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Industrial Hemp Fibers: An Overview

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Received: 16 October 2019; Accepted: 26 November 2019; Published: 2 December 2019

Abstract: Industrial hemp (*Cannabis sativa*) is one of the most available and widely produced bast fibers with high cellulose content. Interest in these fibers is warranted due to environmental protection challenges as well as their inherent properties such as low density, high specific strength, and stiffness. In addition, advanced research and progress have gone into increasing their mechanical performance through surface treatments and in the development of new materials. The most promising application for hemp fibers is as reinforcement in polymeric composites or through hybridization. Nonetheless, more research is needed to improve their properties and expand their range of applications. The biodegradability issue is one problem that must be addressed when considering long life-cycle applications as the reproducibility of these composites' final properties. This review is a comprehensive literature review on hemp fibers. It includes hemp fibers' chemical and mechanical properties, surface modifications, hybrid composites, as well as current and future applications.

Keywords: hemp fibers; surface treatments; hybrid composites; mechanical properties; industrial applications

1. Introduction

Environmental protection is one of the greatest challenges facing the current generation [1]. Due to increasing environmental concern and protection, the number of available studies dealing with the potential use of natural fibers in developing thermoset and thermoplastics composites as well as improving their mechanical performance through physical and chemical surface treatments is growing. Furthermore, natural fibers are getting more attention as possible alternative replacements for synthetic fibers, such as glass fibers [2–7].

Natural fibers are eco-friendly [8], are non-abrasive to the processing equipment, are relatively low cost, are from renewable resources, have low density, and have high specific strength and stiffness [8,9]. On average, natural fiber production uses 60% less energy than glass fiber production, and results in lower air emissions [10]. Moreover, the wastes are mostly organic and 100% biodegradable [7,11].

Joshi et al. [12] compared the life-cycle assessment of three components made from natural fiber-reinforced composites and glass fiber-reinforced composites. They found that natural fiber-reinforced composites emerged more environmentally friendly, mainly for three reasons: (1) natural fiber production had the lower environmental impacts, (2) natural fiber composites had higher fiber content for equivalent performance, which reduced the volume and weight of the base polymeric matrix, and (3) the lower weight of the resultant components reduced the emissions and fuel consumption in its life cycle. The life-cycle assessment, performed by La Rosa et al. [13], showed that hemp mats in glass fiber-reinforced thermoset composites are more environmentally friendly than the conventional single use of glass fiber, due to the reduction of glass fiber and resin content.

While there are a wide number of benefits in using natural fibers, there are also some disadvantages. The major disadvantages of natural fibers are their inherited hydrophilic character, highly anisotropic

nature, low resistance to microorganisms, low thermal stability, variation in mechanical properties, and mechanical properties lower than those of synthetic fibers [6]. Additionally, it is recognized that various aspects such as growth condition, harvesting methods, and maturity often affect natural fiber properties [11].

The hydrophilic character of natural fibers results in poor interfacial interaction between the matrix and fiber and poor fiber dispersion, as well as high moisture absorption, which might lead to fiber swelling and debonding of the matrix-fiber interface [14,15]. The moisture absorption in natural fiber-reinforced composites is governed by three different diffusion mechanisms, namely, (1) water diffusion between the polymer microcaps, (2) capillary transports into flaws and defects at the matrix-fiber interface, and (3) transportation through microcracks formed during the fiber's swelling process [16]. This review article describes the recent research works related to various aspects of hemp fibers and their use in the reinforcement of composites.

2. Natural Fibers: General Considerations

Natural fibers are extracted from different renewable resources and are commonly categorized based on their origin-vegetable, animal, or mineral. Plant fibers are generally referred to as vegetable fibers and contain cellulose as their major structural component and hemicelluloses, lignin (amorphous), pectin, wax, and ash in low amounts as illustrated in Table 1 [11,17].

Table 1. Chemical composition of plant fibers. Data from: [11,17,18].

Fiber	Origin	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)	Ash (%)	Microfibrillar Angle (°)
Hemp	Bast	70–74	3.5–5.7	15–20	0.8	1.2–6.2	0.8	2–6.2
Jute	Bast	61–72	12–13	18–22	0.2	0.5	0.5–2	8
Sisal	Leaf	78	8	10	-	2	1	-
Flax	Bast	64–72	2–2.2	18–20	1.8–2.3	-	-	5–10
Ramie	Bast	69–91	0.4–0.7	5–15	1.9	-	-	7.5
Harakeke	Leaf	56–64	7.8	23–31	-	-	-	-
Coconut Coir	Fruit	36–43	0.15–0.25	41–45	3–4	-	-	30–49
Kenaf	Bast	45–57	22	8–13	0.6	0.8	2–5	2–6.2

The microfibrillar angle is the angle that microfibrils make with respect to the fiber axis [19]. In general, natural fibers with higher strength and Young' s modulus have a higher cellulose content, a longer cell length, and a lower microfibrillar angle, such as in the case of hemp fiber [14,20,21]. The degradation of natural fibers depends on individual chemical composition; lignin is mainly responsible for UV and fire degradation, whereas hemicelluloses are responsible for biological degradation, thermal degradation, and high moisture absorption [11,14,22].

