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Review

Green Composites for Maritime Engineering: A Review

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Abstract: Green composites have gained increasing attention in recent years as a sustainable alternative to traditional materials used in marine structures. These composites are made from biodegradable and renewable materials, making them environmentally friendly and reducing the subsequent carbon footprint. This review aims to provide a comprehensive overview of green composites materials and their applications in marine structures. This review includes a classification of the potential fibres and matrixes for green composites which are suitable for marine applications. The properties of green composites, such as their strength and Young's modulus, are analysed and compared with those of traditional composites. An overview concerning current rules and regulations is presented. The applications of green composites in marine structures are reviewed, focusing on both shipbuilding and offshore applications. The main challenges in a wider application of green composites are also highlighted, as well as the benefits and future challenges.

Keywords: marine structures; lightweight structures; sustainable mobility; green ship; green composites; wood; natural fibre-reinforced composites; advanced composite materials

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1. Introduction

Polymers are widely applied in all industrial fields: it is estimated that since 1950, about 8.3 billion tonnes of plastic have been manufactured, and the current global production of fossil fuel-based polymers account for about 350 million tonnes per year [1]. Despite many benefits, polymeric materials are well known for being the cause of serious environmental consequences. The marine environment is particularly affected by plastic and microplastic (MP, <5 mm) debris aggregation, which jeopardises marine organisms and human lives. As reported by Everaert et al. [2], about 0.17% of the ocean surface is at risk due to microplastics, and this fraction could increase up to 0.52% in 2050, and 1.62% in 2100. The Mediterranean Sea and the Yellow Sea are hotspots of marine microplastic risks [2].

When polymers are destined for marine applications, their choice should carefully consider the compatibility with the marine environment, which produces severe conditions due to several factors (wave loading, underwater pressure, fouling, high salinity, fluctuant temperature, ultraviolet radiation, and moisture uptake).

The most valuable structural application for polymers in the marine industry is represented by composite materials, constituted of polymeric matrices containing different types and amounts of fillers. The growing interest towards composite materials is the result of the necessity to lighten the structures, hence, reducing fuel consumption and therefore the emissions responsible for environmental pollution [3]. Over time, this objective has led to an extraordinary increase in the production and dissemination of composite materials in all industrial sectors and, consequently, in the resulting environmental impact [4–7].

Among composite materials, fibre reinforced polymers (FRP) play a dominant role, and typically include synthetic fibres (e.g., glass, carbon, aramid). The synthetic FRPs are not biodegradable and can stay in the environment for hundreds of years. Moreover, polymer production from fossil fuels releases a significant amount of excess greenhouse gases (GHG), contributing to global warming. Such conventional and synthetic composites are commonly used in marine industry as a result of their interesting properties, such as corrosion resistance and a high strength to density ratio, even if some weaknesses, such as the vulnerability to impact damage [8], should also be considered. Currently, FRPs are the most used materials for small-size vessels (90% of the circulating boats). Glass-reinforced plastic (GRP) is the predominant category of composite, representing approximately 80% of the hulls for vessels up to 20 m in length [9]. FRPs are also used for navy ships [9–11] due to some crucial features for military applications, such as non-magnetic properties for minesweepers [9], and stealth properties, which made them ideal as Radar Absorbing Structures (RAS) [12]. Composites have also gained a role of primary importance in the offshore industry [13].

Despite countless benefits, composites' end-of-life (EoL) management is still an open question. FRPs are hardly recyclable, and the disposal of FRP vessels is dangerous and expensive: the pyrolysis of a 15 m boat requires high temperatures (about 700 °C) and therefore, high energy demand and high associated costs (about EUR 16,000), without mentioning the associated health risks [13–17]. Other alternatives, meant to reduce the environmental impact of the decommissioned FRPs, include the reuse in other composite products, but their value and the mechanical characteristics are significantly low [18–21]. In addition, FRP materials use a significantly high amount of energy for their production. All of these aspects must be considered while approaching the life cycle assessment (LCA) of a vessel, which starts from raw material production to end-of-life (EoL) strategies. The identification of EoL alternatives (reuse, recycling, and disposal) is fundamental to improve the life cycle consequences of vessels [22,23].

The most common EoL solutions for treating composite waste are landfill disposal, incineration, and recycling. Their impact was well represented by Oliveux et al. [24] and shown in Figure 1.

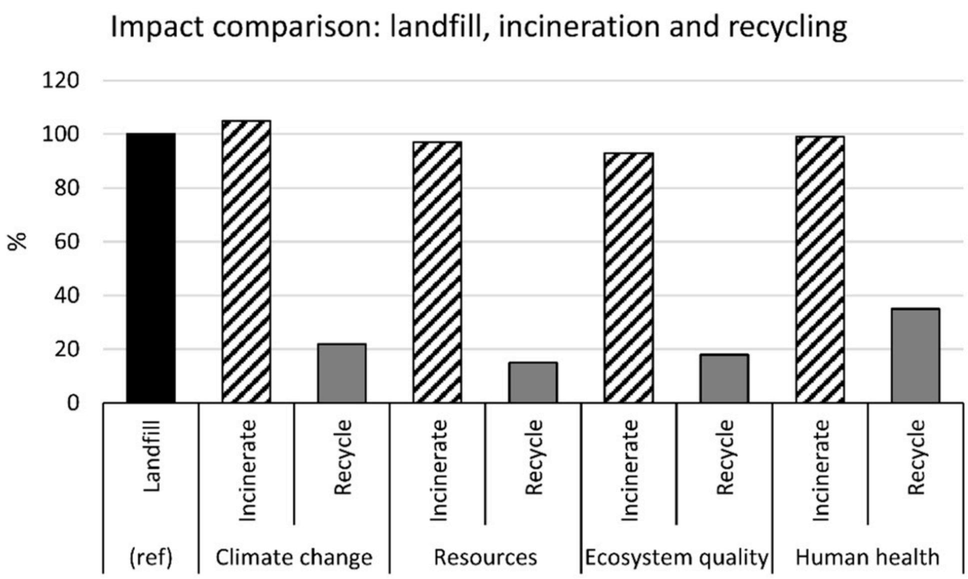


Figure 1. The impact comparison of landfill disposal, incineration, and recycling [24].

Additional EoL solutions for composites include mechanical recycling, pyrolysis, fluidised-bed treatments, chemical solvent processes, and supercritical water methods [25]. The above technologies are often not standard, hence, the literature data on the features of such methods are not always homogenous. In order to suggest a general idea of the environmental consequences produced by EoL processes, data on primary energy demand (PED) and global warming potential (GWP) collected from refs. [16,26–33] were summarised in [34] and shown in Figure 2a,b, respectively.

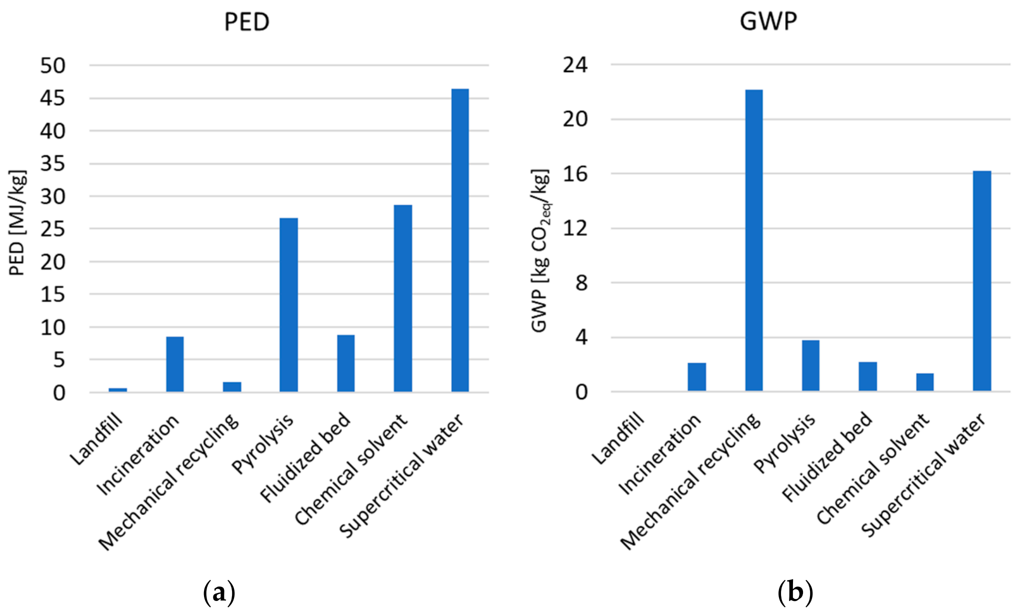


Figure 2. Averaged (**a**) PED and (**b**) GWP of the main EoL methods for composites, according to data from [16,26–33].

