding that using NFRP composites as an alternative resulted in 6.5–7.4% less energy consumed during the lifetime of the composite material. It is also possible to evaluate and quantify the environmental impact of natural fibers to optimize their production process and further minimize their harmful environmental contributions. Van der Werf and Turunen's LCA compared the environmental impacts of flax and hemp yarns [131]. The scenarios considered were water retting as a reference scenario (traditional warm-water retting), bio-retting (hemp green scutching followed by water retting), baby hemp (stand retting before hemp is matured), and flax dew retting (traditional method for harvesting and scutching flax). The retting process is a crucial influential process for preparing the fiber reinforcement; it involves separating the fiber bundles from the core, which undergoes partial degradation [151,152]. The major environmental impact factors were categorized as eutrophication, climate change, acidification, non-renewable energy use, and land occupation. Overall, the LCA found the environmental impacts of the hemp reference scenario and flax dew retting to be very similar, with the notable exceptions being that flax requires higher pesticide use (hemp requires minimal or no pesticides), while hemp requires significantly higher water use during cultivation. Notably, the 400 km transportation of long fibers from fiber processing to yarn processing showed little impact on the environment, with the main energy-intensive stage being the yarn production phase.

As mentioned before in Section 2.2, LCC is a tool used to quantify the total costs associated with the production and usage of a component or product, from cradle to grave, similar to LCA, but instead of focusing on the environmental impact, LCC considers the economic impact represented in financial costs [149]. For example, LCC was employed to compare the cost savings when hybridizing glass with hemp in elbow fittings for seawater cooling pipes, finding a 20% cost saving to complement the 23% weight saving also found [153–155]. By combining LCA with LCC via computational methods, it is possible for manufacturers to increase the sustainability of products such as those used in marine components while also reducing costs and increasing profits [156]. LCA and LCC can also include drivers specific to marine composite components, such as seawater exposure [157,158].

2.3.3. Carbon Footprint

Another metric for measuring the environmental impact of natural fibers is their carbon footprint in comparison to synthetic fibers. Figure 7 shows the comparison between different natural and synthetic fiber reinforcements, in terms of their carbon footprints and costs, to illustrate the substantial advantage natural fibers would have over synthetic fibers if their mechanical properties were comparable. The x-axis shows the price per kg of fibers in GBP, while the y-axis shows the carbon footprint in kg per kg of fiber produced.

Kevlar is by far the most expensive and unsustainable of synthetic fibers, followed by the high-performance, expensive carbon fiber. Glass is more expensive than natural fibers and has a slightly larger carbon footprint in most cases (SF glass has a comparable carbon footprint to hemp), while some natural fibers, such as ramie and sisal, have almost no carbon footprint and negligible costs compared to other fibers.

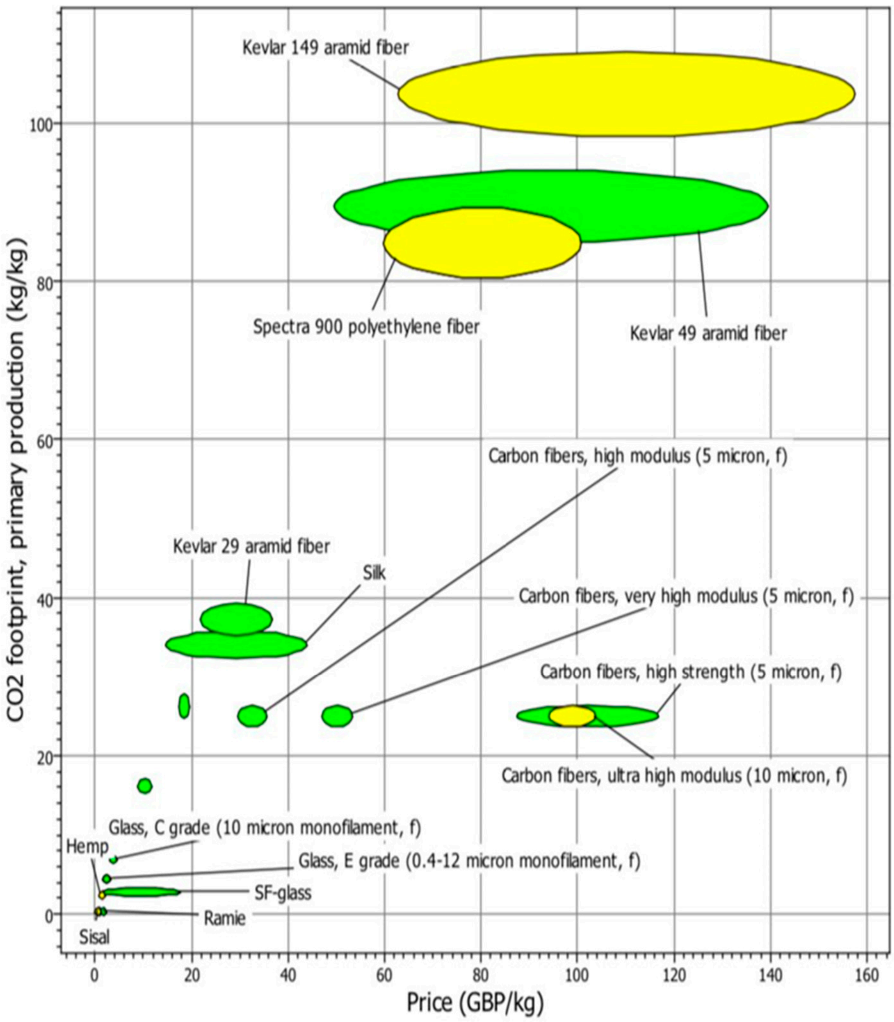


Figure 7. Carbon footprint associated with primary production processes vs. price for different fiber reinforcements for composites [116].

The chart in Figure 7 compares the fibers' carbon footprints for multiple industries and applications, but the carbon footprints of fibers and their resulting FRP composites might differ in each production scenario and industrial application. A study by Barth and Carus [159] provided sustainability data for European automotive and insulation industries, comparing the carbon footprint of synthetic glass fibers with various natural fibers. They estimated that glass fibers produce 1.7–2.2 tons $CO_{2\text{-eq}}$ per ton of glass fiber, compared to 0.5–0.7 tons $CO_{2\text{-eq}}$ per 1 ton of various natural fibers: flax, hemp, kenaf, and jute. The gap in carbon footprints between natural plant fibers and synthetic glass fibers was also shown to translate to their corresponding composites, with NFRP composites estimated to have a 20–50% lower carbon footprint compared to GFRP composites. Shahzad [130] estimated the production of hemp fibers to emit only 0.64 kg $CO_{2\text{-eq}}$ per 1 kg fiber produced, compared to 20.4 kg $CO_{2\text{-eq}}$ per 1 kg glass fiber produced, meaning that glass fiber production can emit more than 30 times the amount of carbon dioxide compared to natural fiber alternatives such as hemp.

The reduced carbon footprint of flax fibers is also evident from their usage in the marine sector for applications that were traditionally implemented using carbon fibers. One example is Bcomp, a Swiss manufacturer that collaborated with many boat manufacturers to produce components with flax fibers, claiming that the use of flax to replace synthetic fibers allows for a reduction of 85% in CO_2 emissions. Bcomp further declared its flax fibers to be carbon-neutral over their lifetime, with the biodegradable natural fibers used for thermal energy recovery at the end of life [127]; this could be explained by the plant fibers removing carbon dioxide from the atmosphere during cultivation, with a rate of 1.3 up to 14 kg CO_2 per kg fibers [160]. With the more widespread utilization of NFRP in components for the marine industry, more accurate calculations can be made regarding their carbon footprints, and more LCA studies can be performed to further reduce their environmental impact. Considering the multiple factors discussed so far in this analysis, NFs are generally much more sustainable than synthetic GFs and CFs, even by conservative estimates, with fewer non-renewable resources used, less harmful effects on the environment, a smaller carbon footprint generated, and all-around more sustainable. As the marine industry follows more complex models for LCAs of components and vessels [161–163], the incorporation of NFRP materials to design components for the marine industry is more likely, as NFRP can be utilized as materials to meet design-for-sustainability principles for product development [164].

2.4. Strategies to Improve Fiber/Matrix Adhesion

The two main challenges for the structural usage of NFRP composites are the variation in the mechanical properties of the natural fibers and poor interfacial adhesion with the matrix.

There have been many attempts to mitigate water absorption by removing the hydrophilic hydroxyl OH groups from the fibers' cell walls and cellulosic structures using various chemical and thermal treatments. Fiber treatment before manufacturing has been recommended by several authors for improving interfacial adhesion [91,165]. Treatments can remove impurities (and hydrophilic elements on the fibers, such as the hydroxyl groups discussed above), reduce fiber surface roughness, and improve the wettability of the fibers, all leading to improved fiber–matrix adhesion.

A critical issue affecting the interfacial adhesion in NFRP composites is the bonding between the hydrophilic natural fibers and the hydrophobic matrix [166]. Chemical treatments and coupling agents are utilized to reduce the hydrophilic nature of the fibers and improve bonding between the cellulosic fibers and polymeric matrices [62].

The optimization of chemical treatment processes to minimize moisture absorption and improve mechanical properties can lead to NFRP being more competitive with GFRP and CFRP performance for marine components.

The more common treatments are described below.

2.4.1. Alkaline Treatment

The process of alkaline treatment, also termed mercerization, is a common chemical treatment for natural fibers prior to composite manufacturing [167–173]. The alkalization process is performed by immersing the fibers in an aqueous sodium hydroxide (NaOH) solution, and the fibers are then washed using distilled water and then dried to remove moisture [174]. The process removes lignin, hemicelluloses, and organic waxes and oils on the individual fibers' cell wall surfaces [175], in turn improving surface roughness and increasing the fiber surface area for bonding [62]. The treatment also chemically alters the cellulosic structure of the fibers, changing the crystalline cellulose order and forming an amorphous region that helps to remove moisture from the fibers.

The concentration of the alkaline solution is important, as a higher concentration of the NaOH solution could lead to fiber degradation due to excess delignification, which will decrease the mechanical properties [68,175,176]. However, using an optimal concentration of the alkaline solution could improve mechanical properties such as tensile and flexural strength and stiffness and impact resistance [66,177,178].

Fiore et al. [179] investigated how a 10% sodium bicarbonate solution can affect the mechanical properties and aging resistance of NFRP composites in a marine environment. The composite samples used flax and jute fibers reinforced in an epoxy matrix. Flax samples were shown to retain their flexural properties better with the treatment in salt-fog conditions expected in a marine environment, and less maximum water absorption was measured at saturation. The treatment reduced the jute samples' flexural properties, increased the deflection at break, and increased the water uptake percentage at saturation, with the authors commenting that the treatment had a slightly worsening effect on the jute composites' durability.