Table 2 shows the physical and mechanical properties of natural fibers and the main type of glass fiber (E-glass). It can be seen that natural fibers have some advantages compared to glass fibers, such as low density and higher specific stiffness. The flax, hemp, and ramie fibers have the highest Young's modulus and specific stiffness, although their strength is lower than that of glass fiber [8,11,18,20,23]. In an attempt to achieve an average performance similar to E-glass, a reasonable choice could be to select hemp, which is stronger than ramie and still stiffer than E-glass.

Table 2. List of plant fibers, physical and mechanical properties (bundles), and glass fiber (E-glass). Data from: [8,11,18,20,23].

Fiber	Length (mm)	Density (g/cm^3)	Failure Strain (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Moisture Content (%)	Specific Stiffness (E/ρ) (GPa)
Hemp	5–55	1.4	1.6	550–1110	30–70	8	21–50
Jute	2–120	1.3–1.5	1.5–1.8	393–800	10–55	12	6–34
Sisal	900	1.3–1.5	2.0–2.5	507–855	9.4–28	11	6–18
Flax	5–900	1.5	1.2–3.2	345–1830	27–80	7	18–53
Ramie	900–1200	1.5	2.0–3.8	400–938	44–128	12–17	29–85
E-glass	Continuous	2.5	2.5	2000–3000	70	<0.1	28

The mechanical properties of natural fibers depend on their physical, chemical, and morphological properties as well as growing conditions, harvesting time, extraction method, treatment, and storage procedures [3,7,17,18,22,23]. Pickering et al. [24] reported that the strength of hemp fibers was reduced by 15% over five days after optimum harvest time, which was found to be 114 days, with an average tensile strength of 857 MPa and a Young's modulus of 58 GPa.

Generally, the properties of a single fiber are calculated based on the total cross-section, despite having a central hollow lumen (Figure 1b) which takes up a significant proportion of the cross-sectional area. The lumen area fraction for harakeke was found to be around 41%, suggesting a true fiber strength of 1308 MPa, instead of a strength of 778 MPa obtained neglecting the lumen [25].

Hemp Fiber

Industrial hemp (*Cannabis sativa*) is an inexpensive and available bast natural fiber. In Europe and Canada, specific *Cannabis sativa* can be cultivated, and it must have no more than 0.2% (Europe) or 0.3% (Canada) tetrahydrocannabinol (THC) [26]. Fiber production from hemp has been conducted over many centuries, for end uses ranging from textiles and papers (hemp paper was used in the first copies of the Bible) to ropes and sails. [27].

The hemp plant is native to India and Persia, although it has been cultivated in nearly all temperate and tropical countries [28,29]. Russia is the largest hemp fiber producer, accounting for about 33% of the annual world production. Other countries such as France, Germany, Italy, Yugoslavia, Chile, China, Japan, and Peru also produce considerable quantities of hemp fiber [30].

Hemp fiber is one of the strongest and stiffest available natural fibers (Table 2) and therefore has a great potential for use as reinforcement in composite materials. Hemp is a tall and annual crop plant, which is normally ready to harvest in two to three months after seeding [31]. Found in the bast of the hemp plant, these fibers have a specific stiffness that is comparable to that of glass fibers (Table 2) [32].

The hemp fiber's cross-section has an irregular shape, which is not constant through its length [33,34]. The phloem (Figure 1a)contains the primary bast fibers, which consist of a bundle of fibers that runs the full length of the plant stem and is made up of approximately 70–74% cellulose, 15–20% hemicellulose, 3.5–5.7% lignin, 0.8% pectin, and 1.2–6.2% wax [18]. The phloem also contains secondary bast fibers that arise from the cambium [35,36].

Hemp fiber has a multi-celled structure, which can be seen as a composite material with numerous lumens side by side (Figure 1b) [18,28,37]. A typical elementary fiber structure of hemp fiber is shown in Figure 1c. The cell wall of the hemp fiber is multi-layered and consists of the so-called primary cell wall (the first layer deposited during cell development) and the secondary wall (S), which is made up of three layers (S1–3). The elementary fibers are bonded together in the middle lamella by lignin (the concentration of lignin is about 90%). On the other hand, the maximum concentration of cellulose is in the S2 layer, at about 50%. S2 is also the thickest layer and, due to higher cellulose concentration, controls the fiber properties [18,28,38,39].

The bond between the fibers is loosened through a microbial process called retting [40]. After the retting processing, the fibers are separated from the hemp stem mechanically or manually [41].

Thamae et al. [28] studied the effect of the retting condition and duration, mercerization with NaOH, and hydrothermal treatment on the tensile properties of hemp fibers. They reported that both mercerization and hydrothermal treatment modified the hemp's surface morphology improving their mechanical properties, which might be related to its microstructure arrangement. The retting processing for up to three weeks did not affect the tensile strength of the hemp fibers.