In the next years, more sustainable composite recycling solutions will be required [13], considering that the following events are likely to occur: the growth of the composite markets, the ban of composite landfilling, the increase in installations of composite wind turbines, and consequently, the first major wave of composite wind turbines reaching their end-of-life and being decommissioned in 2019–2020.

The approx. USD 40.2 billion composite industry consists of ceramic metal composites (approx. USD 3.5 billion) and metal matrix composites (approx. USD 0.6 billion), with the largest portion being polymer matrix composites (PMCs). The PMC end products industry is primarily composed of carbon fibre reinforced polymer (CFRP) products (approx. USD 25 billion), glass fibre reinforced polymer (GFRP) products (approx. USD 50 billion), and natural fibre FRPs products (approx. USD 5 billion) [25]. The worldwide market for end product composites will reach USD 114.7 billion by 2024 [13]. The market comparison by reinforcement fibre type, i.e., glass, carbon, basalt, aramid, and the associated market share (~70% GF, ~12% CF, ~11% BF, ~7% AF), cost range, and mechanical properties were also described in ref. [13]. GFRP is still the dominant material in the composites market, over 90%, even if the CFRP growth rate is the largest. The nature of composites generated by the industry is known to be about one-third thermoplastics and two-thirds thermosets [13].

The mechanical properties (tensile strength and Young's Modulus) and prices of the most used types of fibre are reported in Table 1 [13].

Thus, in order to follow the increasingly important trend of minimising environmental impact and promoting sustainable development in the marine industry, the introduction of both eco-friendly materials and innovative construction technologies is necessary.

All-metal lightweight and green sandwich structures could provide a beneficial alternative in terms of disposability and recyclability, as reported in [35], where an equivalent aluminium honeycomb sandwich (AHS) structure was suggested as a replacement for a GFRP–balsa sandwich on a ship balcony overhang. An overview of the current state of the art for marine applications of sandwich structures with their future perspectives is provided in [36].

Table 1. Properties of several common synthetic fibres (reproduced from [13]).

Fibre Type [1]	Market Share (%)	Cost Range (USD/kg)	Tensile Strength (GPa)	Young's Modulus (GPa)
E-Glass	≈70%	1.3–2.6	3.45–3.5	72.5–73.5
E-CR-Glass		1.2–3	2–3.625	72.5–83
AR-Glass		2.5–3	1.7–3.5	72–175
C-Glass		1–2.5	3.3	69
A-Glass		2–3	3.3	72
S/S-2-Glass		16–26	4.6–4.9	86–89
R-Glass		16–26	4.4	86
PAN Type Carbon	≈12%	15–120	1.8–7.0	230–540
HS Carbon		20–120	3.31–5	228–248
IM Carbon		25–120	4.1–6	265–320
HM Carbon		25–120	1.52–2.41	393–483
UHM Carbon		30–120	2.24	724
Basalt	≈11%	5	4.84	89
Aramid/Kevlar	≈7%	15–30	2.6–3.4	55–127

[1] Fiber type abbreviations expanded: E-Glass [Electric], E-CR-Glass [Electric/Corrosion Resistant], AR-Glass [Alkali Resistant], C-Glass [Chemical], A-Glass [Alkali], S/S-2-Glass [Strength], R-Glass [Reinforcement], HS Carbon [High Strength], IM Carbon [Intermediate Modulus], HM Carbon [High Modulus], UHM Carbon [Ultra High Modulus].

Another solution for obtaining eco-friendly composites could be provided by biocomposites, manufactured using natural fibres as reinforcement materials and with bio-based polymers as a matrix. The bio-based polymer industry is rapidly growing, with an expected 2020 market size of around 1.5 million tons, making it approximately 0.4% of the size of the current fossil fuel-based polymer industry [1]. Spierling et al. [37] reviewed 29 environmental studies of bio-based polymers from social (S-LCA), economic (life cycle costing, LCC), and environmental (LCA) perspectives. Abdur Rahman et al. [38] provided a review on a large number of environmentally friendly green composites. The review included production methods, the currently available configurations, and described the future developments of these general-purpose composites. According to the reviewed studies, a potential annual savings of 241–316 million tonnes of CO_2eq, available by replacing fossil fuel-based plastics with bio-based plastics, is reported. The natural FRP composites market is estimated to reach nearly 3.7 million tonnes in 2022, and is expected to register a compound annual growth rate (CAGR) of more than 9% during the forecast period (2022–2027) [39] (Figure 3).

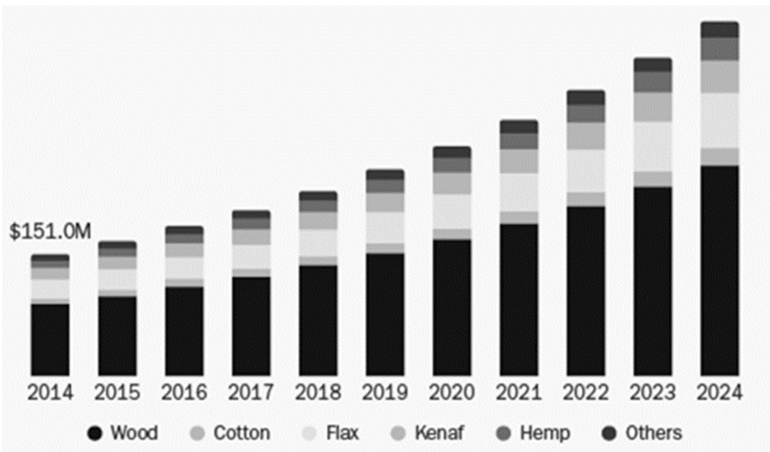


Figure 3. Natural fibres market for composites in 2014–2024 (USD million) [40].

Scope and Research Gap

The current review is aimed at providing an overview of the main aspects and issues concerning the use of green composites in marine applications, to evaluate the current state of the art and identify the challenges and future perspectives.

Although numerous fibrous plants are suitable to produce reinforcements for composites, the overall properties of biocomposites are still far from the conventional high-performance glass or carbon FRP composites, as can be observed by comparing the properties of common synthetic fibres in Table 1 with those of several natural fibres in Table 2 [41]. Therefore, researchers and composite manufacturers are still endeavouring to find a balance between composite performance and biodegradability [42,43].

Table 2. Mechanical properties of several natural fibres (data reproduced from [41]).