Chethan et al. [68] investigated the mechanical properties of treated hemp/epoxy in a marine environment. The hemp fibers were treated with alkaline treatment, a 5% Potassium Hydroxide (KOH) solution, and the hemp/epoxy composite laminates were manufactured by compression molding. The composite samples were immersed in natural seawater for 150 days at room temperature. Tensile properties, flexural properties, and moisture content were analyzed in samples with and without alkaline treatment. The alkaline treatment was shown to make little difference in moisture absorption, but it also deteriorated tensile and flexural properties. Untreated dry samples showed tensile strength and stiffness of approximately 36.5 MPa and 0.855 GPa, respectively, and after 150 days of seawater immersion, the tensile strength and stiffness decreased by 13.7% and 10.5%, respectively. For dry alkalized samples, the tensile strength and stiffness were found to be around 32.2 MPa and 0.754 GPa, respectively, decreasing by 28% and 9.7%, respectively, after seawater immersion. Untreated dry samples also had better flexural strength at around 84 MPa compared to 64 MPa for alkalized samples, with both untreated and treated samples showing a reduction in flexural strength of 17% and 22%, respectively. The better mechanical properties for untreated samples were explained by the high concentration of the alkaline solution used for fiber treatment, which decreased fiber/matrix interphase adhesion, with SEM (Scanning Electron Microscopy) imaging confirming this conclusion. The strong alkaline solution reduced the fiber surface roughness by removing lignin and hemicelluloses, thus affecting fiber interlocking with the matrix compared to untreated samples. Chetan et al.'s research showed the importance of optimizing the treatment's solution concentration and process for different NFRP composites.

2.4.2. Silane Treatment

Silane compounds are hydrophilic silicon-based coupling agents that improve bonding between the fiber surface and the matrix [176]. Silane coupling agents reduce the hydrophilic hydroxyl OH groups on the fiber surface and serve as a chemical link between the hydrophilic fiber and the hydrophobic matrix.

Vigneshwaran et al. [180] tested the hardness and erosion resistance of jute/polyester composites using alkaline and silane treatments. Samples undergoing both treatments showed the minimum erosion rates and improved hardness.

Sepe et al. [166] compared the effect of alkaline and silane treatments on hemp-fiber-reinforced epoxy composites, commenting that alkaline treatment removes lignin and hemicelluloses from the fiber surface, leading to easier fiber pull-out (fibrillation), consequently reducing the tensile strength of the composite samples. Meanwhile, silane-treated samples showed tensile stiffness and flexural strength compared to untreated samples and caused less reduction in tensile strength compared to alkaline-treated samples. Silane solutions with 1%, 5%, and 20% concentrations were tested, with the 1% concentration silane solution used for fiber treatment producing samples with better mechanical properties. Figure 8 shows SEM images of alkaline- and silane-treated fibers, both using a 5% solution.

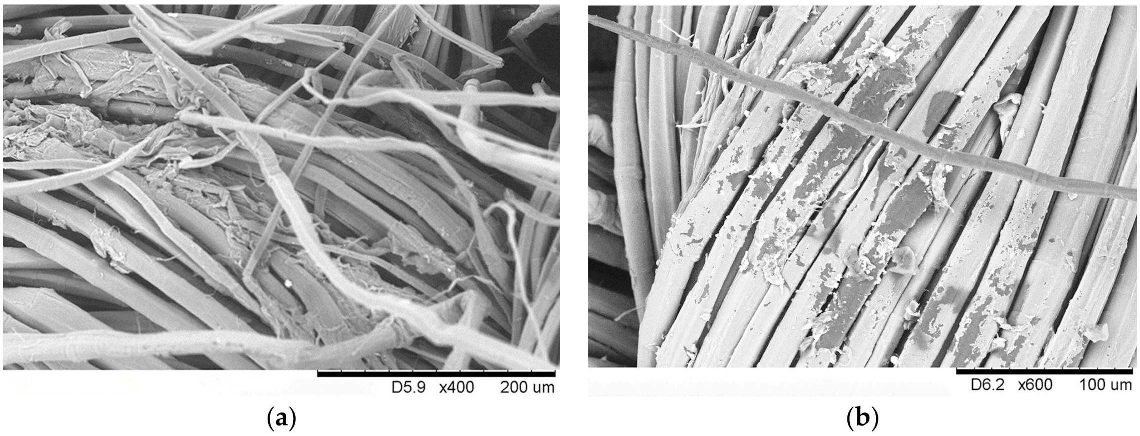


Figure 8. SEM images of hemp fibers treated with (**a**) 5% alkaline solution; (**b**) 5% silane solution [166].

For jute-reinforced epoxy composites, Seki [181] reported that silane treatment using a 1% concentration solution improved flexural properties by 11% and 7% for strength and stiffness, respectively, compared to alkalized samples. Jute-reinforced polyester composite samples' flexural properties showed 20% and 7% higher strength and stiffness, respectively, compared to their alkalized counterparts. The tensile properties of silane-treated samples were further improved relative to alkaline-treated samples, with tensile strength being 22% and 24% higher and tensile stiffness being 8% and 10% higher for epoxy and polyester composites, respectively. Sever et al. [182] tested 0.1%, 0.3%, and 0.5% silane solutions for treating alkalized jute/polyester composites, with the 0.3% solution shown to be the optimal concentration, improving the mechanical properties of tensile strength, flexural strength, and interlaminar shear strength by around 40%, 30%, and 55%, respectively.

2.4.3. Acetylation

Another approach using chemical treatment is the esterification of the hydrophilic hydroxyl groups using acetylation treatment. Acetylation removes moisture from the fiber surface; removes waxes, hemicelluloses, lignin, and other impurities; and reduces fiber surface roughness, allowing for better mechanical bonding. These effects all serve to increase interfacial adhesion, improving mechanical properties [62,183].

El Boustani et al. [184] used an environmentally friendly solvent-free acetylation process for treating flax/epoxy and flax/wood fiber/epoxy composites, improving interfacial adhesion, reducing fiber roughness, and improving wettability at the expense of slightly reducing tensile properties and possible fiber damage at high acetylation levels.

Bledzki et al. [185] showed that acetylation increases the tensile and flexural strength of flax/polypropylene composites at up to 18% acetylation; however, the impact strength decreased with the increasing level of acetylation. They also discovered that the addition of malleated polypropylene increased tensile and flexural properties by 20 to 35% according to the level of acetylation. The acetylation treatment of flax fibers was also reported to have reduced moisture absorption by up to 50%.

2.5. Hybridization Strategies (Synthetic/Natural Reinforcement)

As discussed in the previous sections, the economic and environmental appeal of NFRP composites for a circular economy is becoming too difficult to ignore in manufacturing composites for sectors such as the marine industry, but the issue with developing composite structures fully reinforced with natural fibers persists due to natural fibers' lower structural mechanical properties in comparison with synthetic fibers, the variability of such properties, and most critically, for marine environment applications, the hydrophilic nature of natural fibers. To overcome the technical disadvantages of natural fibers and, on the other hand, the environmental disadvantages of synthetic fibers, hybridization is being introduced as a possible solution. Hybridization in this section refers to the inclusion of more than one type of reinforcement in the composite material, usually merging glass fibers (or less commonly carbon fibers) and natural fibers, aiming at combining the advantageous properties of natural fibers (NFs) (such as their environmental benefits and damping characteristics [186,187]) with the favorable mechanical properties of synthetic fibers [91,188]. In addition, there are also some chemical and physical advantages specific to the marine environment that hybridization can improve, such as resistance to fire, corrosion, fungus, microbial degradation, and aqueous delamination [189].

Hybridizing hemp with glass fibers was found to significantly improve the mechanical properties of the composite laminates, especially in terms of impact strength, showing the potential of this process [126]. The combination of two types of natural fibers has also been researched to maximize the advantages of the two types of natural fibers, although this can lead to further deterioration of mechanical properties due to water absorption in some cases.

Fiore et al. [190] analyzed the dynamic properties (storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$)) of flax, jute, and their hybrid composites after exposing them to salt-fog conditions for 30 and 60 days. The natural fibers were treated with sodium bicarbonate ($NaHCO_3$) prior to the composite samples being manufactured by vacuum-assisted resin infusion. All samples had a decrease in the storage modulus and glass transitions temperature and an increase in the loss factor proportional to the salt-fog exposure period and moisture content. The sodium bicarbonate treatment was shown to help flax fibers retain their damping properties while not affecting jute fibers. A similar study by Fiore and Calabrese [191] investigating glass, flax, and their hybrid composites, under the same salt-fog exposure conditions and for the same length of time, analyzed the mechanical properties and durability of the composites and their suitability by performing pinhole bearing tests using a steel pin. Different geometrical configurations were investigated with variation between the hole diameter (4–10 mm) and edge distance (2–20 mm), for a total of 30 different joint configurations that were investigated with 270 samples. The flax samples showed a significant bearing strength decrease of around 29%, double that of the glass samples, which had a reduction of 14%. The hybrid samples had a less severe bearing strength reduction of around 20% with the inclusion of glass fibers. The bearing fracture failure modes were also influenced by the inclusion of glass fibers in the laminate. With the increase in exposure to salt-fog conditions, the flax samples showed catastrophic fracture by shear-out and net-tension modes, showing poor durability and mechanically unstable behavior. Such premature fracture behavior is undesirable for mechanical joints [192]. The glass samples' exposure period had a minimal effect on the fracture modes. For the flax/glass hybrid samples, the inclusion of glass skins on the outer surface of the laminate decreased water diffusion, limiting the causes of the bearing strength decrease, such as reducing the fiber–matrix interfacial adhesion and the matrix stiffness [193]. The result is the non-catastrophic, progressive failure of the hybrid composite bearing, which is more desirable in design and application than catastrophic modes of failure [194,195]. The hybrid samples also had a lower rate of bearing strength deterioration with salt-fog exposure in comparison with flax samples.