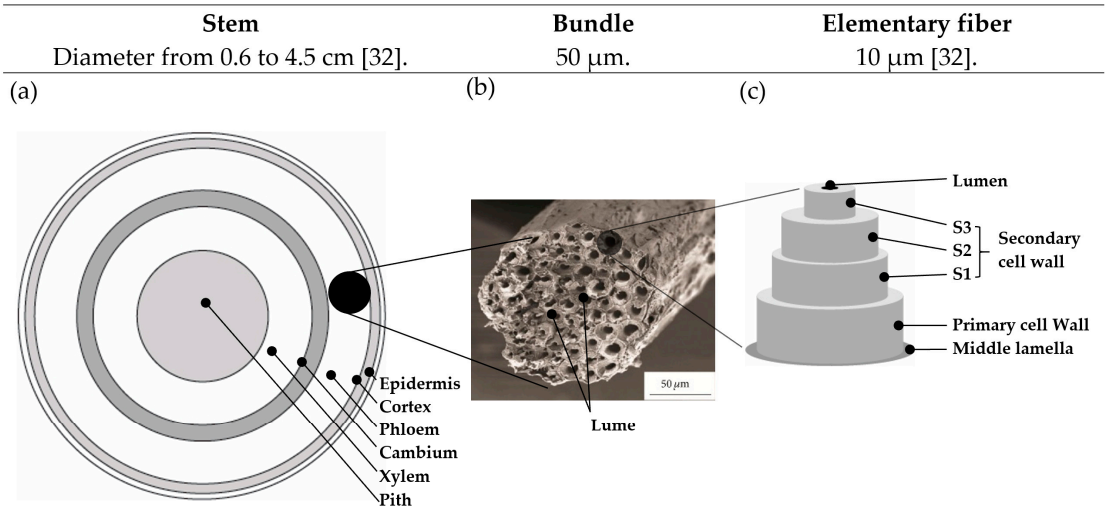

Figure 1. Structure of hemp fiber: (**a**) transverse hemp stem section (adapted from [42]), (**b**) cross-section morphology of the hemp fiber bundle [37], and (**c**) schematic depiction of hemp elementary fiber (adapted from [38]).

The effect of temperature on the mechanical properties of hemp fibers was studied by Teixeira et al. [43]. It was observed that hemp fibers' tensile strength increased (approximately 18%) when they were exposed to 100 °C for 24 h, whereas the Young's modulus decreased. At 200 °C for 24 h, hemp fibers became fragile and brittle with a decrease in mechanical stiffness. Shahzad [44] evaluated the physical and mechanical properties of hemp fibers. He observed that the thermal degradation of hemp was around 150 °C, the decomposition of hemicelluloses and pectin occurred at around 260 °C, and that of cellulose started at 360 °C. Moreover, it was found that the cross-section of hemp fibers was polygonal and the tensile strength of a single hemp fiber (mean fiber width of 67 ± 26 μm) was 277 ± 191 MPa, as well as a tensile modulus and a strain to failure of 9.5 ± 5.8 GPa and 2.3 ± 0.8%, respectively.

3. Hemp Fiber-Reinforced Composites

When two or more different materials are combined in order to produce a new engineered material, they are called composite materials. In general, this refers to a matrix material which is reinforced with fibers [45]. The mechanical properties of composite materials, depend on the dispersion and distribution of reinforcements, the interfacial adhesion between matrix and reinforcements, the material's mechanical properties, the fiber surface modification, the fiber dimension and orientation, volume fractions, and test conditions [6,8].

Hemp fibers have been used to reinforce materials for more than 1000 years [1]. Low prices and the steadily increasing performance of technical and standard plastics have resulted in a renewed interest in hemp fibers. Currently, the interest in hemp fiber composites is growing both in terms of their industrial applications and fundamental research as they have the potential to replace synthetic fibers as reinforcement materials at a lower cost and with a better environmentally friendly approach to product making [46]. Wambua et al. [47] tested and compared the mechanical properties of sisal, kenaf,

hemp, jute, coir fibers, and glass fiber-reinforced polypropylene composites. The composites reinforced with hemp fibers displayed the highest (52 MPa) tensile strength, whereas the coir composites displayed higher impact strength. Some specific properties of hemp fiber composites were found comparable to those of glass fiber. The advantages and disadvantages of hemp fiber composites are summarized in Table 3 [19].

Table 3. Advantages and disadvantages of hemp fiber-reinforced composites. Data from: [4,11,19].

Advantages	Disadvantages
Low density, high specific stiffness and strength.	Lower durability when compared with synthetic fiber, but can be improved through chemical and physical treatments.
Are from a renewable resource, therefore little energy is required for their production.	High moisture absorption, which results in swelling. Dimension instability.
The production costs of natural fibers are lower than those for synthetic fiber.	Lower strength.
Low health hazards during the manufacturing processes.	High variability of properties such as growth condition, harvesting methods, and maturity.
Low emission of toxic fumes when subjected to heat and during incineration at end of life.	Matrix options are limited due to lower processing temperatures.
Are less abrasive to processing equipment than synthetic fibers.	Poor matrix-fiber interfacial adhesion.
Good thermal and acoustic properties.	Flammable, sensitive to UV, microbial, and fungus attack.