Fibre	Density (g/cm^3)	Elongation at Break (%)	Elastic (Young's) Modulus (GPa)	Tensile Strength (MPa)
Cotton	1.2–1.6	7.0–8.0	5.5–12.6	250–500
Coir	1.2	24–51	6	140–593
Flax	1.2–2.4	2.3–3.2	27.6–80	500–1500
Hemp	1.3	2–40	45	530–1100
Jute	1.2–1.8	1.5–2.5	10–55	325–800
Kenaf	1.2–1.6	1.6	41	745–930
Sisal	1.2–1.5	2.0–3.2	9.4–22	310–855
Abaca	1.5	3.4	41	410–810
Henequen	1.4	4.8	13.2	500
Pineapple	1.5	0.8–3.2	82	1020–1600
Banana	1.3	2.0–3.7	27–32	720–910
Nettle	1.5	1.7	38	650
Ramie	1.4	1.2–3.7	23–44	500–915

The possibility to obtain a biocompatible replacement for traditional synthetic fibres is deeply promoted in developing countries, where the availability of large quantities of natural materials, to be used as reinforcement, (natural fibres of thatch, pineapple leaf, coconut husk, coconut coir, sisal, banana stems, jute, sugar cane, raffia, seagrass, and sea-lettuce) could represent an interesting opportunity to support the manufacturing sector [44]. Another attractive perspective is represented by the possibility to create a marine closed-loop through the development of natural fibres from aquatic organisms. *Posidonia oceanica* is now attracting the attention of researchers, as evidenced by some studies focused on the mechanical characteristics assessment of composites reinforced with such fibres, including the degradation process up to one year in the marine environment [45,46]. Some researchers are trying to reproduce the structures of natural fibrous materials, which have proven remarkable characteristics. This led Palomba et al. [47] to carry out a testing campaign on bamboo, with the aim to understand its behaviour under impact loading and to imitate its architecture in protective structures to be introduced in marine environment.

The first step, which could enhance the use of biocomposites in marine structures, regards the study of the production and characterisation of components with proper performance for ship construction. Qin et al. [48] published a study on the selection of the most suitable monomer to perform in situ infusion for thermoplastic composites reinforced with natural fibres, to be used in marine applications. Thyavihalli Girijappa et al. [49] proposed a comprehensive review of the available natural fibres, including kenaf, hemp, jute, flax, ramie, nettle, pineapple, sisal, date palm, cotton, coconut, kapok, bamboo, and silk. They showed the chemical treatments aimed to improve the characteristics of these fibres, then the possible applications, and finally the effect of degradation of the atmospheric agents.

The weakest feature of natural fibre composites is the resistance to the degradation in harsh conditions, such as the marine environment. The most comprehensive attempt to explain the behaviour of these materials in the maritime environment was made by Dabrowska [50], who discussed the interaction between green composites and seawater, highlighting the aspects that could avoid the microplastic pollution, in order to improve their sustainability. Malmstein et al. [51] discussed the hygrothermal ageing of plant oil-based composites in marine applications. Plant oils offer many opportunities to obtain natural fibres and bio-based resins. Dabrowska [52] investigated these opportunities with the aim to build boat hulls made entirely of plant oil-based products. Another solution to improve the performance of the biocomposites is represented by hybridisation. In this method, it is possible to combine natural and traditional fibres in order to obtain both environmental impact reduction and mechanical properties enhancement. Nurazzi et al. [53] collected the mechanical performances in structural applications of hybrid natural fibre composites, showing some configurations that are intermediate between traditional and natural composites, such as rubber, elastomer, metal, ceramics, glasses, and plants. Routray et al. [54] proposed a sisal–glass epoxy composite configuration and studied its behaviour during 30 days of seawater immersion.

Finally, it is crucial to pay attention to the environmental impact of these composite materials during the whole lifecycle, in particular, when the final aim is to replace traditional composites with bio-based ones in the perspective of product sustainability improvement. Maiti et al. [55] discussed the importance of finding a compromise between the performance and biodegradability of natural composites. Curto et al. [56] focused on the long-term durability and ecotoxicity of natural fibre-reinforced composites in marine environments.

The application of green composites in shipbuilding and marine structures should be supported by a deep knowledge of the achievable strength and long-term durability, considering the exposure to harsh marine environments and service loading conditions. Assessing the response of green composites to marine loading conditions and their long-term durability is crucial to establish their potential to replace conventional petroleum-based composite materials in marine applications.

The main shortcomings, and what is required for a wider use of green composites for marine structures, are the following:

- A better knowledge of the mechanical properties and the long-term durability of the green composites;
- Innovative green composites with improved mechanical properties and compatibility with the marine environment;
- The application of disruptive technologies such as additive manufacturing;
- An update of the current rules and standards;
- Eco-design methodologies, based on life cycle assessment, which consider the environmental impacts of the green and sustainable product during the whole life cycle and recycling solutions.

2. Green Fibres

The global natural fibre composite market was valued at USD 4.46 billion in 2016. It is likely to experience an annual growth rate (CAGR) of 11.8% from 2016 to 2024. The sky-rocketing demand for lightweight products from the automotive industry, and the growing awareness of green products, are among the key factors boosting the growth of this market. However, the moisture sensitivity of these materials is bound to hinder this growth.

Natural fibres (NF) are bio-based materials made from products such as wood, cotton, flax, kenaf, and hemp. All are less harmful to the environment and more easily available than synthetic ones. The raw materials used for the production of natural fibre composites are environmentally friendly and have the potential to replace synthetic fibres in the years to come. The growing awareness of green products, the increase in disposable income of consumers, the growing inclination towards eco-friendly products, and the urgent diffusion of recyclable products are likely to play a vital role in the growth of this market.

A summary of the classification of natural and synthetic fibres, with some examples of natural fibres to be potentially used in the marine industry, is reported in Figure 4.

Figure 4. Summary of fibre classification.

Benefits and Drawbacks of Green Fibres

Natural fibre composites (NFRCs) are reported to be potentially 25 to 30% stronger than composites containing the same quantity of glass fibres [57]. Composites made from natural fibres also help reduce component weight and, consequently, the total energy consumption. Finally, the NFC moulding process consumes less energy than fibreglass moulding, lowering production costs by 10%. However, the sensitivity to moisture and weak bonding to polymeric matrices could hamper the growth prospects. The tendency of natural fibres to absorb moisture, which results in swelling of the fibres, limits an effective application in the automotive industry, except for the interiors.

On a general basis, it should be noted that the mechanical properties of natural fibres, which are at the centre of numerous recent studies, are inferior to those of synthetic fibres. On the other hand, natural fibres are reported to have lower density than synthetic fibres, hence, a rational application in composites materials could be beneficial in the perspective of weight reduction goals. In order to provide a critical comparison among the properties of natural, synthetic, and mineral fibres, Figures 5–7 report the maps correlating tensile strength, Young's modulus, and density. When the data reported in the maps refer to more than one source, the average value was considered.

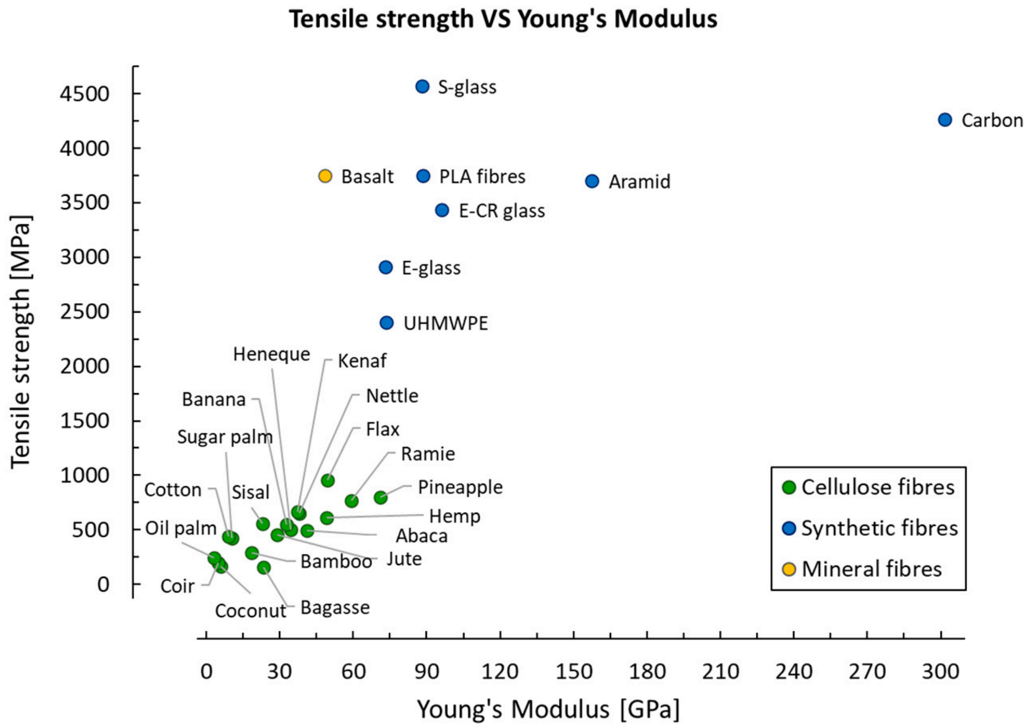


Figure 5. Map of the tensile strength against Young's modulus for several cellulose, synthetic, and mineral fibres. Data from [52,55,58–63].