Another possible hybrid configuration is the combination of natural fibers and wood reinforcement for a composite laminate exposed to the marine environment. Valencia et al. [196] constructed a Fiber–Wood Laminate (FWL), inspired by fiber/metal laminates. The FWL consisted of two thin pinewood veneer layers on either side of a three-ply flax-reinforced bio-epoxy laminate. The laminate was manufactured by vacuum resin infusion, with several holes drilled on the lateral side of the wood layers to ensure resin infusion in the vertical direction, with a net bleeder placed over the peel to ensure in-plane resin infusion. A five-ply flax-reinforced laminate was manufactured with the same matrix and resin infusion method for comparison. Flexural testing found the FWL to have an increase in flexural strength and stiffness of 41% and 28%, respectively, compared to the pure-flax-reinforced samples. Impact testing found the FWL to compare unfavorably to the flax composite, reducing the peak force, penetration, and perforation energy thresholds by around 30%. The authors recommended using thicker wood layers to improve the impact properties, as 0.5 mm thick wood layers were used, 50% less than the flax fabrics' 0.75 mm. The effects of seawater immersion were also investigated. The samples were immersed for 6 months between April and October, the peak period for marine bioactivity in the Cantabrian Sea north of Spain, with the samples clamped at the edges to avoid water absorption by the exposed fiber ends. The conditions were sought to simulate those experienced by a ship hull. All composite samples experienced discoloration due to photo-oxidation. The flax samples' thickness increased by 2.6%, while the FWL had a negligible increase in thickness. The epoxy matrix had effectively impregnated the cellular structure of wood during the resin infusion process, making the wood layers an effective barrier to water absorption by the flax fibers. The results are encouraging for further research to optimize the thickness of the wood layers and the FWL laminate layup and orientation to improve mechanical properties.

Hybrid carbon and natural fiber composites have also been developed for different applications, including utilization in a marine environment, as will be discussed further in the Applications section. In a case study analyzing the mechanical properties of a carbon/flax hybrid, Zouhar et al. [197] researched replacing carbon-fiber-reinforced parts of an electric surfboard with a hybrid carbon/flax twill and biaxial fabrics to improve the damping of noise and vibration from the electric engine. Zouhar et al. first tested tensile properties for different flax, glass, carbon, and carbon/flax reinforcements, obtaining the stress–strain curves shown in Figure 9. Carbon fiber had the most favorable tensile properties, followed by the carbon/flax hybrid, while both glass and flax biaxial samples had notably similar curves. The carbon, glass, flax, and carbon/flax hybrid samples were then subjected to tensile and flexural tests in a humid environment, and vibration damping was analyzed for the samples with the engine operating at its maximum setting of 7200 RPM. It is important to mention that the test was performed in a closed room while the watercraft was not on the water, possibly affecting the vibration-damping results. The results showed the carbon/flax parts to reduce noise and vibrations in comparison to pure- carbon-reinforced parts. The frequency response function measurement was found to be 50% lower for the carbon/flax part compared to the carbon-reinforced part. The carbon/flax twill composite sample was found to retain 72% tensile strength and 60% flexural strength of the pure carbon fiber samples, significantly higher than both flax and glass samples, which were all lower than 35% of the carbon fiber samples' properties. After humidity conditioning, the hybrid and flax samples were compared for tensile and flexural strengths. The flax samples showed minimal changes in tensile strength, with the carbon/flax sample's tensile strength decreasing by 28% with humidity conditioning. The flexural strength of the carbon/flax sample decreased by 40%, significantly lower than that of flax samples, which lost up to 64% of their flexural strength.

Cheng et al. [198] also looked at thermoplastic polypropylene composites reinforced with carbon/flax hybrids with carbon or flax plies on the outer surface, as well as a pure- flax-reinforced laminate. The samples were exposed to hygrothermal treatments with prolonged water immersion at an elevated temperature, for 289 h at 60 °C. Water absorption, tensile, and flexural properties were analyzed. Having the carbon layers on the outside was found to reduce the moisture mass absorption to 15.8%, compared to 18.4% when having flax on the outside and 21.8% with only flax reinforcement. The inclusion of carbon fibers significantly increased the tensile and flexural properties and reduced their deterioration after hygrothermal conditioning in comparison to the flax samples. The samples having carbon on the outside contained three carbon plies, which led to significantly better mechanical properties compared to the samples having flax on the outside and containing only two carbon plies. All three laminates had five plies of fiber reinforcement.

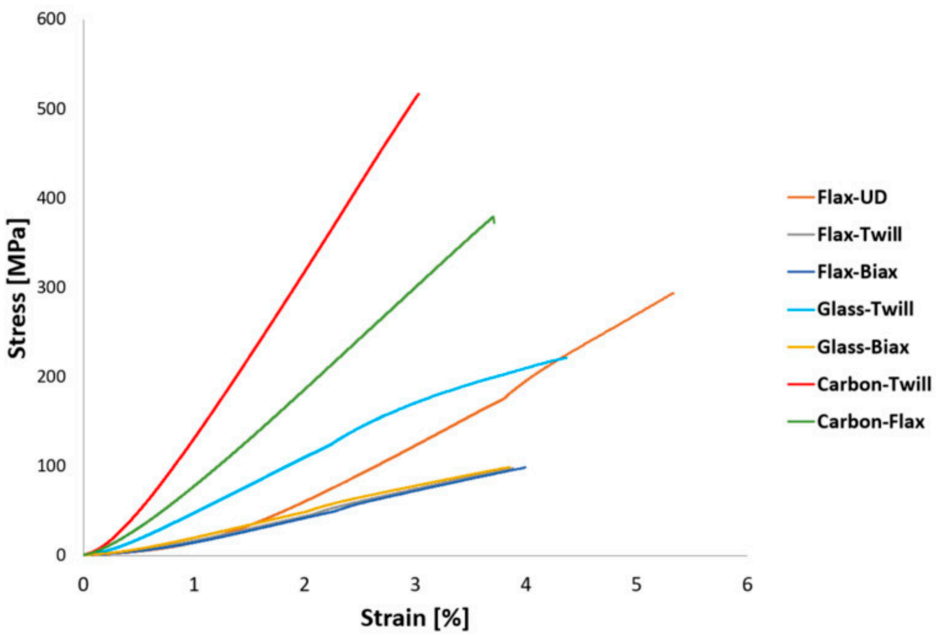


Figure 9. Tensile test stress–strain curves comparing different flax, glass, carbon, and carbon/flax fiber reinforcements [197].

Carbon and hemp hybrid composites were also considered for marine applications. One of the useful functions of CF/NF hybridization is combining the impressive strength and stiffness properties of CF with the interesting damping and impact energy absorption mechanism that limits damage propagation [199]. Flexural, interlaminar shear stress (ILSS), damping, and impact tests were performed to analyze the failure modes of the laminate for different layups. The results showed that placing hemp layers in the middle of the laminate could improve the flexural modulus to almost the same value as that of the pure CF while having different failure mechanisms that allow for damage propagation within the limit, unlike the more brittle failure of CF. Low-velocity impact (LVI) tests also showed that hemp layers in the middle of the laminate absorb a similar amount of energy to the pure CF samples. Placing hemp layers higher in the laminate (closer to the impact surface) resulted in a larger damage area but greater energy absorption for the hemp layers, reducing the propagation of internal damage through the laminate by 40% for the 10 J impact, thus showing that tailoring carbon/hemp composites could control composite failure modes and reduce damage propagation. Boccarusso et al. [200] further analyzed carbon/hemp hybrids for structural applications by optimizing sandwich panels using hemp grids as the core for damage propagation, and they found that using a low-density hemp grid for the core resulted in relatively ductile behavior with large deformations compared to the high-density core (double the number of hemp tows per unit area), which resulted in a stiffer, more brittle response. LVI tests also showed the low-density core samples to be more efficient at dissipating impact energy, as illustrated in Figure 10, which shows energy absorbed per energy level for low-density and high-density samples.

Figure 11 shows the failure modes of both low-density (LD) and high-density (HD) hemp core samples after being impacted at 10, 25, and 45 J impact energy levels, with evident crack propagation found as a result of the composite skin failure, but also skin-core debonding due to poor interfacial adhesion. The low-density core samples also had larger deformation areas and a more elastic response, while the more rigid high-density samples showed a stiffer response with skin–core debonding. The high tailorability of these hybrid materials to control mechanical properties and failure modes is interesting for structural marine applications.

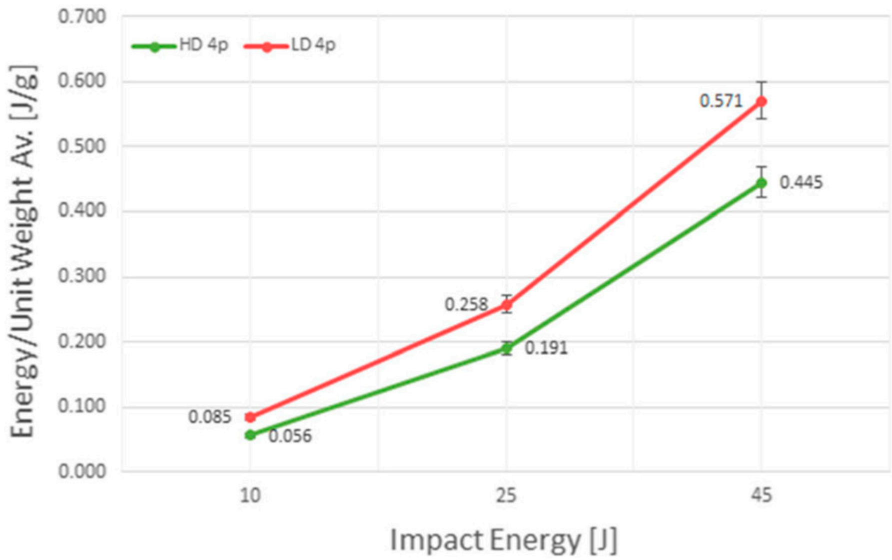


Figure 10. Energy absorbed per unit of weight for 3 energy levels, 10, 25, and 45 Joules, in low-density (LD) and high-density (HD) hemp core samples [200].