Long-term performance or durability is one of the major concerns to be considered for hemp fiber-reinforced composites in outdoor applications. Weathering conditions such as humidity, temperature, and UV radiation impact adversely on the service life of the composite. In addition to that, under constant stress, hemp fiber-reinforced composites are more vulnerable to creep than glass fiber-reinforced composites. These factors hinder the acceptance of hemp composite products industrially. To overcome the detrimental effects of weathering conditions, the properties of hemp fiber composites are usually enhanced by using coupling agents, UV absorbers, etc., during the manufacturing process [48].

3.1. Thermoplastic and Thermoset Polymeric Matrices

The role of the matrix is to protect the fibers from the environment and pack them in a fixed arrangement, transfer the loads to the fibers, as well as govern the composite shape and surface appearance [45]. The properties of the matrix will also determine the maximum service temperature, moisture and chemical resistance, and thermal stability. The most common matrices currently used in hemp fiber composites are polymeric, both thermoplastic and thermoset, as they are light weight and can be processed at low temperature [20]. Table 4 presents the properties of thermoplastic and thermoset polymeric matrices used for hemp fibers [23].

Table 4. Properties of thermoplastic and thermoset polymers used for hemp fibers. Data from: [4,7,8,23,49].

Polymer	Price (kg) (USD)	Density (g/cm^3)	Failure Strain (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Glass Trans. Temp. (Tg °C)	Melting Temp. (Tm °C)
Thermoplastics							
PP	1.65	0.89–0.92	20–400	30–40	1.1–1.6	−10 to −23	161–170
HDPE	1.76	0.94–0.96	2–130	14.5–38	0.4–1.5	−100 to −60	120–140
PS	2.14	1.04–1.06	1–2.5	25–69	4–5	100	110–135
PLA	2.42	1.21–1.25	2.5–6	21–60	0.35–3.5	45 to 60	150–162
Thermosets							
Epoxy	-	1.1–1.4	1–6	35–100	3–6	60 to 170	-
Polyester	-	1.2–1.5	4–7	40–90	2–4.5	−47 to 120	-

3.1.1. Thermoplastic Matrices

Both linear and branched polymers are thermoplastic, which means that they can be melted or softened and reversibly hardened as a function of temperature [50]. Natural fibers generally have a higher modulus than thermoplastics, thus the combination of both may result in a higher modulus [51]. Melt compounding and melt pressing are the processing techniques used the most for hemp fiber composites. The melt compounding processing technique includes a single- or twin-screw extruder and an internal melt mixer, which can be used alone or in combination. Melt pressing is generally used with loose chopped fiber or mats of short or long fiber. The fibers are stacked alternately with thermoplastic matrix before pressure and heat are applied. Good quality composites can be produced by controlling viscosity, pressure, holding time, and temperature, taking into account both the fiber type and the matrix [11,52].

The most extensively studied thermoplastic matrices are polypropylene (PP), polyethylene (PE), polystyrene (PS), and polylactic acid (PLA) [11,52]. Polypropylene is used the most as a thermoplastic matrix for natural fiber composites, due to its low density, low cost, processability, tensile strength, and heat and corrosion resistance compared to other thermoplastic matrices. However, the lack of interfacial adhesion of PP (hydrophobic) with the hemp fibers (hydrophilic) is problematic due to its different chemical structure, which may lead to an ineffective stress transfer between both [52]. Coupling agents such as maleated polypropylene (MAPP) for polypropylene have been used to increase interfacial bonding between fiber and matrix [19,24,53,54]. Their extensive use is due to manufacturing economy and effective interaction of the anhydride with the fibers' hydroxyl groups [55].

The effect of maleated polypropylene on the mechanical properties of hemp fiber-reinforced PP composites was investigated by Mutjé et al. [56]. The obtained results were compared with the composites without a coupling agent. The addition of 4% *w*/*w* (with respect to hemp fiber) maleated polypropylene in the formulation with 40 wt % of hemp fibers was reported to have enhanced the tensile strength and flexural strength up to 49% and 38%, respectively.

The melting point of polymeric matrix and the temperature below which the thermal degradation of natural fibers occurs are the main parameters to consider. The higher melting point of some thermoplastics may induce the thermal decomposition of hemp fibers, which most likely occurs at 260 °C in the hemicelluloses and at 360 °C in the cellulose [44]. When fibers are subjected to heat, the physical and/or chemical structural changes are depolymerization, hydrolysis, oxidation, dehydration, decarboxylation, and recrystallization [57]. Polyethylene and polypropylene melt below 200 °C; therefore, both polymers can be used as matrices for hemp fibers [11,20].