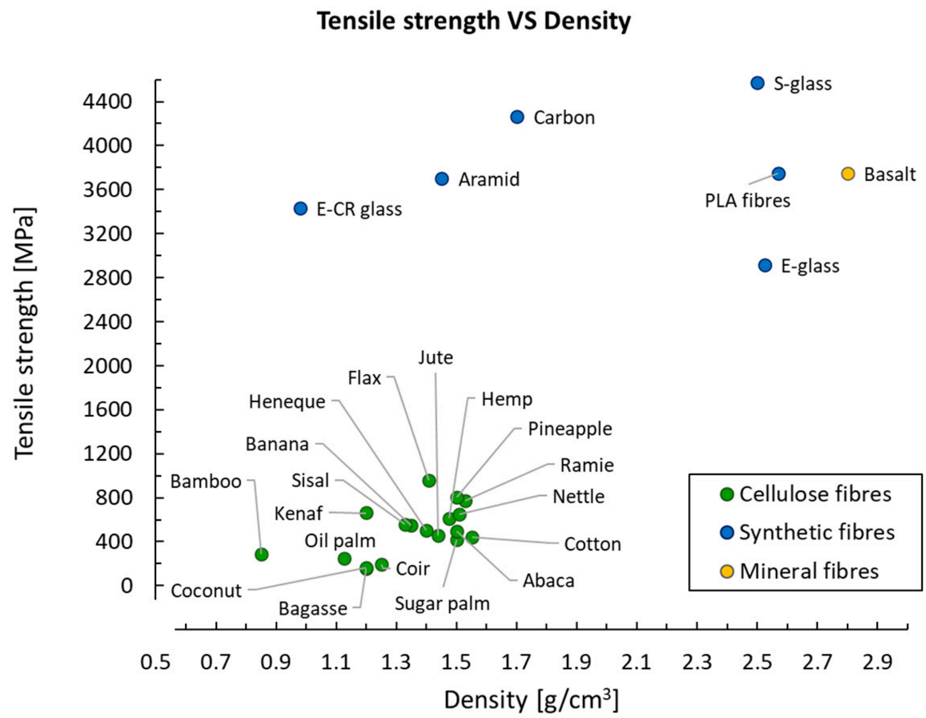


Figure 6. Map of the tensile strength against density for several cellulose, synthetic, and mineral fibres. Data from [52,55,58–63].

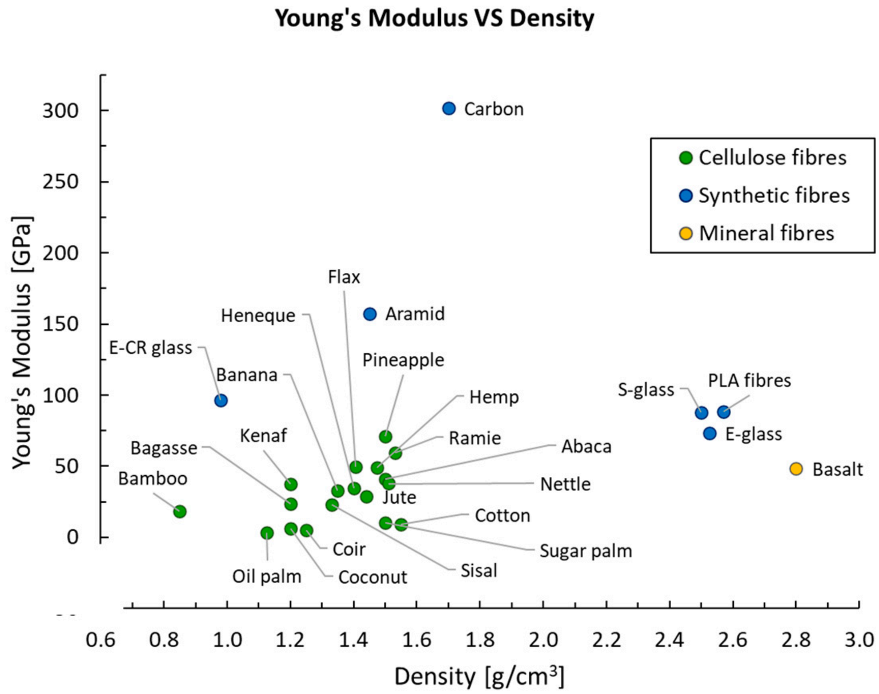


Figure 7. Map of the Young's modulus against density for several cellulose, synthetic, and mineral fibres. Data from [52,55,58–63].

Improved mechanical features of composites are accomplished if the fibres align with the applied load direction. Nevertheless, achieving such an arrangement with natural fibres is complicated, considering an intrinsic inclination to random orientation. As a result, FRP tensile performances decrease considerably as the fibre orientation angle, compared to the test direction, increases [64]. NFs are often arranged in layers before resin impregnation, to achieve a high degree of orientation [65].

It is frequently noted that humidity in the fibre prevents the ultimate strength of the final materials. NFs are generally hygroscopic, influencing the components' mechanical features. Fibre distribution and volume fraction are also significant aspects that affect the properties of short natural fibre-reinforced composites, usually consisting of hydrophilic fibres embedded in hydrophobic matrices. The excellent fibre distribution promotes great interfacial adhesion, decreasing voids by guaranteeing fibre impregnation [66]. Additionally, the impact strength of the composite materials is a significant drawback. Low-velocity impact (LVI) behaviour of green epoxy biocomposite laminates, reinforced by sisal fibres, was investigated in [67].

In the maritime sector, attention is also paid to the possible use of basalt fibres, which show interesting static and dynamic mechanical properties [68]. The static mechanical characteristics of these composites are placed in an intermediate range between the properties of GFR composites and CFR composites, while the costs, which are constantly decreasing, are closer to those of glass fibres. Even more interesting are their dynamic characteristics, which respond well to mechanical impact stresses, as recently shown in ref. [69]. The results showed how, when glass fibres and basalt fibres are subjected to the same stresses, the areas impacted on the latter are more limited, with advantages in terms of safety and residual strength.

Satish et al. [43] reviewed the extraction methods, chemical treatments, and applications for NFRCs. The conclusion was that chemical treatment can improve the physical, mechanical, and thermal properties of NFRCs. NFRCs are replacing petroleum-based fibres (e.g., glass, carbon, aramid, and Kevlar fibres), being cheap, abundant, eco-friendly, biodegradable, sustainable, and hygienic. The environmental sustainability of composite materials depends on three main factors: (a) the materials used, (b) the manufacturing process, (c) and EoL and recycling. The carbon footprint of natural fibres is lower in comparison to that of glass fibres during the fibre production stage, as shown in Table 3 [55], but it is higher during composite manufacturing. In addition, the production of natural fibres also requires fertilisers and pesticides.

Table 3. Carbon footprints of FRP composite components: natural and synthetic fibres and conventional epoxy resin polymer (data reproduced from [55]). (< is the "less-than sign").