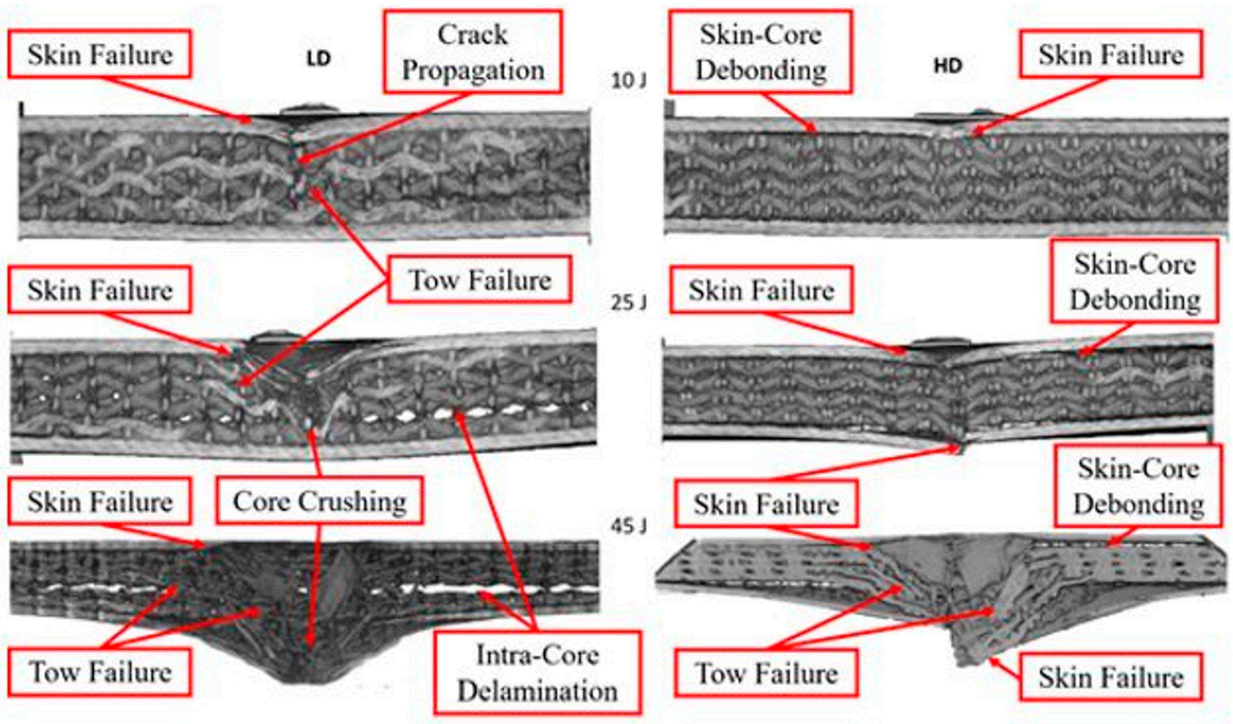


Figure 11. CT scan results for low-density (LD) and high-density (HD) hemp core samples impacted at 10, 25, and 45 J [200].

3. Matrix Selection Criteria for NFC in Marine Applications

Matrices for FRP composites used in the marine environment are required to have not only good mechanical properties but also good thermal properties and, more importantly, limited water absorption. For manufacturing purposes, matrices are also required to be easily processed and laminated, possibly with processes that allow room-temperature curing, with the ability to be repaired swiftly and easily after manufacturing [9]. Furthermore, the chemical structure of the matrix is an influential factor for compatibility with the fibers [62], as well as for water absorption throughout the composite laminate, with the crystallinity and orientation of the molecules in the polymeric matrix also being highly influential on the moisture absorption rate [65]. Indeed, the maximum moisture content $M\%_{max}$ varies with different polymeric matrices [64,201], as indicated in Table 3 below.

Table 3. Polymeric matrices. Data from Summerscales [201] and Colin and Verdu [64].

Matrix Type	Examples	Water Weight Percentage
Non-hydrophilic	Polyethylene, polypropylene, polytetrafluorethylene, Polydimethylsiloxane.	<0.1 wt%
Moderately hydrophilic	Polyethylene, polycarbonates, polyesters	<3 wt%
Strongly hydrophilic cured network polymers	Amine-cured epoxies	<7 wt%
Strongly hydrophilic crystalline thermoplastics	Polyamides	<10 wt%

As explained in the previous section, natural fibers are highly hydrophilic due to the presence of hydroxyl groups, which can be removed by several chemical treatments. Some matrices can be highly hydrophilic as well, as shown in Table 3, and just as natural fiber selection is critical, matrix selection is also important to ensure that the resultant composite's mechanical properties do not deteriorate when exposed to high moisture concentrations, as expected in a marine environment.

3.1. Polyester

Polyester is a polymer commonly used in boat manufacturing in conjunction with glass fibers for boat components such as decks and hulls [202]. Polyesters have also been used with other fiber reinforcements and with hybrid natural–synthetic reinforcements, such as wood/glass hybrids, where they can be applied as an adhesive layer to limit water absorption [203]. There are also examples of hybrid GF/NF/polyester composites in boat manufacturing, such as the boat made by Misri et al. [204], which is discussed later in the Applications section. Multiple authors have analyzed the mechanical properties of NF/polyester composites in the literature. Dhakal et al. looked at moisture absorption's effect on the performance of hemp/polyester composites (as discussed in Section 2.1.1.). Shah et al.'s [100] work comparing the fatigue of different natural fibers with polyester was also previously discussed, as well as Vigneshwaran et al.'s [180] research on the erosion and hardness of jute/polyester composites. Lu et al. [81] compared the moisture absorption of flax composites and found similar moisture absorption rates with epoxy and polyester as matrices, while Seki [181] tested the effect of alkali and siloxane treatments on jute composites, also comparing epoxy and polyester as matrices. In this work, the author showed that, although jute/epoxy has better tensile, flexural, and shear properties compared to jute/polyester, chemical treatments can significantly improve jute/polyester's properties, leading to higher values of the tensile modulus (up to 1 GPa higher, although this was with a 7.5% higher volume fraction of fibers). Sever et al. [182] optimized the chemical treatment process for jute/polyester composites, as previously discussed in the silane treatment section (Section 2.4.2). The addition of nanofillers to the matrix can also improve the mechanical properties of NF/polyester composites, with examples in the literature that include nano-clay, carbon, or graphene [98].

Rouison et al. [205] also analyzed the moisture absorption of hemp/unsaturated polyester composites, exploring two moisture absorption scenarios: immersion in water or exposure to the air with an RH of 94%. The water absorption rate was found to be more dependent on the hydrophilic natural fibers in the longitudinal direction, with a diffusion coefficient β of 3×10^{-11} m^2/s compared to the polyester's 2.6×10^{-13}. Numerous authors have also looked at different, less common natural fibers combined with polyester in a marine environment. For instance, Nurazzi et al. [206] studied a hybrid sugar palm/glass-reinforced unsaturated polyester composite and found glass to increase the density but, at the same time, improve mechanical properties and reduce water absorption.

Sindhu et al. [207] studied the aging of coir/polyester and glass/polyester composites under water, acid, and seawater effects. Seki et al. [208] studied *Luffa cylindrica* (snake plant) fibers with polyester under seawater aging at an elevated temperature.

There are also thermoplastic polyesters such as polybutylene succinate (PBS), a semi-crystalline thermoplastic polyester formed by the polycondensation of 1,4-butanediol with succinic acid. Interest in natural-fiber-reinforced PBS composites has increased in recent years due to the possibility of producing PBS from bio-sources [35], its biodegradability, and its biocompatibility with natural fibers such as flax, which improves the interfacial adhesion of flax/PBS composites in comparison with flax/PP, flax/MAPP, and flax/PLA [209,210]. Furthermore, PBS also possesses high heat resistance, higher impact resistance, and higher elongation at break (nearly 200%) compared to PLA [211]. Such mechanical properties are desirable for applications in the marine sector.

3.2. Vinyl Ester

The mechanical properties of vinyl esters lie halfway between those of polyesters and epoxies [212]. Vinyl esters offer good resistance to chemical erosion, moisture absorption, and hydrolytic attacks, making them a favorable choice for boat hulls [9]. Boat hulls and decks using vinyl ester matrix composites show increased fatigue resistance compared to polyester [114].

A recent European research project termed FIBRESHIP tested the fire performance of laminates using different resins by measuring their time to ignition, heat release, and smoke production [213]. The phenolic resin system showed the best fire performance, followed by the vinyl ester resin system, leading to the vinyl ester system being chosen to manufacture laminates for the ship vessels in the project, owing to their better mechanical properties. The project also tested an acrylic resin (Elium), which showed the shortest time to ignition, an intermediate level of heat release, and low smoke production compared to the epoxy resin tested, which showed the worst performance, with a similarly short time to ignition but with relatively high levels of heat release and smoke.

Visco et al. [214] showed that glass/vinyl ester composites have better moisture resistance and mechanical properties in a marine environment compared to glass/polyester composites. However, the processing of vinyl esters is complex due to the processing conditions and the high level of toxic styrene involved, which are subject to increasingly stringent industrial regulations. Polyesters and vinyl esters are widely used by boat manufacturers to produce composite components, as they have good mechanical properties and good water resistance, are easy to laminate, and have a short curing time. However, they have high shrinkage (7–10%), which causes surface imperfections, and the high levels of styrene associated with using polyesters and vinyl esters necessitate proper ventilation systems to limit worker exposure to toxic chemicals [215].

Desnoes et al. [216] compared the mechanical properties of composites using traditional synthetic materials such as glass fiber and unsaturated polyester with more sustainable vinyl ester composites reinforced with microfibrillar cellulose at 1% and 2% weight filler contents. Petroleum-based vinyl ester was used along with a more sustainable bio-based vinyl ester made using cardanol, a phenol organic compound that is the main component of cashew nutshell liquid. Figure 12 compares the flexural properties of bio-based vinyl ester (BVE) and vinyl ester (VE) composites reinforced with microfibrillar cellulose (MFC), along with unsaturated polyester reinforced with 0.5–2% wt glass as a benchmark. MFC reinforcement increased BVE's flexural stress at break from 25 to 39 MPa and VE's flexural stress at break from 63 MPa to 88 MPa, while the flexural stiffness was increased with the addition of MFC from 2.2 GPa to 4.8 GPa and from 3.8 GPa to 4.9 GPa for BVE and VE, respectively.

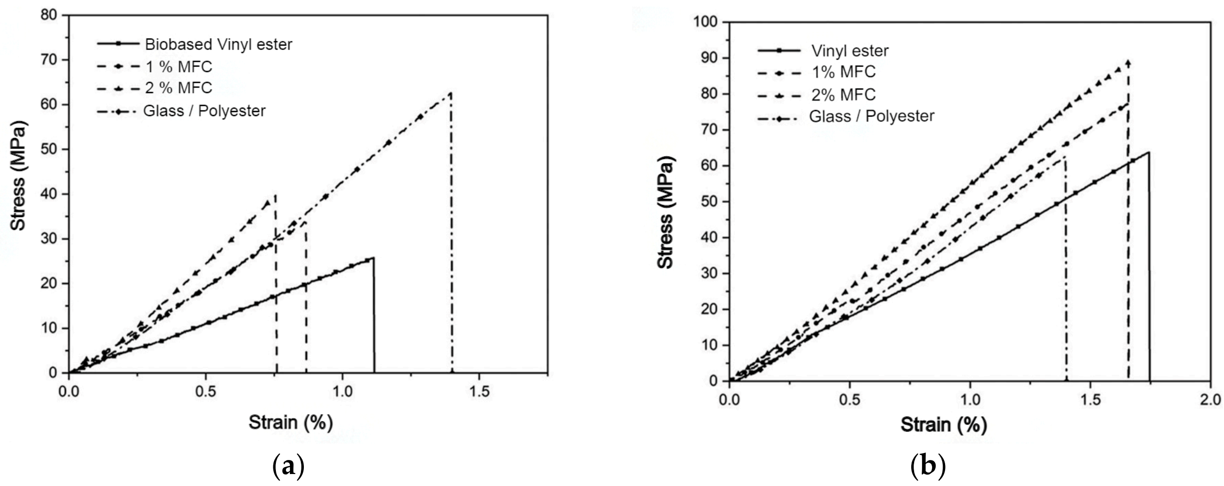


Figure 12. Flexural stress–strain curves of (**a**) bio-based vinyl ester; (**b**) petroleum-based vinyl ester [216].