Green composites (100% bio-based composites) such as polylactic acid (PLA) have been emerging as a promising thermoplastic biopolymer matrix. PLA has singular qualities, such as good transparency, glossy appearance, and high impact resistance. However, PLA has some limitations, which are associated with its inherent brittleness and poor toughness as well as low melt viscosity, high price (Table 4), and its decomposition nature, when considering long-life applications [58,59]. The high price makes PLA unaffordable even for large-scale productions. As an example, while PLA has a higher strength than PP, its price is very high. PLA is at least 1.5 times more expensive than PP (Table 4) [59].

3.1.2. Thermoset Matrices

Thermoset matrices are cross-linked polymers and become permanently hard through a reaction with a second component, which is known as a hardener or curing agent. Thermosets are being used for advanced composite applications, such as aerospace technology, insulation materials, and the construction industry due to their high mechanical properties, dimension stability, and chemical resistance [11]. Vinyl esters, epoxies, polyimides, and phenolics are some examples of thermoset composite matrices. Common examples of hardeners are multifunctional amines, anhydrides, and acids [60].

Polyester and epoxy are the sturdiest reinforced thermosets for natural fibers. The processing temperatures (ranging from 25 °C to above 100 °C) are below the degradation temperature of hemp

fibers (that begins around 150 °C) [23]. Therefore, the advantages of thermosets over thermoplastics are processing at a lower temperature, the avoidance of thermomechanical degradation, and a larger amount of natural fibers that can be added to the composite matrix. However, the efficient recycling of thermosets is still a challenge and thermoplastics have also the advantage of providing a greater flexibility in the design [11,30].

Resin transfer molding, sheet molding compound, pultrusion, vacuum-assisted resin transfer molding, and hand layup are the most common processing methods for thermoset composites. Vacuum-assisted methods are used to produce thermoset composites for high-end applications. The advantages of vacuum-assisted methods are the following: (1) high fiber content laminates, (2) lower void contents, and (3) improved fiber wet-out due to pressure [11,61]. Sèbe et al. [62] manufactured hemp fiber-reinforced polyester composites using resin transfer molding (RTM). They obtained good quality parts with high flexural properties. However, the impact strength of these materials was found to be fairly low to compete with glass fiber in structural applications.

3.1.3. Recycling of Thermoplastic and Thermoset Polymeric Matrices

Recyclability is becoming increasingly important. A major advantage of thermoplastics over thermosets is the ability to reuse the material. Thermoplastics can be heated above their melt temperature and reformed into a new shape. The thermoset composites can be recycled by three methods: (1) chemical recycling refers to processes like pyrolysis in which the material is heated in an oxygen-free environment to produce one or more recoverable substances, (2) in particle recycling, the thermoset composite is mechanically milled into particles to be used as a filler in new plastic or composite applications as a replacement for calcium carbonate or talc, and (3) energy recycling refers to the possibility of incinerating the material to recover energy from its organic portion [63]. Similar to thermoset composites, thermoplastic composites can also be recycled by chemical or energy methods as described above. In addition, thermoplastic composites can also be recycled by grinding followed by reprocessing by a number of techniques such as injection molding [64].

Hemp fibers are renewable and can be incinerated at the end of the material lifetime. From an eco-performance point of view, mechanical recycling is favored over thermal recycling in the case of natural fiber-reinforced composites. Problems associated with thermal degradation during recycling and reprocessing may significantly lower the eco-performance of natural fiber composites. Life-cycle assessment studies show that the advantage of natural fibers over glass fibers are mainly related to their low weight rather than recyclability [65].

4. Hemp Fiber-Reinforced Hybrid Composites

Hybridization in polymeric materials can be extended to a blend of one or more polymers reinforced with one or more types of fibers. Hybridization provides new opportunities to broaden the applicability and improve the properties of composite materials, especially in high-end applications [3,7]. Hence, hybrid composites can provide a high stiffness and strength, improve the impact and fatigue resistance, provide high fracture toughness, and simultaneously cut the weight and/or total cost [66,67].

In addition, textile engineering has provided affordable solutions for producing hybrid fabrics, with controlled fiber content, fiber orientation, and roving texture. The most commonly hybrid fabrics used as reinforcement are plain (warp fibers alternately weave over and under the weft fiber in a regular pattern), twill (one or more warp fibers alternately wave under or over the weft fibers and are repeated in a regular manner), and satin (twill weave modified with fewer intersections of weft and warp) [4,68].

Song et al. [69] investigated the mechanical properties of hemp fiber-reinforced PLA composites, with a focus on the viscoelastic and thermal behavior. Twill and plain-woven hemp fabrics were used as reinforcements. The twill fabric was found to be suitable for reinforcing a PLA resin with higher impact strength and better thermal and viscoelastic behavior than the plain woven one, due to fewer intersections and closer packing of the twill fabrics.

4.1. Synthetic and Hemp Fiber-Reinforced Composites

Synthetic and hemp fiber-reinforced composites have been used to enhance the performance and properties of the resultant composite materials as well as reduce moisture absorption and balance the fiber's cost [70]. As suggested by Sature and Mache [31], the reinforcement of natural fibers with glass fibers may work as a skin protection.