Composite Components	Energy Intensity [MJ kg^{-1}]	CO_2 Emission [kg CO_{2eq}/kg of Fibre]
Glass fibre	13–32	1.4–2.95
Carbon fibre	183–286	29.4
Recycled carbon fibre	<250	4.65
Jute fibre	9.6	0.97
Flax fibre	6.5	0.90
Epoxy resin	76–80	6.70

3. Bio-Based Matrices

The recent literature shows that bio-based thermoplastic composites are suitable for high structural performance engineering applications [70,71]. Thermoplastic polymers, such as polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), acrylonitrile butadiene styrene (ABS), polyether ether ketone (PEEK), and nylon, are the bio-based resins of this category.

Benefits and Drawbacks of Bio-Based Matrices

Thermoplastic polymers offer greater design flexibility and ease of processing than thermosetting resins. Thermoset polymers are also responsible for end-of-life criticalities and are generally not environmentally friendly. Compared to synthetic polymer resins, biofibres and bio-based resins, with similar properties, result in superior compatibility and interfacial fibre–matrix adhesion. The low mechanical and thermal properties and the limited long-term durability are, to date, the major obstacles to the full success of biocomposites. Furthermore, most bio-based resins and biofibres are unstable at high temperatures (above 200 °C), at which they cannot be processed.

The recycling of biocomposites is another crucial aspect for their success, as a result of the increasing lack of resources and the consequent need to use them efficiently, in addition to the growing problem of waste disposal [72]. Thermal, mechanical, and chemical technologies are usually used to recycle thermoplastic resin composites. Thermal and mechanical recycling usually degrades the properties of the fibre, destroying the matrix [73]. The chemical treatment, based on the use of chemical dissolution reagents, allows the recycled fibre to keep its properties, and the matrix to keep its monomers intact [74]. The efficiency of the chemical dissolution process depends on the type of organic resin. Cicala et al. [75] concluded that the recycling of the Connora bio-based resin, using separable amines, opens technically and scientifically interesting scenarios for future applications.

The mechanical properties of selected polymer matrices are shown in Table 4 [55].

Table 4. Summary of some key properties of polymer matrices (reproduced from [55]).

Matrices	Resin	Density [g/cm^3]	Tensile Strength [MPa]	Elongation at Break [%]	Young's Modulus [GPa]	Compression Strength [MPa]	Properties
Thermoplastic	Polyethylene (PE)	0.91–0.95	25–45	150	0.3–0.5	-	Low cost, good solidity, chemical resistance, ageing resistant
	Polypropylene (PP)	0.90–0.91	20–40	80	1.1–1.6	-	Low cost, good solidity, chemical resistance
	Polyvinyl chloride (PVC)	1.3–1.5	52–90	50–80	3.0–4.0	-	Low cost, weather resistant, non-inflammable, good haptics
	Polystyrene (PS)	1.04–1.05	35–60	1.6	2.5–3.5	-	Lightweight, water resistant, excellent shock absorption, anti-bacterial

Table 4. *Cont.*

Matrices	Resin	Density [g/cm^3]	Tensile Strength [MPa]	Elongation at Break [%]	Young's Modulus [GPa]	Compression Strength [MPa]	Properties
Thermoset	Unsaturated polyester (UPE)	1.2–1.5	40–90	2	2.0–4.5	90–250	Poor linear shrinkage, excellent wettability of fibers, room temperature curable by addition of hardener
	Epoxy (EP)	1.1–1.4	28–100	1–6	3.0–6.0	100–200	Low cost and low toxicity, high strength, low shrinkage, excellent adhesion to fibers, chemical and solvent resistant
	Phenolic (PH)	1.3	35–62	1–2	2.8–4.8	210–360	Good strength and dimensional stability, heat, solvent, acid, and water resistant
	Vinyl ester (VE)	1.2–1.4	69–86	4–7	3.1–3.8	86	Good strength and mechanical properties
Bio-based	Polylactic acid (PLA)	1.2–1.3	57–185	2.1–30.7	5.1–19.5	-	High strength, high modulus, good appearance, highly biodegradable, less green-house gas emission
	Polybutylene succinate (PBS)	1.26	39–55	5–12	3.6–7.4	-	Inherent biocompatibility and biodegradability
	Polyhydroxy alkanoate (PHA)	1.2–1.3	10–39	2–1200	0.3–3.8	-	Biodegradable with lack of toxicity, reduction of fossil fuel usage
Recycled	High-density polyethylene (HDPE)	0.9–1.0	32.0–38.2	150	1.3	-	Stiff, durable, high-temperature stability, UV resistant, easily recycled
	Polyethylene terephthalate (PET)	1.5–1.6	55–159	300	2.3–9.0	-	Highly rigid, good tensile strength, good barrier effect, easily recycled

The degradation and fragmentation of bio-based plastics in the marine environment produce microplastics and leachate, which could induce toxic effects in aquatic organisms, even if the number of ecotoxicological data points of bio-based MPs is substantially lower than for fossil fuel-based polymer materials and limited to a restricted number of organisms [56]. As reported in [56], the potential ecotoxicological effects of leaching substances and microplastics derived from biocomposites require a deeper discussion, based on a significant amount of ecotoxicological data and evidence to establish their toxicity in the environment.

4. Green Composites

Sustainable FRP composites from renewable and biodegradable fibrous materials and polymer matrices are of great interest, as a result of the potential reduction of the environmental impacts. Composites containing at least one of these components (matrix or reinforcement) obtained from natural resources are categorised as partially biodegradable composites, and composites with all of their constituents from natural resources are called fully biodegradable green composites. Green composites merge plant fibres with natural resins to produce ecological composite materials. Natural fibres are developing as low cost, lightweight, and ecologically excellent options compared to synthetic fibres. Green composites are employed in several applications, ranging from vehicles to smartphones. Maiti et al. [55] provided an overview of sustainable FRP composites in terms of manufacturing techniques and sustainability in general, at the materials, manufacturing, and end-of-life levels (Figure 8).

Benefits and Drawbacks of Green Composites

Biocomposites have some serious drawbacks, such as moisture and humidity absorption, flammability, matrix–fibre incompatibility, highly anisotropic properties, difficult processability, etc. [76], which can hinder their use in primary engineering applications. The origin of the natural fibres is a decisive factor for the properties and durability of biocomposites. The presence of cellulose, hemicellulose, lignin, pectin, etc., makes biofibres hydrophilic, with a consequent poor ability to adhere to the interface with host polymeric matrices, which are usually hydrophobic. This drawback yields poor mechanical and thermal properties, restricting their potential use, especially in particularly demanding fields of applications. Therefore, the current research interest is still focused on overcoming these limitations through surface treatments, hybridization, nanoengineering, etc. [77,78]. In particular, materials science aims at the understanding and knowledge of what occurs at a micro-structural and morphological level following the above treatments. These treatments, which essentially alter the carboxyl and hydroxyl groups on the surface of the fibres, appear vital to broaden the applications of biocomposites. These techniques can also roughen the fibres, encouraging interfacial interlocking phenomena.