3.3. Epoxy

As previously discussed, despite the advantages of polyester and vinyl ester resins for marine applications, their environmental credentials are poor due to high styrene emissions. Therefore, there is a shift toward using epoxy resin as a more environmentally friendly alternative in marine composite production in order to satisfy administration protocols in the United States and the European Union [114]. Epoxy is also one of the most widely used matrices in sea vessel manufacturing, along with polyester, due to its availability, processability, relative sustainability, and good mechanical properties. Cavalcanti et al. compared the tensile properties of epoxy and polyester composites reinforced with jute, jute/curauá, and jute/sisal natural fibers, finding epoxy samples to have higher tensile strength, while polyester samples had higher tensile stiffness, as shown in stress–strain curves in Figure 13. Natural fiber hybridization of curauá and sisal with jute was also found to increase mechanical properties [217].

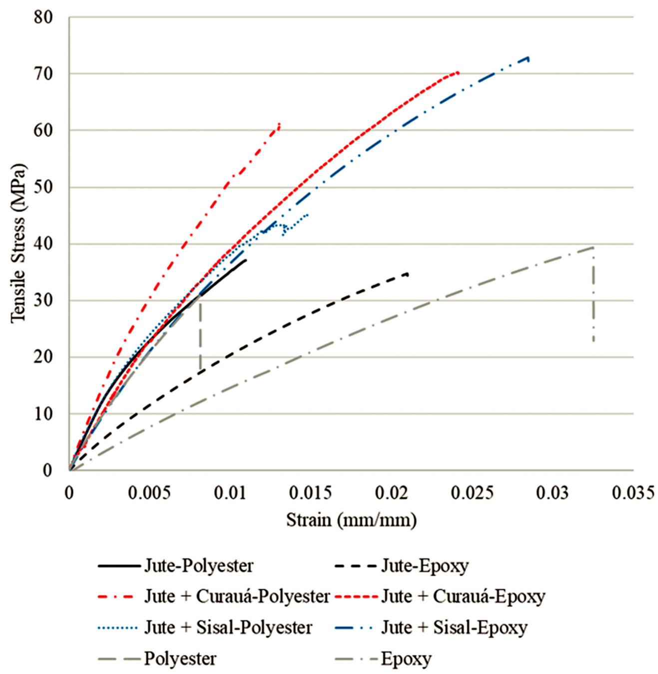


Figure 13. Stress–strain curves of jute/polyester with jute/epoxy, as well as jute/curauá/polyester and jute/sisal/polyester [217].

Some epoxy matrices can be developed from bio-sources, improving their sustainability and, consequently, the environmental credentials of the NFRP composite materials [218,219]. Water-based epoxy is possible to synthesize for usage in structural parts, as it has good mechanical properties in terms of strength and durability and low toxicity [220]. Epoxy requires a hardener to cure properly, like most thermosets, but the chemical hardener can also be derived from bio-sources [221], as shown in the work by Benega et al. [222], who studied the effects of bio-based hardeners made from cashew nutshell liquid on epoxy resin for marine applications. The bio-based hardener was compared to a conventional hardener for an epoxy resin system made for composite manufacturing using the infusion process. The results showed that when using the bio-based hardener, the stiffness of the final composite was not reduced, but at the same time, it was possible to reduce moisture uptake rate, thus especially encouraging its application for components that will be submerged in water for long times.

There are various marine applications that utilize epoxy resin as the matrix for NFRP composites. For example, Scouts Boats switched from polyester and vinyl ester to epoxy for manufacturing the largest yacht in its fleet, a 42-foot-long sport fishing yacht [215]. The epoxy resin was used in conjunction with the resin infusion process for a better surface finish due to epoxy having less shrinkage (less than 2%) compared to polyester and vinyl ester (7–10%) [9]. Lightweight boat and yacht manufacturers are increasingly using epoxy resin via resin infusion processes for easier, more adjustable, environmentally friendly processability with a better surface finish. This, along with the more favorable mechanical properties of epoxy, such as elongation, tensile strength, and stiffness, allowed for the production of lighter composite boat parts than those utilizing vinyl ester and polyester matrices, as the laminate can be produced with higher fiber content, and, therefore, the total thickness of the component can be reduced. Some epoxy matrices also have the ability to be cured at room temperature without autoclave curing [215]. Such simple processing for the composite material is critical for manufacturers, as it reduces manufacturing time, costs, resources, and hazards.

3.4. Polyamides

There is great potential for using some polyamide matrices for bio-based composites in the marine industry due to considerations related to cost savings and ecological concerns [223], even though some polyamides (PAs), such as PA6, PA 6–6, and PA 4–6, form some of the most hydrophilic linear polymers used in composites [64]. Indeed, polyamides suffer from hydrolysis during fabrication under high-moisture and high-temperature conditions; therefore, moisture needs to be greatly minimized during fabrication, for example, by adding a vacuum pump to the extruder to remove water vapor [224]. In one example, Vold et al. [225] used torrefaction at 400 °C for 30 min to remove moisture from the "biomass" flax shive and sunflower hulls and used them as fillers in PA6 composites. Torrefaction decomposes the hemicellulose and amorphous cellulose while gradually degrading the lignin and mildly degrading the crystalline cellulose [226]. Compared to pure PA6, the composite samples showed a decrease in water absorption of 50%, which led to an increase in tensile and flexural moduli of approximately 150%, but also to a decrease in the tensile and flexural strength of 30% and 6%, respectively. In a similar study, Sridhara and Vilaseca [227] reinforced PA6 with cellulose pulp fiber via melt-compounding and injection molding. PA6 was previously dried for 8 h at 80 °C to remove moisture. Tensile and flexural tests were performed under dry conditions, and samples were also conditioned at 50% relative humidity for 48 h. The results showed that the tensile stiffness for dry and conditioned samples was similar and proportional to the fiber content percentage, with the maximum at 25% fiber content being around 4.5 GPa. Similarly, the flexural properties also increased with the fiber content percentage, with the humidity conditioning reducing flexural strength by 6% and flexural stiffness by 18.5%.

3.5. Phenolics

Phenolic matrices are recommended for applications that need to comply with fire resistance standards [228,229], as they resist up to 200 °C while emitting minimal smoke and toxic fumes, satisfying requirements for fire hazard areas in ships. The main disadvantage of using phenolic matrices is, however, the absolute values of their mechanical properties, as in-plane properties are 20% lower compared to polyesters [9], even though they are not affected by high temperatures. Moreover, it is possible to improve the mechanical properties of natural-fiber-reinforced phenolic matrix composites, minimizing their water absorption and density and taking advantage of their fire resistance properties [230].

Choosing a matrix with good fire resistance that is compatible with natural fibers is a key consideration, as NFRP composites score the lowest on fire performance in comparison with other FRP composites due to the degradation of the natural fibers' chemical components, such as cellulose, hemicellulose, and lignin [231]. Natural fibers and the polymer matrix are usually both flammable, but they are both flammable at different temperatures and ignition rates, making it difficult to predict their combustion behavior [119,232].

Kashizadeh et al. [233] studied the mechanical properties and water absorption of date palm trunk fiber-reinforced phenolic matrix composites and found that alkaline treatment can halve the water uptake rate from 30% to 15%. The high rate of water absorption was attributable to the use of long fibers and also due to the fact that the date palm fibers obtained from the trunk of the tree were more hydrophilic than those obtained from other parts of the palm [234].

Li et al. [235,236] developed flax-fiber-reinforced phenolic composites, improving their flame retardancy by adding Dimethyl Methyl Phosphonate (DMMP), a widely used phosphorus-containing flame-retardant material, regarded as being a low-smoke, low-toxicity flame retardant. However, the addition of such flame retardants to natural fiber composites can decrease mechanical properties, as DMMP can increase water absorption due to the hydrophilicity of the material while simultaneously decreasing fire retardancy [237]. A solution was found by adding nano-montmorillonite (MMT) particles to the phenolic matrix. This reduces water absorption by decreasing DMMP precipitation within the composite, thus improving the fiber–matrix interfacial adhesion and enhancing mechanical properties. The addition of MMT also increased fire retardancy by forming more carbonization layers in the composite.

3.6. Hybridization Strategies (Matrices/Nanoparticles)

As seen in the previous paragraphs, along with choosing a suitable matrix to minimize water absorption and optimize mechanical properties, another possible method to maximize NFRP performance in a marine environment is the addition of nanoparticles. An example is represented by the study by Alamri and Low [238], who added different concentrations of nano SiC particles to recycled cellulose fiber/epoxy composites to reduce water absorption and improve mechanical properties. The results showed that after being immersed in water at room temperature for about 133 days, the sample with the inclusion of SiC particles positively affected the maximum water absorption rate $M\%_{max}$ of 23.28, and the addition of higher concentrations of SiC decreased $M\%_{max}$ proportionally, with a minimum value of 12.23%. Nano SiC was found to improve the interfacial adhesion between fibers and the matrix.

However, the addition of engineered nanoparticles (ENPs) is accompanied by a caveat, as their harmful environmental effects and toxicity to fish and other biological organisms in natural aquatic environments need to be considered. Nanoparticles can be transformed into different forms in a marine environment via processes such as dissolution, agglomeration, aggregation, absorption, and chemical reactions. After transformation, the toxic nanoparticles can be internalized by fish through dietary consumption or respiration, leading to harmful effects on fish in a natural aquatic environment not accustomed to such particles. Therefore, nanoparticles in a marine environment need to be considered with caution in regard to their quantity and ecotoxicity in a marine environment [239].

The material selection process for the composite has been discussed, involving the natural fiber reinforcement, the chemicals used for its treatment, matrices suitable for binding the fibers, and some additives and fillers used in the matrix to improve properties. After the materials have been chosen for the suitable application, the manufacturing processes for the composite materials will be discussed.

4. Processing of NFC in Marine Applications

As discussed in part 1 of this review, both fiber volume fractions and laminate layups influence the rate of water absorption and, therefore, the mechanical properties of the final composite material. Indeed, the orientation of each layer (and the mismatch between consecutive layers) needs to be optimized to limit water absorption since natural fibers absorb moisture along their length and expand radially with water absorption, affecting fiber–matrix adhesion. Similarly, the manufacturing methods used to produce the final part will also affect moisture absorption and therefore will be discussed in this section, analyzing some of the processes that natural fibers undergo from their cultivation, all the way to the specific technologies used for the preparation of the final composites.