Samanta et al. [71] performed a comparative study on hemp/glass fiber and bamboo/glass fiber hybrid reinforced epoxy composites. It was found that hemp/glass fiber hybrid composites have a higher strength under compressive load than bamboo/glass fiber hybrid composites, whereas under tensile load the opposite scenario was observed.

The effects of water absorption on the mechanical properties of hemp and hemp/glass fiber hybrid reinforced polypropylene composites were investigated by Panthapulakkal and Sain [26]. Hemp fiber-reinforced PP composites showed a significant reduction in strength and stiffness due to the absorbed moisture, which resulted in the debonding of the matrix–fiber interface. The hybrid composites had a significantly decreased water absorption by 40%, although the incorporation of glass fiber did not have any significant effect on the strength properties of the aged composites.

Akil et al. [16] studied the effect of water aging on the mechanical properties of pultruded hemp and hemp/glass fiber hybrid reinforced polyester composites. It was observed that the addition of glass fibers reduced water absorption, thus delaying the aging degradation of the hybrid composite material. In addition, the hybrid composites showed a superior strength retention.

4.2. Natural and Hemp Fiber-Reinforced Composites

Natural fibers can be blended with other natural fibers and be embedded in a polymeric matrix to form a hybrid composite. Many researchers have investigated the mechanical properties of natural with hemp fiber hybrid composites [11,68,72]. Chaudhary et al. [73] studied and compared the mechanical properties of natural fiber-reinforced epoxy composites (jute fiber/epoxy matrix, hemp fiber/epoxy matrix, and flax fiber/epoxy matrix) and hybrid composites (jute and hemp fiber/epoxy matrix, hemp and flax/epoxy matrix, as well as jute, hemp, and flax fiber/epoxy matrix). Jute fiber-reinforced epoxy composites have better flexural strength (85.59 MPa), and hybrid composites also showed improvements in mechanical properties, where hemp and flax fiber hybrid reinforced epoxy composites had the highest tensile strength, elastic modulus, and impact strength of 58.59 MPa, 1.88 GPa, and 10.19, kJ/m^2, respectively, while jute and hemp fiber hybrid reinforced epoxy composites achieved the maximum flexural strength of 86.6 MPa.

Similar results were found by Maslind et al. [74] in their research, in which they investigated the effect of water absorption on tensile and flexural properties of hybrid composites consisting of interwoven kenaf/jute and kenaf/hemp yarn-reinforced epoxy matrix. It was observed that the mechanical (tensile and flexural strengths) and water-resistant properties of the interwoven hybrid composites were superior to those of the individual woven composites.

5. Hemp Fiber Surface Modifications

Significant research has been carried out on improving the interfacial bonding between the natural fibers and matrix, which can be divided into three different approaches—hybridization, physical treatment, and chemical treatment [2,4,7]. Hemp fibers contain large amounts of cellulose, hemicelluloses, lignin, and pectin. Consequently, they have hydroxyl groups in their structure and tend to behave as polar hydrophilic material, while polymeric materials are polar due to their hydrophobic, long aliphatic primary chain [2]. The combination of both hydrophilic and hydrophobic materials in the composite processing results in poor matrix–fiber interfacial adhesion, leading to ineffective stress transfer between the matrix and fiber and loss of the composite materials' final properties [4].

Chemical and physical treatments can improve the matrix–fiber interfacial bonding, by changing the surface polarity and increasing fiber roughness, allowing a better wettability of the fibers in

the matrix. In the literature, more research has focused on chemical treatments than on physical approaches with better improvements [19]. Chemical treatment involves the modification of the fiber's hydroxyl and carbonyl groups, introducing other interacting groups that effectively interlock with the polymeric matrix at the interface [75]. Chemical treatments include alkali, acetyl, silane, benzyl, acryl, permanganate, peroxide, isocyanate, titanate, zirconate, and acrylonitrile treatments, whereas physical treatments include corona, cold plasma, ultraviolet (UV), and heat treatment electron radiation [19,76].

Alkali treatment, also known as mercerization, is one of the most used chemical treatments for natural fibers. KOH, LiOH, or NaOH is usually used in the process of mercerization [6,77]. Alkali treatment removes a fiber's chemical constituents, such as hemicellulose, lignin, and pectin, which increases the fiber surface roughness topographies as well as modifies cellulose structure by increasing its crystallinity [40]. Different studies on alkali treatments have reported both improvements in interfacial shear strength, thermal stability, and moisture absorption reduction as well as improvements in the composites' final properties, such as the tensile and impact strengths, elastic modulus, and fracture toughness [19,78,79].

Beckermann and Pickering [80] observed improvements in tensile strength and elastic modulus, lignin and pectin reduction, and higher thermal stability for hemp fibers treated with a solution of 5 wt % NaOH/2 wt % NA_2SO_3. Furthermore, the crystallinity index increased by 4.4% when compared with untreated hemp fibers. The increase in crystallinity index is thought to be due to the removal of lignin and pectin, which allowed a better packing of the cellulose chains [24].