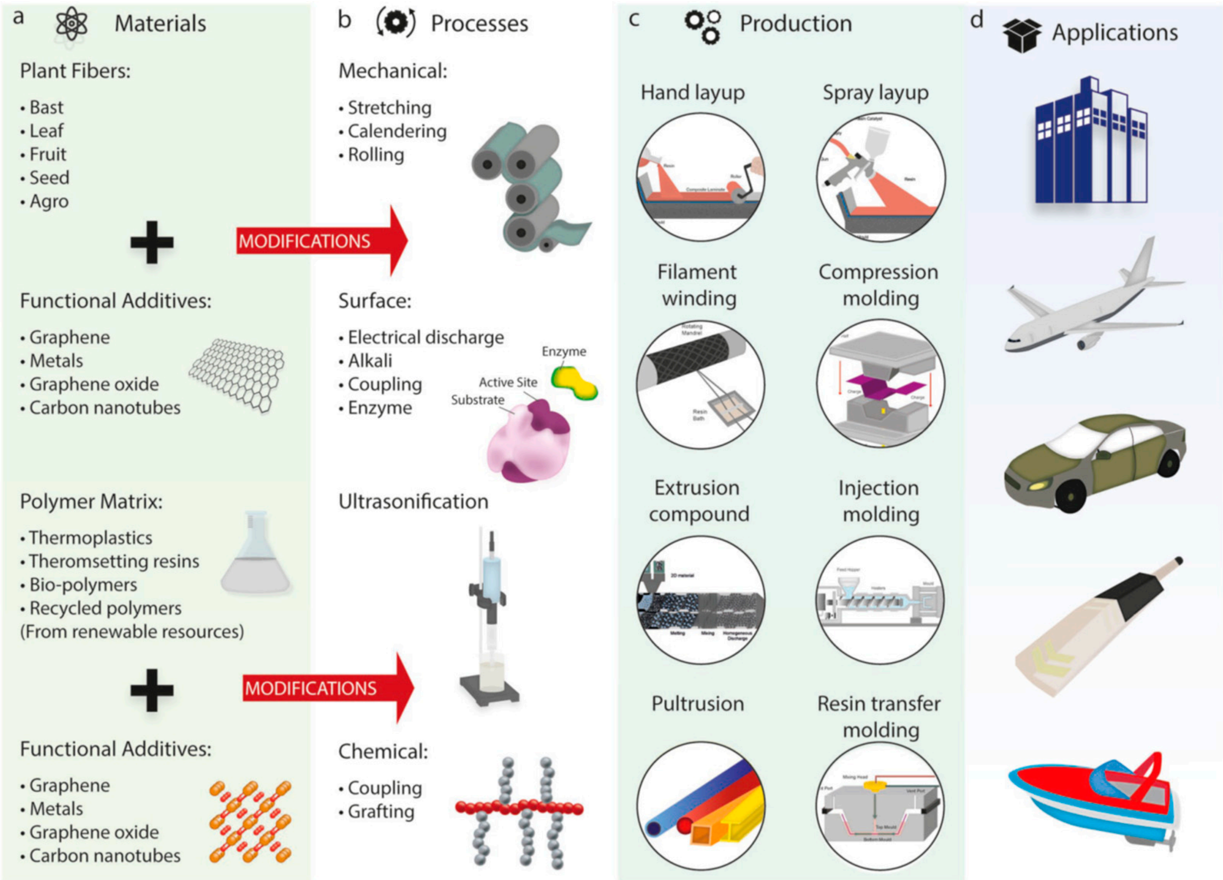


Figure 8. Sustainable FRP composites: (**a**) materials, (**b**) modification processes, (**c**) composite manufacturing methods, and (**d**) applications of fibre-reinforced composites [55].

The marine environment is extremely hostile, with humidity, UV, physical stresses, and degradation processes [79]. The effects of ageing circumstances may induce the thermal and mechanical degradation of polymers or biocomposites exposed to various ageing conditions, limiting their general environmental stability. Regarding the mechanical degradation of hemp fibre-reinforced unsaturated polyester composites, Dhakal et al. [80] showed that water uptake increases with the increase of voids and cellulose content. In general, different researchers have shown that biocomposites made with natural fibres are subjected to significant water absorption, resulting from the fibres' chemical constitution and from the multi-layered construction [81]. Most of the polymers suggested as possible biocomposite matrices are hydrophobic, inducing a poor fibre–matrix adhesion. The chemical hydrophilic nature of fibres [82] affects the fibres' conditioning before the composite manufacturing process. Baley et al. [83] performed an extended analysis on the drying of flax fibres and its effect on the composite features. The impact of these factors on the mechanical properties of polyester/hemp fibre composites was evaluated at room and higher temperatures [80]. The presence of hemp fibre aids the mechanical features of the UP matrix, but the composite mechanical properties were predominantly affected by marine conditions. The decrease of mechanical characteristics was explained as the consequence of weakened fibre–matrix interfaces, due to moisture access (Figure 9).

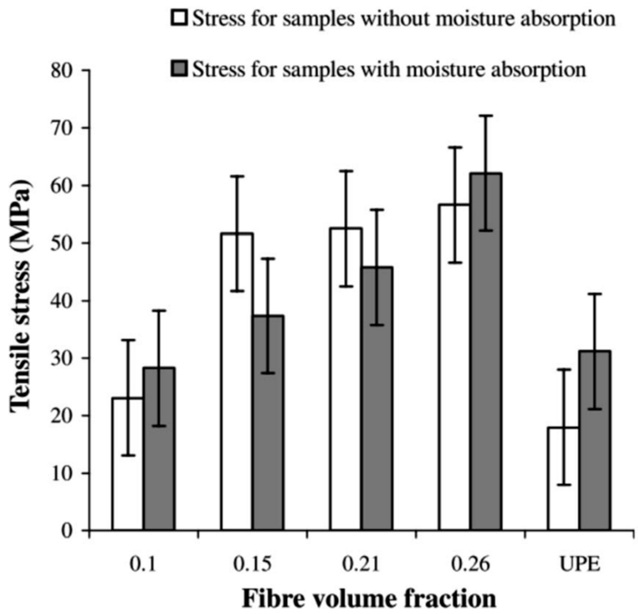


Figure 9. Moisture effect on the tensile strength of hemp/UP composites (reproduced from [56]).

However, when accessible material improvement strategies are available, the effect on mechanical properties produced by exposure to the marine environment will be reduced. An interesting property to investigate for maritime applications is the impact strength, which is often a critical issue for composites. The impact strength of composites is dependent on countless features, including fibre orientation, fibre volume fraction, the number of plies, or manufacturing technology. Several studies in the scientific literature were focused on the investigation of impact properties for bio-based composites [84–89]. Figure 10 shows a general comparison between traditional composites [88,90,91]. It is interesting to observe that impact strength of biocomposites is similar to that achievable with traditional composites.

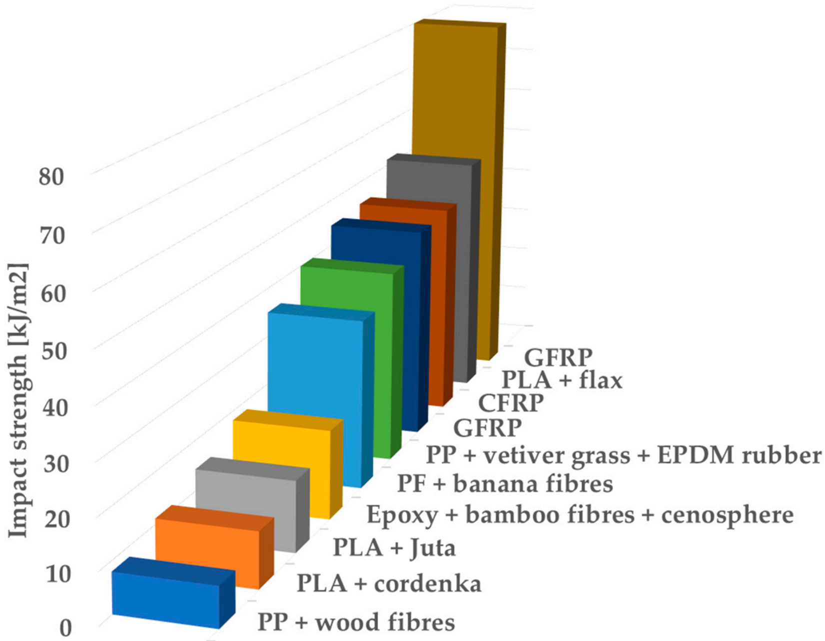


Figure 10. Impact strength of bio-based and traditional composites. Data from Refs. [84–91].