4.1. Natural Fiber Processing from Plants

The first processing parameter that influences natural fibers is the cultivation and extraction of the fibers from the plant, as previously shown in Figure 6. The process of extracting fiber bundles from flax/hemp plants is called retting, a complex procedure that highly influences the mechanical properties of the final fibers. Traditionally, retting takes place in the field as a natural biological process that separates the fiber bundles from non-cellulosic materials thanks to enzymes produced by bacteria and fungi [240]; nonetheless, this process can be optimized to improve fiber quality and production, thus reducing the costs and carbon footprint [241].

Mazian et al. [242] analyzed the upstream processing parameter of field retting for hemp fibers and studied how the process can impact the mechanical properties of the consequent NFRP composites. Increasing the duration of field retting was found to improve the tensile properties of the fibers, owing to the increase in cellulose content and its crystal structure as a result of microorganisms such as fungi and bacteria producing enzymes that alter the biochemical structure of the fibers during the field retting process. The optimal duration for field retting in this study was found to be 5 weeks when harvested at the flowering stage in summer conditions. The retting duration was also found to be influential on properties such as color, fiber morphology, and thermal stability. Further research is recommended on the effect of the retting duration, considering different natural fiber types and varieties, and different weather conditions, considering geography, temperature, humidity, etc. This will contribute to the ongoing improvement of the natural fibers' mechanical properties. Furthermore, it could pave the way for more consistency in the natural fibers' morphology, dimensions, and mechanical properties, which are some of the main reasons for their utilization in industries such as the marine industry, as natural fibers are notorious for having variable properties based on their varieties and harvesting conditions.

4.2. Composite Production Processes

After having analyzed the influence of retting on the performance of the final natural fibers, it is now important to analyze the manufacturing process used for producing the actual composite component and its key parameters and consider how to improve its performance and mechanical properties while reducing moisture absorption.

It is worth noting that, owing to the high sensitivity of natural fibers to moisture, the absorbed moisture must be controlled before processing to avoid defects in the composite, such as pores and low adhesion between fibers and the matrix. Therefore, in contrast to synthetic fibers, NFs must be thermally treated in a climatic chamber to remove the moisture content. For example, Prasad and Sain thermally treated hemp fibers in an inert atmosphere at 180 °C, above lignin's glass transition temperature, causing lignin to migrate to the surface of the fiber, which improves hydrophobicity, and opening up fibers in both the length and width directions [243]. Thermal treatment in an inert environment was found to increase the tensile properties of strength and stiffness, possibly due to the opening of the fibers increasing the fiber count and decreasing the fiber diameter. In contrast, thermal treatment in the presence of air was found to decrease strength due to the oxidation of fibers. Another form of thermal treatment for NFs is steam explosion, where steam is employed at a similarly elevated temperature to separate fiber bundles into smaller cleaner fibers with rough surfaces [244]. Steam explosion (STEX) can take place in the presence of various chemical agents to simultaneously chemically and mechanically treat natural fibers such as hemp [245] and flax [246].

Van de Velde and Kiekens [247] studied flax/polypropylene laminates manufactured using compression molding with variations in processing parameters such as time, temperature, and MAPP treatment. In addition, the experimental campaign also included the inclusion of different flax fabrics obtained from fibers that were subjected to different retting processes, such as normally retted, boiled, and bleached. The fiber orientation effect was also studied, along with the needle-punching effect on the fabric. The results indicated a processing temperature of 190–200 °C for the fibers and identified the use of boiled flax treated with MAPP as the best combination of materials and processes to optimize the final mechanical properties.

Another important factor is constituted by the fact that NFRP manufacturing processes are highly reliant on processing temperatures, as cellulose, the main component of natural fibers, decomposes in air at 200 °C [248]. Indeed, while significant weight losses of around 70% are reported at over 220 °C, color changes are also reported at 180 °C [165,249]; therefore, the temperature and environmental conditions such as air exposure need to be carefully monitored during fabrication.

In terms of the manufacturing process, there are still multiple marine structures that are manufactured via hand layup. This process is regarded as the simplest and earliest method in manufacturing composite components for the marine industry, producing composite laminates as well as sandwich panels that can be suitable for boat hulls or other small components [91]. Hand layup is carried out in a mold that is cleaned and waxed, and then the resin is poured over the reinforcement fabrics and rolled over so that it spreads the resin, after which increasing the pressure, temperature, and catalyst content can be used to optimize curing, depending on the matrix used [176]. Although hand layup is simple and cost-effective, there are some drawbacks, such as inhomogeneities throughout the laminate, a low fiber fraction, and a high concentration of voids, which increases the water absorption rate [65].

While wet layup is still used for small, low-cost marine applications, when good mechanical properties are required, RTM is often regarded as the most efficient process to produce large composite parts with high fiber volume fractions, a requirement that is expected for large structural marine components [250,251]. Indeed, one case study investigated the mechanical properties of a composite laminate for a high-speed boat using hand layup and RTM, finding a 45% higher thickness efficiency for RTM compared to hand layup [252].

A cheaper alternative to closed mold processes such as RTM is resin infusion under flexible tooling (RIFT) [253] or vacuum-assisted resin transfer molding (VARTM) [254] due to simpler cost-effective tooling and lower styrene emissions [255]. Indeed, RIFT is gaining traction as a favorable RTM variant for manufacturing complex structural composite parts due to the replacement of the upper solid mold tool with flexible vacuum bags [256]. A diagram showing the RIFT process is shown below in Figure 14.

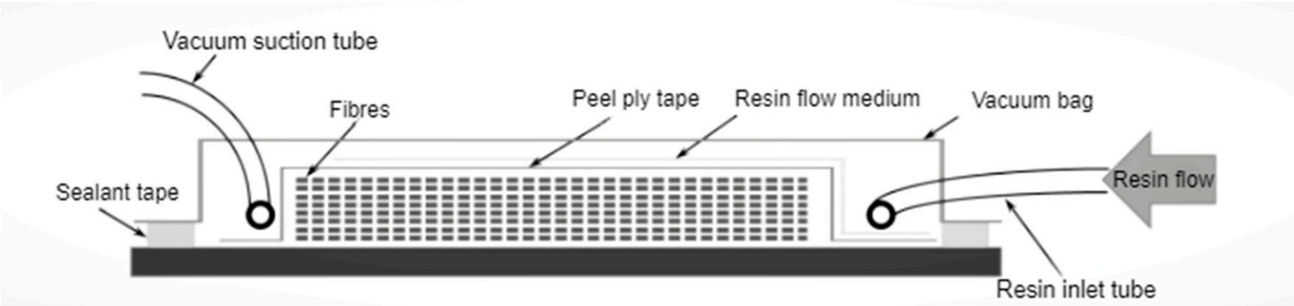


Figure 14. Schematic of resin infusion under flexible tooling (RIFT) [117].

The laminate sealed on the top face by vacuum bags is able to be visually inspected, leading to a more efficient resin infusion process with low void defect rates and reduced thickness variability across the laminate [257]. There are several RIFT processing parameters that can produce higher-quality composite parts, such as fiber preform permeability, temperature, resin injection point locations, and the materials used [258].

RIFT is mainly used for thermoset resin composites; however, for sustainable marine composites reinforced with natural fibers, a thermoplastic matrix is more desirable due to its repairability, cost, and environmental credentials [259]. A modified version of RIFT, Monomer Infusion under Flexible Tooling (MIFT), was proposed by Qin et al. as a manufacturing process to integrate a more sustainable thermoplastic matrix utilizing the highly efficient, cost-effective RIFT method [117]. They proposed a solution involving in situ polymerization by MIFT, considering various monomers to acquire the best solution for marine composites. They considered parameters such as the processing temperature, process open window, monomer viscosity, mechanical properties, moisture absorption, cost, bio-based availability, and recyclability. The monomer selection process proposed a number of options, such as a commercial acrylic resin, although not commercially available in bio-based form yet, and PLA, although requiring a relatively high processing temperature and having issues with durability.

5. Applications of NFC in Marine Applications

The analysis of processing parameters and the optimization of the manufacturing process will improve NFRP performance in the marine environment. Such optimizations in the manufacturing process, along with strategies to limit moisture absorption and improve mechanical properties, could lead to the utilization of NFRP materials for various applications. However, each application requires a different set of mechanical properties and different responses from the material. The most prominent applications in a marine environment for NFRP composites are the construction of components in sea vessels. However, there are various other possible applications that NFRP composites can expand to; some of these applications will be discussed in this section.

5.1. Boat Hulls

Several types of natural fibers have been used around the world to manufacture components for sea vessels, such as boat hulls, decks, and sail masts. The natural fiber selection process tends to rely on the geography and the natural fibers available, as discussed before, along with the mechanical properties, costs, and environmental suitability.

Corradi et al. [260] manufactured and tested a 6 m boat hull and a spinnaker pole using natural bamboo fibers. The bamboo fibers were made using bamboo strips and tested for mechanical properties. Composite laminates were then manufactured with epoxy resin, using both compression molding and vacuum bagging processes, and different pressures to analyze the most favorable processing methods. The samples were then subject to tensile tests, which found high-pressure compression molding to decrease the stiffness of the samples. For the flexural and environmental tests, sandwich panels were made using balsa as a core. The sandwich panels were subjected to water absorption and accelerated weathering tests, which found the composite to have good resistance to the marine environment, even though marine applications would require further treatments to exposed and submerged parts. The ILSS of the bamboo was found to be over 3.5 MPa without any chemical treatment, which is an encouraging figure for its utilization as a sandwich skin. The spinnaker pole made from the bamboo laminate was subjected to compression tests and then later achieved a compressive stress of 70 MPa. Samples of the bamboo sandwich panels were tested for their performance in the boat hull, and flexural and impact tests found the mechanical properties to be comparable to traditional boat hull materials. Subsequently, the complete 6 m boat hull was analyzed for critical lamination points, vacuum bagging efficiency, and final surface finish, as shown in Figure 15.

Figure 15. Complete 6 m bamboo composite boat hull [260].

In another case study, Collotta et al. [115] analyzed the manufacturing of a racing boat hull made using natural flax fibers, epoxy resin, and a cork core to make sandwich panels. The sandwich skin layers were a four-ply flax laminate infused with epoxy and then placed on the cork core to cure for 24 h at room temperature. The samples were subjected to tensile and flexural tests. The tensile tests found lower stiffness compared to glass-fiber-reinforced samples, although similar specific stiffness values were observed for glass fiber laminates with a similar stacking sequence. The elastic moduli were measured to be 1140 $\pm$ 40 MPa for the sandwich panels and 4800 $\pm$ 300 MPa for the laminate skins, while the bending stiffness was measured to be 1860 $\pm$ 150 MPa for the sandwich panels. The flexural tests caused the cork core to fail, although the outer flax skins did not. Thus, other core options should be explored for the sandwich panels. An FEA analysis was then performed to examine the boat's performance in racing conditions and found the performance to be comparable to similar boats made from other composite materials, with a 28% cost reduction for the boat made from the more sustainable NFRP composite material. A skiff prototype was unveiled in Brescia using the sandwich panels, as shown in Figure 16.