The properties of untreated and alkaline-treated hemp fiber/carbon fiber hybrid reinforced polyester composites were investigated by Ramesh et al. [81]. The mechanical properties of the alkali-treated hemp/carbon fiber-reinforced hybrid polyester composites were found to be superior as well as have long-term moisture resistance as compared with the untreated fibers.

However, at high concentrations of NaOH, Mwaikambo and Ansell [82] and Pickering et al. [24] observed a reduction in thermal resistance and a decrease in strength in the hemp fibers, which were attributed to the degradation of cellulose. Sawpan et al. [83] demonstrated that alkali and silane treatments applied to hemp fiber-reinforced PLA composites improved tensile strength and Charpy impact properties as the result of better wettability of the fibers in the matrix and an increased matrix crystallinity index.

Sullins et al. [54] studied the effects of 5 wt % MAPP (maleated polypropylene), 5% and 10% NaOH-treated hemp fiber, and 5% NaOH + 5 wt % MAPP on the mechanical properties of hemp fiber-reinforced PP composites, with 15 wt % and 30 wt % hemp fiber. It was found that the surface treatments resulted in composites with better mechanical properties compared to the composites without any treatments, and the composites with 5 wt % MAPP showed the best mechanical properties.

Physical methods such as plasma discharges have been comprehensively reviewed by Baghaei et al. [78] and studied by Mwaikambo and Ansell [79]. Plasma discharge can be generated by either corona treatment or cold plasma treatment. The distinguishing feature between the two categories of plasmas is the frequency of the electric discharge. High-frequency cold plasma can be produced by microwave energy, whereas a lower frequency alternating current discharge at atmospheric pressure produces corona plasma. Plasma treatment can result in changes of the fiber's surface characteristics as chemical and mechanical as well as increase the polarity, the surface roughness, and dimensional stability of the fibers. Plasma treatment is an attractive method and has many advantages compared with chemical treatments, such as simplicity, low energy consumption, short treatment times, and low cost, and it does not require water or any potentially hazardous chemicals [80,81,83]. Corona-treated fibers were studied by Ragoubi et al. [84]. It was shown that the corona treatment allowed a greater improvement in the hemp fiber-reinforced PP composites' properties with an enhancement of 32% and 30% of tensile strength and Young's modulus, respectively, to those of untreated corona fibers.

6. Fiber Dispersion, Length, Orientation, and Volume Fraction

Fiber dispersion, length, orientation, and volume fraction in the matrix have a significant effect on the mechanical properties of the composites [2,77]. Increasing the hemp fiber length and/or decreasing its diameter increase the fiber aspect ratio (length/diameter), which induces a positive effect on the mechanical properties of polymer composites [85]. Decreasing the fiber length more than the critical length over which the fiber stress is decreased from the maximum value reduces the stress transfer between matrix and fiber [2].

Ensuring a good fiber dispersion in the matrix results in a better wettability of the fibers with the matrix, reduces the void content by ensuring that fibers are surrounded by the matrix, and also leads to an increase in interfacial bonding between matrix and fibers. The use of a twin-screw extruder with thermoplastic matrices leads to better fiber dispersion; however, this can cause fiber damage and fiber length reduction [20,24].

In injection molding, the fibers are aligned along the flow direction. In this process, the fibers' alignment depends on matrix viscosity, mold design, fiber volume fraction, and fiber length [20]. The best mechanical properties of composite materials are obtained when the fiber is aligned parallel to the direction of the applied load [86]. Large reductions in tensile strength and elastic modulus have been observed with an increasing fiber orientation angle relative to the principal loading direction (on-axis direction). Baghaei et al. [78] investigated the influences of different orientation off-axial directions of aligned hemp fiber-reinforced PLA composites. The results showed that the mechanical properties of the composites were affected by the fiber direction. Tensile, flexural, and impact values of the composites demonstrated a decreasing trend for off-axial composites (fiber orientation angles of 45° and 90°) compared to the principal fiber direction (on-axis direction). The authors' justification for the results was based on the fact that, along the on-axis direction, the composite properties are strongly dependent on fiber and matrix properties, whereas in the off-axis direction the composite properties are controlled by the matrix properties rather than the fiber. Other reported works on natural fiber-reinforced polymeric composites reached the same conclusion, such as in Brahim and Cheikh [87].

The increase in fiber volume fraction leads to high mechanical properties of composite material; however, over a specific value the fiber volume fraction deteriorates the composite's mechanical properties, due to poor fiber distribution and wettability with the matrix [88]. Additionally, water absorption is increased with an increase in fiber content, leading to swelling of the natural fibers and debonding of the matrix–fiber interface as well as deteriorating the mechanical properties of the composite [89,90]. Dhakal et al. [89] studied the effect of water absorption on the mechanical properties of nonwoven hemp fiber-reinforced unsaturated polyester composites, containing 0 wt %, 10 wt %, 15 wt %, 21 wt %, and 26 wt % of fiber. It was shown that moisture absorption increased with fiber volume fraction increases, due to a higher void and cellulose content. Furthermore, the tensile and flexural properties were found to decrease due to the debonding of the matrix–fiber interface.