5. Wood

Wood is the oldest material used for boatbuilding [92] and has interesting properties in an environmental perspective, as it is a low energy material, a renewable resource, and has a negative net carbon footprint. Similarly, in the use of natural fibres, wood–composite hybrids [93] are interesting for maritime applications, both onboard and for mobile structures, as well as for fixed structures.

The knowledge of the quality and mechanical properties of wooden laminates is extensive, and several studies reporting various wood essences exist in the literature. In particular, the mechanical properties of Iroko wood [94] and Iroko laminates [95], Douglas fir and Mahogany Sapele [96], used in boatbuilding, were already investigated by some of the authors. Figure 11 shows the phases of the construction of a strip-planked hull. The strip-planking technique is a wood construction method, which consists of stratifying a number of wood strips and veneers with different thickness. This construction technique (Figure 11) involves the preparation of a series of transversal frames, in order to reproduce the boat hull form (Figure 11a). These frames serve as a support for the long and narrow pieces (strips) of wood running in the fore-aft direction and joined on their edges using a proper adhesive (Figure 11b,c). Then, the strip planking is covered by layers of laminated wood veneers, running perpendicular to the strips (Figure 11d). Finally, a gel-coated layer and antifouling paint are applied to the external surface of the hull.

Figure 11. Phases of the construction of a strip-planked hull [96]. (**a**) transversal frames. (**b**,**c**) wood strips. (**d**) wood veneers.

As reported in [97] "forestry management should prioritize 'win–win' strategies—those that increase both forest stocks and timber harvest, through measures such as protecting trees from animals, or replacing dying or low productivity forests".

Some of the limitations of wood are related to its strength and toughness, and therefore wood may not be suitable for many applications [98–100]. The majority of dominant wood modification systems (chemical modification, thermal modification, and polymer or resin impregnation) have sought to alter the relationship between wood and moisture and, as a result, to restrict dimensional change and reduce susceptibility to decay. Song et al. [101] describe a straightforward and efficient approach to change bulk natural wood into a high-performing mechanical material with a more than optimum increase in strength, toughness, and ballistic resistance, and with more dimensional solidity.

6. Marine Applications of Green Composites

6.1. Current Rules and Standards

Classification societies, such as the American Bureau of Shipping (ABS), Lloyd's Register (LR), and DNV GL, have established guidelines and rules for the use of composite materials and structures in marine structures. Class rules address the design, fabrication, inspection, and testing of composites, including requirements for materials selection, manufacturing processes, quality control, and inspection methods. The specifics of the rules can vary between classification societies and are subject to changes and updates, aimed at ensuring high standards of safety and reliability. A common principle of the current rules is that when the use of unusual materials is proposed, special tests or examinations before and during service may be required. Hence, the application of green composites in marine structures should at least guarantee the minimum requirements established for traditional composites, but could be also subjected to additional checks. Despite some particularities and differences among class rules, the general approach recommended to achieve composite certification includes the following steps:

1. Tests on the matrix;
2. Tests on the reinforcements;
3. Tests on composites samples and/or specific tests on components or parts.

Test procedures are usually defined in accordance with international standards (e.g., ISO standards).

A summary of the steps for composite certification, including the most crucial properties to be assessed according to some of the classification societies [102–105], is reported in Figure 12.

In addition to the requirements on constituent materials, classification societies usually provide rules or guidelines on the design and calculation of composite construction [102–105].

6.2. Green Composites for Boat Building

There is a growing interest in replacing fossil fuel-based polymers and composites with more sustainable and renewable fully bio-based composite materials in marine applications, aiming at reducing the carbon footprint and the environmental impact. The typical service life for ships and offshore structures is 20 years, during which, structures are subjected to different harsh conditions, hence, the assessment of the long-term durability according to marine applications is necessary, in order to evaluate the related degradation mechanisms. The relevant literature on the long-term durability of biocomposites specific for marine environments is reviewed in [56]. Among the prototypes reported to have good potentials in terms of durability when exposed to the marine environment, there is a flax/PLA canoe and a flax fibre-reinforced trimaran, displayed in Figure 13.

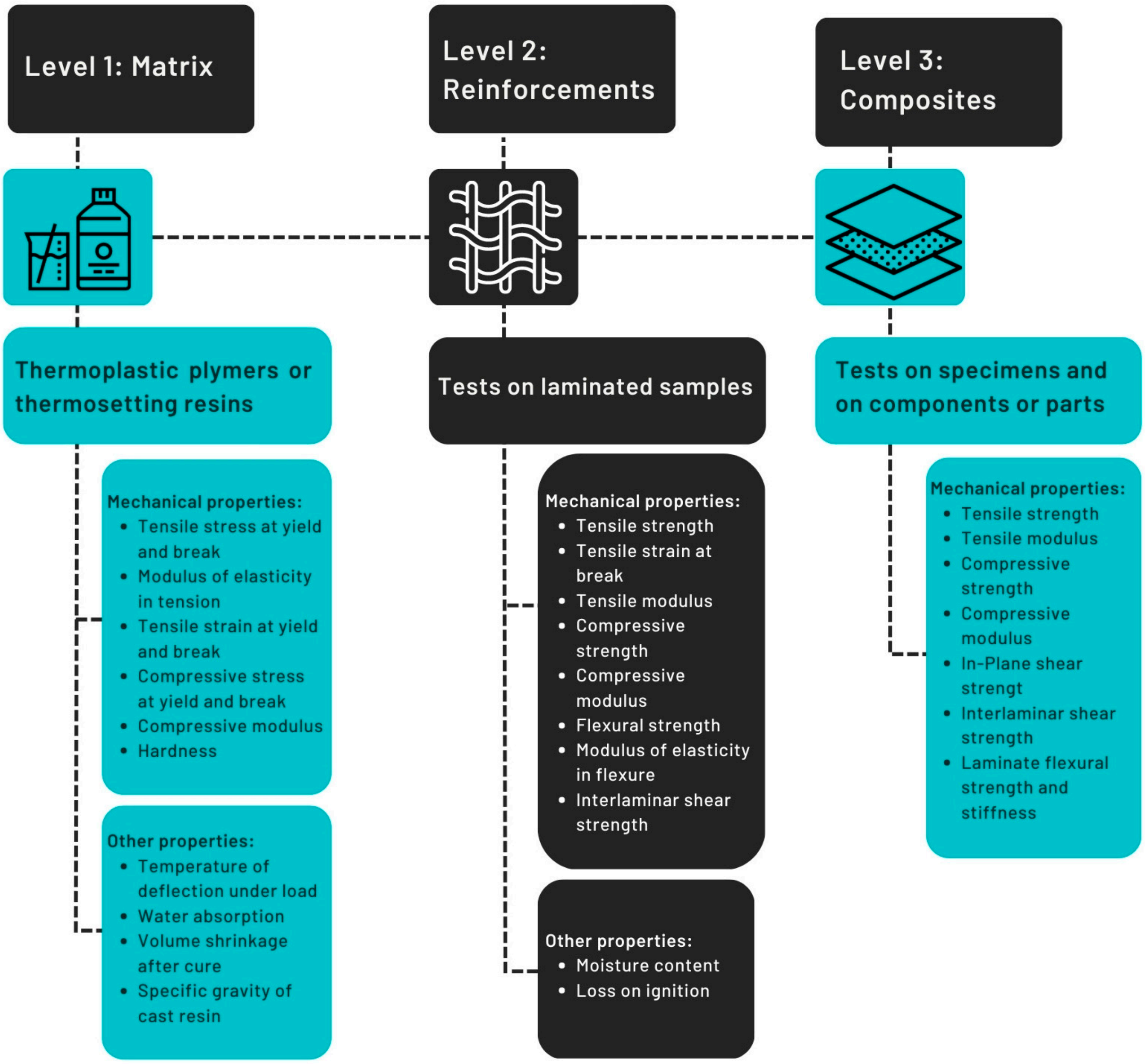


Figure 12. Summary of the properties to be assessed for composites to be used in marine structures, according to classification societies.