Figure 16. Skiff racing boat, 4.6 m long, in Brescia, Italy [261].

Misri et al. [204] made a boat from a hybrid glass/sugar palm layup with an unsaturated polyester matrix using the compression molding method, as shown in Figure 17. Using the hybrid laminate reduced the usage of glass fiber by 50% and reduced the boat's weight as a result; jute is about half as dense as glass, 1.22–1.26 kg/m^3, compared to 2.55 kg/m^3 for commercial E-glass fibers [262].

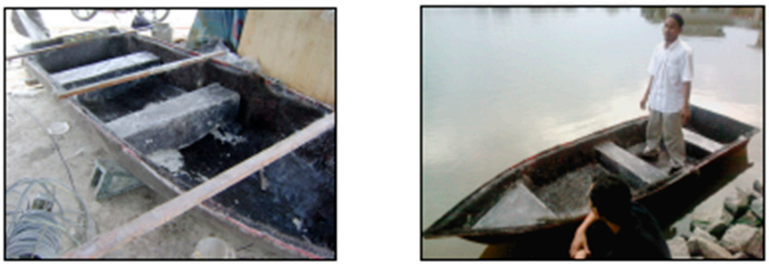


Figure 17. Hybrid glass/sugar palm boat made by Misri et al. [204].

More recently, Bcomp collaborated with Baltic Yachts to make the hull of its flagship racing yacht (the Baltic 68 Café Racer, as shown in Figure 18) out of its ampliTex flax fabrics [263]. The replacement of the carbon- and glass-fiber-reinforced composite parts with flax led to reduced weight, significantly better vibration damping, and better sound insulation performance. The yacht's deck is made from cork as a more sustainable alternative to tropical hardwoods found in similar yachts. The environmentally sustainable natural fiber choice was combined with the on-board hydro generator and solar panels to operate the yacht on clean energy with minimal emissions.

Figure 18. Baltic 68 Café Racer Pink Gin Verde. Photo Credits: Baltic Yacht/YachtShot.

Bcomp's ampliTex flax fabrics were also used by another sustainable boat manufacturer called Greenboats. For the Greenboats Flax27, shown in Figure 19, the hull is made from sandwich panels, with flax skins vacuum-infused with a plant-based epoxy resin [264,265]. The core of the sandwich panel is made from recycled polyethylene terephthalate (PET) bottles. Much of the deck is also made from cork, similar to the Baltic 68 Café Racer. Sicomin's bio-based epoxy (GreenPoxy InfuGreen 810) was used for the flax composite laminates. The GreenPoxy InfuGreen 810 resin was also used for the manufacturing of the Fly 86/2600 motor yacht by Couach [266]. The yacht's hull is the largest bio-epoxy hull to date, and the GreenPoxy was also used in the manufacturing of the deck and superstructure of the Flax27. Couach and Sicomin worked on developing an efficient vacuum infusion process to incorporate the GreenPoxy into the composite parts' manufacturing processes.

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

Figure 19. (**a**) GREENBOATS Flax 27 sailing; (**b**) Flax 27 surface showing flax laminate [265,267].

Sicomin's GreenPoxy 33 resin was used in the manufacturing of the FLOKI 6.5, a sustainable Mini 6.5 class yacht [268]. The Mini 6.5 class yacht is designed to compete in the highly competitive biennial transatlantic Mini-Transat 6.5 race, which usually features innovative composite materials and designs. The FLOKI bio-composite hull, deck, and roof panel parts were reinforced with bamboo fibers; a 2 × 2 twill weave bamboo fabric was supplied by Cobratex. The bamboo strips in the fabric resemble a sandwich structure and are not fully covered by the resin, thus having a high fiber ratio in the laminate. The bamboo structure helps achieve high vibration damping and sound insulation properties for the structure. A secondary +/−45° flax fabric was also used for bonding and taping in the yacht structure. For an even more sustainable design, the core of the sandwich panels on the FLOKI is made from Airex AG's T92 PET foam, which is made from recycled PET drinking bottles. The lamination process used to manufacture the FLOKI 6.5 is shown in Figure 20, as well as the hull structure while being manufactured.

Alternative Energie Company worked on developing an electric-powered catamaran using natural flax fibers as a sustainable material. These biologically sourced composite materials consist of flax fiber reinforcement, a 30% bio-sourced polyester matrix, and also balsa and cork for the sandwich panels. The boat's cabin, roof, and bulwark are designed to be made from the bio-sourced composite [26].

5.2. Canoe

There are multiple cases of lightweight canoes built using natural fibers and sustainable resins. Flaxland, an artisan natural fiber grower and processor run by Simon and Ann Cooper, grows flax and linseed fibers on their farm in the southwest of England. Flaxland has also built lightweight canoes using flax fabrics and flax linseed oil resin, as shown in Figure 21 [269]. NavEcoMat, a collaborative research project between industry and research based in Bretagne, France, developed the Naskapi canoe. The canoe was made from natural flax fibers reinforced with bio-sourced PLA films using RTM [165]. The project was finished by Kairos Inc. and the Ifremer Company, which characterized various bio-based polymers, composite materials, and sandwich cores for commercial boat applications, and considered various natural fiber reinforcements, such as flax, hemp, jute, and other cellulose fibers in unidirectional, woven, and fiber mat forms [26]. One case study manufactured two boats, with the same weight, fiber content, and epoxy matrix but different fiber reinforcements: glass and cellulose fibers. The boats were fully immersed in natural seawater at 40 °C. The research projects found the cellulose fiber-reinforced boat and the Naskapi canoe to have comparable performance and quality with the glass-fiber-reinforced alternatives [270], paving the way for more possible industry and research collaborations to gradually replace GFRP with NFRP in such small marine vessels.

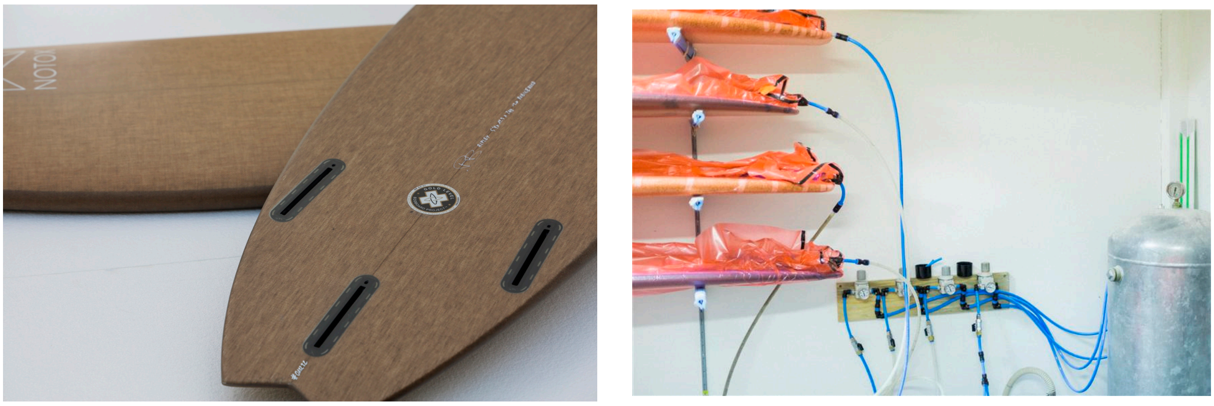
(a) (b)

Figure 20. (**a**) Manufacturing laminates for FLOKI 6.5; (**b**) hull panels while manufacturing FLOKI 6.5 [268]. Photo credit: Sicomin.

Figure 21. Flaxland canoe, built using flax natural fibers. Photo credit courtesy of Flaxland.

5.3. Surfboard

Surfboard manufacturing has produced various innovative solutions to incorporate sustainable biodegradable materials in its designs [271]. A case study compared the manufacturing of surfboards using widely used, industry-standard synthetic materials and more sustainable natural fibers and foams. Samples were made using hemp fabrics, a sustainable bio-foam (made from 45% vegetable oil instead of petroleum-based oil), and epoxy resin. The samples were tested against industry-standard materials made from glass fiber, polyurethane foam, and polyester resin. The flexural strength and stiffness of the hemp samples were found to be significantly lower than those of the glass fiber samples, but the quality of the hemp composites was limited due to the materials being available only by donation [272]. More recently, Michelena et al. designed a flax/epoxy composite system for surfboard production, using alkaline and silane solutions to improve fiber–matrix adhesion and mechanical properties [273]. NOTOX's Greenone surfboard (Figure 22a) is manufactured out of flax fabrics, with a 50% recycled polystyrene foam core and a 56% bio-based epoxy matrix, using a vacuum infusion method, as shown in Figure 22b. The surfboard is 20% lighter than other NOTOX surfboard options and is claimed to allow easier boarding due to flax's vibration-damping properties [274]. Samsara Surfboards also manufactured surfboards from flax fibers [273,275]. Predn and Ertha Surfboards have also included Bcomp's ampliTex flax fabrics to manufacture more sustainable surfboards using natural flax fibers.