Extensive studies have been conducted to find the optimum relation between volume fraction and optimal mechanical properties [8]. For injection-molded thermoplastic matrix composites reinforced with natural fibers, the maximum fiber content is usually between 40% and 55 wt % of fiber content [19]. Hargitai et al. [90] found that the optimum volume fraction of hemp fiber-reinforced PP composites was between 40% and 50 wt % of fiber, and Hu and Lim [91] showed that the hemp fiber-reinforced PLA composites with 40 wt % volume fraction of alkali-treated fiber had the best mechanical properties.

7. Industrial Applications

Industrial hemp is being used in a number of industries such as textiles, automotive, composites, fiberboard, heat-insulating materials [25,42], and building construction, for example, in fiber-reinforced concrete [19,25,92]. Tran et al. [93] showed that hemp concrete can decrease daily indoor relative humidity variations and reduce energy consumption by 45% as compared to cellular concrete. Recent

studies have shown that hemp fibers can also be employed for sound insulation and/or sound absorption [94].

New research for hemp fiber applications are in sporting goods or musical instruments due to their higher vibration-damping capacity than that of synthetic fibers [43] as well as reinforcements in brake pad applications. The modified formula for brake pads contains natural hemp fibers and a geopolymer as a fraction replacement for synthetic Kevlar fibers and phenolic resin, respectively [95]. The automobile industry is constantly searching for eco-friendly materials to use in its products; therefore, the most researched and expanding application for hemp fibers and natural fibers, in general, is as reinforcement in polymeric composites in automotive applications, such as those described in Table 5 [27,29,96]. Composites reinforced with natural fibers such as hemp can be an alternative to glass fiber-reinforced composites, because they can be 25% to 30% stronger for the same weight and exhibit a non-brittle fracture on impact, which is an important requirement for interior automotive plastic components [97].

Table 5. Natural fiber-reinforced polymer composite in different automotive applications. Data from: [46,98].

Manufacturer	Model	Application
Audi	A2, A3, A4, A4 Avant, A6, A8, Roadster, Coupe	Trunk liner, spare tire lining, side and back door panel, seat back, and hat rack
BMW	3, 5, and 7 series	Seat back, headliner panel, trunk liner, door panels, noise insulation panels, and molded footwell linings
DaimlerChrysler	A, C, E, and S class, EvoBus (exterior)	Pillar cover panel, door panels, car windshield/car dashboard, and business table.
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156, 159	Door panel
Mercedes Benz	C, S, E, and A classes	Door panels, glove box, instrument panel support, insulation, molding rod/apertures, seat back rest panel, trunk panel and seat surface/backrest
	Trucks	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, and roof cover.
Volvo	V70, C70	Seat padding, natural foams, and cargo floor tray

An increasing number of car models are using natural fiber-reinforced polymeric composites in door panels, instruments panels, engine covers, sun visors, and air filters, and the number of applications are expanding to more structural components such as seat backs and exterior underfloor paneling [20,46].

8. Conclusions

Industrial hemp (*Cannabis sativa*) has been extensively researched over recent years for the development of new materials and is getting more attention as a possible alternative replacement for synthetic fibers. Interest is warranted due to its low density, high specific strength and stiffness, as well as the fact that hemp fibers have a relatively low cost, are from renewable resources, and the wastes are 100% biodegradable. However, the major disadvantages of hemp fibers are their inherited hydrophilic character, low resistance to microorganisms, low thermal stability, and variability in their properties because they depend on growth conditions and maturity.

Advanced research and progress have gone into increasing hemp fibers' mechanical performance through surface treatments in order to improve their wettability and dimensional stability as well as increase the interfacial bonding between matrix and fibers. The most promising application for hemp fibers is as reinforcement in polymeric composites or through hybridization. Hybridization allows the possibility of overcoming the limitations and provides new opportunities to broaden the applicability of hemp fibers in high-end applications. It is worth mentioning that hemp fiber hybrid composites bring a competitive market to various industrial applications.

Industrial hemp is being used in a number of industries such as textiles, automotive, composites, fiberboard, heat-insulating materials, in fiber-reinforced concrete, sound insulation and/or sound absorption as well as in sporting goods or musical instruments or as reinforcements in brake pad applications. However, more research is needed to expand their application range and improve their properties. The biodegradability issue is one problem that must be explored when researching hemp fiber composite applications and considering long life-cycle applications. Another aspect to be addressed is the reproducibility of these composites' final properties.

Author Contributions: All authors contributed extensively to this study, discussed the results and reviews, prepared the manuscript and agreed to the amendments at all stages of the paper.

Funding: The present research work was financially supported and funded by the INTERREG SUDOE NABITEX project: Innovative technical textiles, developed from natural fibers, for application in the habitat, SOE2/P1/P0524.

Conflicts of Interest: The authors declare no conflict of interest.

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