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

Figure 13. (**a**) Flax/PLA canoe manufactured during the NAVECOMAT project; (**b**) Gwalaz, flax fibre-reinforced trimaran [56].

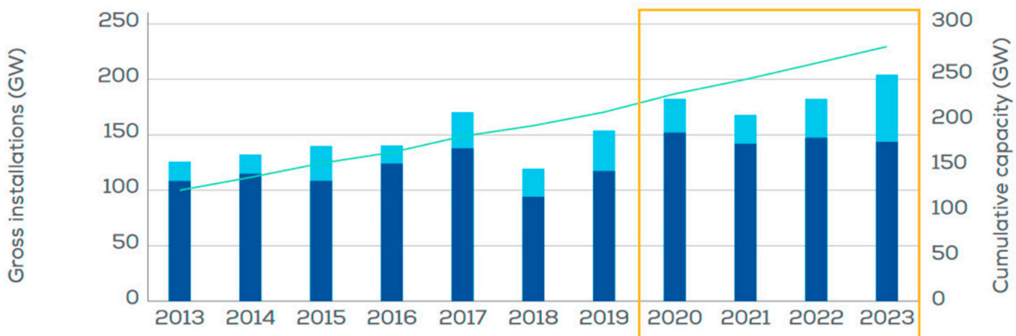
The compatibility of flax fibres with the marine environment attracted the attention of Živković et al. [59], who evaluated the influence of moisture absorption on the impact properties of flax fibre composites, along with basalt and hybrid flax–basalt fibre composites. The low environmental impact of the tested composites was guaranteed, not only by natural fibres, but also by the use of a low styrene emission vinyl ester matrix. According to the impact testing on both dry and conditioned samples, flax fibre specimens experienced an increased impact resistance after accelerated aging in salt water, whereas basalt fibre composites had worse impact properties after conditioning. Hybrid flax–basalt fibre specimens, on the other hand, had similar impact strength in dry and aged conditions, a more uniform response, and a more stable behaviour in term of moisture absorption.

The necessity to thoroughly investigate the properties of bio-based composites, in order to guarantee high reliability standards for shipbuilding, has so far limited the use of similar materials in small boats. In addition, bio-based composites with potential shipbuilding applications are countless, hence, specific assessment of their properties and the best manufacturing technology for each type is required.

An example of natural fibre-based composite testing and subsequent manufacturing of a small boat was offered by Misri et al. [106]. The referenced analysis suggested a woven glass–sugar palm fibre-reinforced unsaturated polyester hybrid composite to manufacture a small boat with the compression moulding technique. The conclusions highlighted that the mechanical properties of the hybrid composite were higher than composite based only on the natural woven sugar palm fibres. However, it should be observed that the environmental sustainability of such a solution was not optimal.

6.3. Green Composites for Offshore

In recent years, composite materials have expanded to applications where the corrosion resistance is an appreciated property: the offshore, marine, and wind energy industries [13,107–109]. Composites are employed in wind turbine blades thanks to their high specific strength [13]. The gross annual wind turbine installations in Europe are shown in Figure 14 [13], where the yellow box refer to the last four years (2020–2023).



	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023
Offshore	1.5	1.5	3.0	1.6	3.2	2.7	3.6	2.9	2.7	3.4	5.9
Onshore	11.0	11.6	10.9	12.3	13.9	9.4	11.7	15.2	14.2	14.7	14.5
Cumulative	122	135	148	162	178	190	205	222	238	255	275

Figure 14. Gross annual wind turbine installations in Europe [13].

The Global Wind Energy Council (GWEC) reported that there are more than a third of a million utility-scale wind turbines installed around the world, most of which are designed for a service life of 20–25 years. Turbines from the first major wave of wind power in the 1990s are currently reaching their expected end of life [13]. According to [25,110], the usage of blade material waste is expected to grow from 1,000,000 t in 2020 up to 2,000,000 t in 2030, doubling within the current 2020 decade. It is predicted that a quarter of this EoL waste will be in Europe.

In this frame, recycling will become an even more pressing matter in the 2020s.

According to Wind Europe, there will be around 14,000 blades (about 40,000–60,000 t) planned for decommissioning by 2023, and their recycling is a top priority for the wind industry [13].

7. Challenges and Future Perspectives

Innovative alternatives for marine applications may be suggested by the observation of solutions provided by nature, according to the principles of biomimetics [47].

The interest towards bio-inspired engineering solutions is also rising, thanks to the growing accessibility of additive manufacturing (AM) techniques, which allow the production of complex design solutions, such as bio-inspired structures.

The widespread additive manufacturing technology for producing components having complex geometries has resulted in increased attention towards new reinforced materials. A composite's internal structure can be designed ad hoc on the required mechanical performance. Moreover, fused deposition modelling (FDM) technology allows the building of continuous fibre-reinforced thermoplastic composites [111,112]. Carbon fibre-reinforced thermoplastics, produced by additive manufacturing, were proposed in [113] for a structural joint, connecting the cockpit frame to the cross beams of a small racing boat.

Natural fibres have been growing in interest as fillers for FDM composites, but the mechanical properties of the printed components are low, due to poor fibre characteristics, the low volume fraction, fibre arrangement, and the high porosity content relative to the technology. Matsuzaki et al. [114] were the first authors to suggest the printing of continuous jute fibres and a PLA matrix using a synchronised impregnation technique. The achieved mechanical performance exceeds all the available data for 3D printed discontinuous natural fibre composites. Additionally, Le Duigou et al. [112] evaluated the mechanical performance of a novel high-performance 3D printed biocomposite based on a continuous flax yarn embedded in a PLA matrix. The road to using natural fibers in 3D printing is still long, but with excellent precautions it is possible to obtain satisfactory results.

A wider use of green composites for marine structures will be possible only as a result of two conditions. These conditions are: the development of reliable knowledge of the benefits offered by green composites, and an increased awareness of the environmental consequences produced by traditional materials. In order to implement such conceptions in the actual design of marine structures, an implementation of dedicated methodologies, such as LCA, should be required by the class rules. A standardisation of such methodologies would promote more responsible choices right from the design phases, supporting numerous decisions ranging from materials selection [115–117] to manufacturing processes [118,119].

8. Conclusions

This review analysed the current state of the art of green composites, and provides a collection of bio-based materials with promising mechanical and environmental performances, which make such materials potentially suitable for marine applications. Most of the green composites have mechanical properties still far from the high-performance synthetic FRPs and are hydrophilic, resulting in a decrease of the mechanical strength when exposed to the marine environment. The impact of these factors limits the applications and the benefits of green structures in maritime engineering.

This state of the art literature review demonstrates a significant lack of studies that have investigated the mechanical and environmental performances of eco-friendly structures. Therefore, future researchers should be focused on eco-friendly marine structures, aiming at increasing the mechanical properties and long-term durability in the marine environment. Moreover, a responsible development of structures produced by green composites also requires the full analysis of the environmental footprint, so that other studies are necessary to deepen this aspect, in the view of a circular economy having a proper EoL approach. A wider use of green composites for marine structures requires an update of the current standards and the development of eco-design methodologies, based on life cycle assessment, which consider the environmental impacts of green and sustainable products during the whole life cycle, as well as recycling solutions.

In this vision, the rediscovery of wood, a natural eco-friendly material, well-known for marine applications, can play an important role. Such a goal can be reached thanks to the increasing progress in woodworking machines and technologies, such as strip-planking, along with the development of bio-based adhesives, which allows the production of wood-based laminates possessing interesting mechanical properties.

A milestone towards the manufacturing of marine structures with complex geometries is represented by the development of disruptive technologies, such as AM, which allows the tuning of the geometry, of the stacking sequence, of the fibre's orientation, and of the resulting mechanical properties. Some solutions for the design of AM structures could be suggested by nature, according to the principles of biomimetics.

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