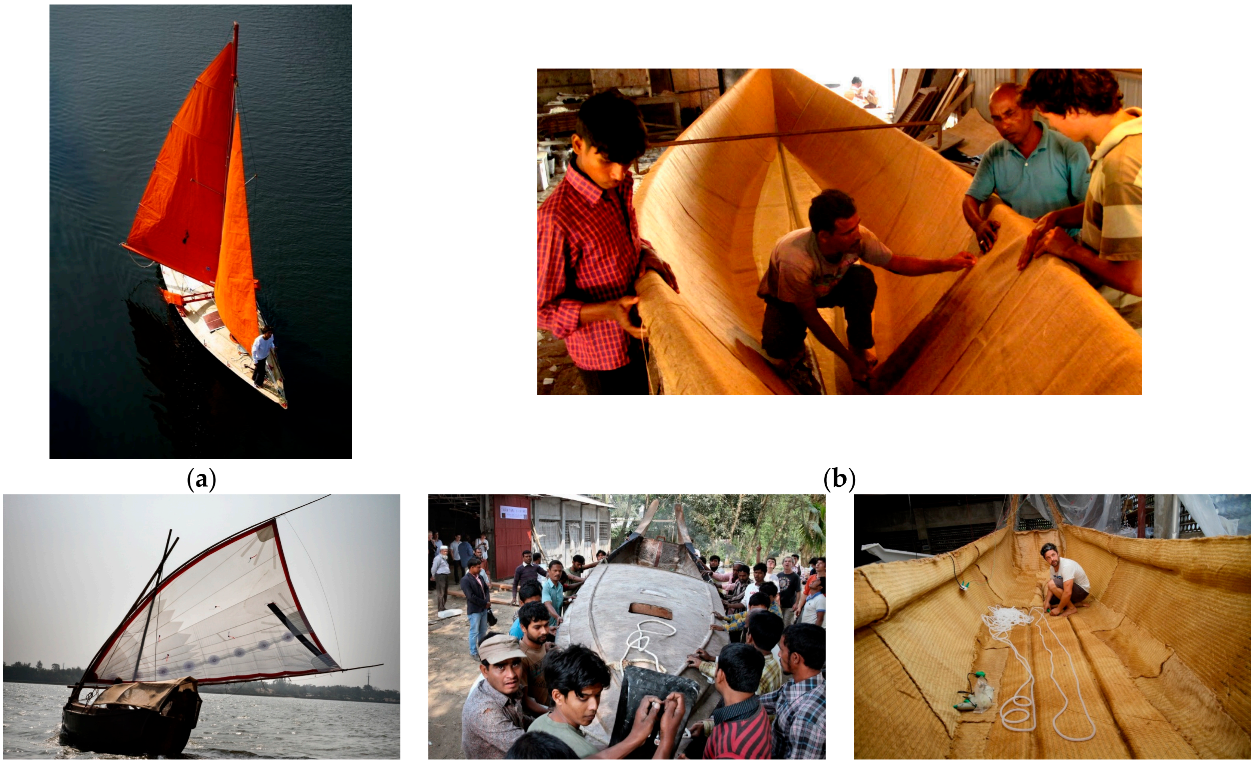


(**a**) (**b**)

Figure 22. (**a**) NOTOX Greenone surfboard; (**b**) vacuum infusion method used for NOTOX surfboards. Photo credits: NOTOX.

5.4. Other Marine Applications for Natural Fibers

One of the first projects to utilize a natural fiber composite in sailboats is the TaraTari (Figure 23a), built in 2010 from a hybrid jute-and-glass laminate. The boat sailed over 14,000 km in 186 days from Bangladesh to France [276,277]. Jute fibers have been the primary industry in Bangladesh for centuries, but the decline in jute in favor of imported synthetic fibers, such as glass fibers, has contributed to the deterioration of the locals' economic, ecological, and manufacturing environment. Figure 23b shows the construction of the 9 m long TaraTari in Bangladesh using mostly local materials (boosting its economic and environmental sustainability profile) and around 40% jute fibers. TaraTari's successful sailing voyage to France inspired a more ambitious project for a truly sustainable environmentally conscious product for the marine industry [278]. In 2013, Corentin de Chatelperron, the builder of the TaraTari, constructed a boat called the Gold of Bengal (Figure 23c), made entirely from jute-fiber-reinforced composite with polyester resin [279]. The Gold of Bengal was claimed to be the first boat in the world made entirely from natural fiber reinforcement. The project was supported by various governmental and humanitarian institutions as well as local talent, as shown in Figure 23d. Simple technology and cost-effective manufacturing processes were used to make the boat structure, as shown in Figure 23e. De Chatelperron successfully managed to sail the boat for 6 months in the Bay of Bengal [280]. The success of the Gold of Bengal spawned other similar projects by de Chatelperron, including the Nomade des Mers, which is an organization promoting low-tech environmentally sustainable solutions around the world, such as the construction of a 70-square-meter buoy made from bamboo. In 2018, de Chatelperron ventured on a 4-month solo experiment with the bamboo buoy just off the coast of Thailand [281].



(a) (b) (c) (d) (e)

Figure 23. (**a**) TaraTari, a 9 m long boat built using jute fibers; (**b**) construction of the TaraTari using local materials; (**c**) Gold of Bengal, made entirely from jute fibers and polyester matrix; (**d**) locals in Bangladesh working on the Gold of Bengal boat; (**e**) low-technology manufacturing processes used for the Gold of Bengal, made entirely from jute fibers and polyester matrix. Photo credits: Corentin de Chatelperron/Gold of Bengal Association.

Shortly after the construction of the TaraTari, in 2011, the Araldite, a 6.5 m long racing sailboat made from 50% flax and 50% carbon fiber reinforcement and an epoxy matrix, competed in the Mini Transat, a solo transatlantic race from France to Brazil, arriving in 15th place [276]. Huntsman Advanced Materials helped manufacture the boat prototype components (including the deck, hull, helm, and toe rails) using prepreg flax fibers provided by LINEO [41,282]. LINEO's line of flax fabrics and flax/epoxy prepregs have also been used in the manufacturing of various boats, canoes, and yachts. Figure 24a shows work being performed on the hull's structure, while Figure 24b shows the completed Araldite prototype in operation. The external hull was constructed using sandwich panels using flax fabrics and structural foam, as well as epoxy resin, which was vacuum-infused and cured at 50 °C [41], while the internal framing used CFRP, as shown in Figure 24a.

Most recently, in 2022, Grand Largue Composites (GLC), a French composite manufacturer, produced Crosscall, shown in Figure 25 below, the first Class40 racing yacht with flax fibers as a cheaper, lighter, more sustainable alternative to carbon fiber reinforcement in many non-structural parts. The yacht was designed so that the cockpit is a non-structural component and is made from a hybrid biaxial fabric with 50% flax fiber reinforcement. GLC used a high-modulus structural epoxy (Sicomin's SR 171) as an infusion resin. The boat's ballast tanks, cap, engine cover, and tunnel also included flax fiber reinforcement in their design. Crosscall won the Class40 World Championships in June 2022. GLC has since started building a second Lift V2 Class40 yacht and is planning a third one based on the success of the Crosscall prototype [285].

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

Figure 24. (**a**) Working inside the hull of the Araldite [283]; (**b**) Araldite sailing on the water [284].

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

Figure 25. Crosscall racing yacht. (**a**) Prototype; (**b**) sailing. Photo credits: Sicomin/Grand Largue Composites.

The successes of such high-performance marine vessels incorporating natural fibers in their components will bring great publicity to NFRP composites, leading to their further development and encouraging the marine industry to adopt such materials across various applications and sectors. The goal of this review is to highlight such successes after discussing at length the critical points of improving NFRP materials' performance in a marine environment.

6. Conclusions

In this review, the state of the art of NFRP composites utilized in the marine industry was discussed.

The most prominent concerns about NFRP composites for applications such as the marine industry were addressed; such concerns mainly lie in the variability of the mechanical properties of natural fibers and their hydrophilic nature, which affects their structure and damages fiber–matrix interfacial adhesion, which is key to the mechanical properties of NFRP composites. Consequently, it was pointed out that there are available strategies, such as different treatments and processes, to mitigate these problems, as well as moisture absorption. This literature review reveals how the hybridization method is an appealing solution to expand the application of NFRP composites. Hybridization allows the improvement of certain mechanical properties of composites, combining the sustainable credentials of natural fibers with the favorable mechanical properties of synthetic fibers, possibly improving damage resistance and damping performance compared to traditional FRP composites utilizing one material as reinforcement.

Regarding the economic and environmental credentials, it was found that natural fibers can be more sustainable than glass and carbon fibers by analyzing the environmental impact using many environmental sustainability metrics, such as energy consumption, life cycle analysis, chemical effects on the environment, and the carbon footprint. Considering all discussed factors, natural fibers offer a desirable alternative to synthetic fibers to reinforce composites for applications in the marine environment, as demonstrated by numerous applications of NFRP composites found in the marine industry. The diversity of natural fiber applications and their potential in the marine industry were highlighted, from relatively small and lightweight surfboards and canoes to large yachts and racing boats. The appeal of including natural fibers in lightweight sea vessels is demonstrated by cost-effective, socially driven environmental projects, as well as in large-scale commercially viable luxurious yachts. The potential of adopting natural fibers is increasing exponentially for various manufacturers and projects in the marine industry, and with efforts to reduce moisture absorption effects and improve mechanical properties, the prominence of NFRP composites in the marine industry is likely to increase in the future.

7. Future Recommendations

There are further applications that are considered ancillaries to marine composite products that can be further developed to be manufactured from natural fiber composites, such as fishing rods. For example, Edge Rods, a subsidiary of Northfork Composites, used Ekoa, a material made from flax linen fiber and bio-based resin prepregs, to manufacture more sustainable, lightweight composite fishing rods, which are claimed to have a fast recovery, dampening, and feel similar to carbon fiber composite rods [286,287]. There are also possibilities of producing paddles and oars for kayaking using natural fiber composites, as Stu Morries has designed a lightweight, stiff, sustainable paddle for kayaking using flax and thermoset resin as an alternative to carbon and glass fiber composite alternatives [288].

Offshore wind turbines are also a major application that natural fiber composites should expand toward after further research and development to improve their mechanical properties, as components used in wind and tidal energy generation are required to have good durability, high specific strength and stiffness properties, and resistance to corrosion, moisture, and fatigue [9,289]. Some limited attempts exist in the literature at manufacturing and testing wind turbine components from natural fiber composites, such as Holmes et al., who manufactured and tested a bamboo/epoxy composite laminate for wind turbine blades, finding high specific strength and stiffness and potentially good fatigue resistance with further research and optimization [290].

Another attempt was made by Shah et al. to manufacture a full-scale 3.5 m composite rotor blade made from flax/polyester and glass/polyester, and the flax/polyester blade was found to be 10% lighter but with much lower stiffness. The flexural rigidity of the flax blade was found to be 24.6 kN m^2, compared to 43.4 kN m^2 for the glass blade. However, design modifications were proposed to improve the flax's blade performance, and the development of the flax-reinforced composite's mechanical properties will work toward reducing the gap in mechanical properties and performance compared to synthetic composite wind turbine blades.

There have also been instances of small-scale, low-cost wind turbine blades made from locally sourced and produced timber, such as wind turbines manufactured using timber in Nepal [291]. Such innovative components and manufacturing methods offer a significantly cheaper, significantly more sustainable alternative while also offering the social contribution of utilizing local talent and sources to benefit local society and offer truly sustainable products, similar to the TaraTari previously discussed in the Applications section. A wind turbine component utilizing sustainable natural fibers for renewable energy generation should also be explored and developed further in the future, as well as other composite marine applications to renewable energy, such as tidal energy generation.

Finally, it is also important to highlight that future academic end-industrial activities will most likely study the possibility of optimizing known manufacturing processes to increase the productivity and mechanical properties of the final composite products, but they will also investigate and implement new manufacturing technologies for the production of these components. For example, the usage of additive manufacturing techniques. According to the online article published in the Seapower magazine [292], the University of Maine's Advanced Structures and Composites Center in Orono has already printed two of the largest 3D-printed vessels for the U.S. Marine Corps for testing the potential of additive manufacturing.

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