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Extraction and refinement of agricultural plant fibers for composites manufacturing

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ABSTRACT

Because of their excellent tensile properties, low density, and natural abundance, cellulose-based plant fibers are a sustainable and biodegradable alternative for synthetic fibers in fiber-reinforced composite materials. However, the extraction of plant fibers can be costly and difficult to control because the fibers are enmeshed in a complex network of biopolymers (principally lignin, pectin, and hemicellulose), which serve both to strengthen the fibers and to bind them to their parent organism. It is necessary to extract or degrade these biopolymers to produce fine plant fibers without adversely altering the fibers themselves in the process. In particular, it is important that both the molecular weight and the degree of crystallinity of the cellulose in the fibers be kept as high as possible. This article reviews chemical treatments, which have been used to extract and refine fibers both from purpose-grown fiber crops, such as hemp and flax, and agricultural waste such as coconut husks and pineapple leaves. The treatments are discussed in terms of changes in the mechanical properties and surface chemistry of the fibers.

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1. Introduction

Plant fibers are a biodegradable and sustainable substitute for synthetic fibers. They have relatively low density, are abundant in nature, and their tensile properties are comparable to those of glass and carbon fiber. Reviews have already been published on the use of plant fibers as reinforcement in concrete [1,2] and in polymer matrices [3–5]. There have also been considerable studies on the cultivation and cellular structure of plant fibers [6–11].

Virgin plant fibers have several shortcomings which adversely affect their performance in many value-added applications (e.g., in composite materials). Because they are hydrophilic, the fibers do not adhere well to common polymer resins. Their capacity for moisture retention can also lead to void spaces being formed at the fiber−matrix interface. The fibers also swell when wet, which can result in internal stresses developing in materials which contain the fibers. Natural fibers can also be difficult to refine because of the pectin- and lignin-rich gum which binds clusters of fibers together. If this gum is not removed, it can be difficult to disperse individual fibers during compounding.

A wide array of treatments has already been applied to plant fibers to make them suitable for use in a variety of roles, most notably in the production of paper [12–14], textiles [15,16], and high-voltage insulation [17]. Treatment of plant fibers to improve their performance in composites is a subject which has received relatively poor attention. Moreover, the body of academic literature on plant fibers contains relatively little discussion of how the performance of composite materials is affected by a given fiber treatment. This review presents the effects of chemical and enzymatic refining processes on the cellular structure and composition of plant fibers in the context of their use in composite materials.

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2. Plant fiber–reinforced composites

2.1. Plant fibers as substitute for glass fiber

Fiber-reinforced composites (referred to here as FRCs) contain rigid fibers, which are responsible for the tensile strength of the material, contained in a polymer matrix which can easily be molded to a desired shape and transfers stresses to the embedded fibers. The fibers must be very stiff, so they are typically made from a material with high elastic modulus and tensile strength. Table 1 compares the tensile strength, modulus, and density of some commonly used fiber reinforcements with other common building materials for reference. The polymer matrix which coats the fibers tends to be significantly weaker but protects the fibers from wear and degradation and distributes load evenly across the array of fibers.

2.2. Fiber–matrix interaction

The performance of FRCs also depends on strong fiber–matrix adhesion [22]. If adhesion is poor, then the fibers will be more likely to aggregate during compounding rather than dispersing in the matrix. Void spaces are also more likely to form at the fiber–matrix interface. Both of these phenomena result in reduced surface contact, and therefore less efficient stress transfer, between fiber and matrix. This is a considerable problem for plant fibers because their hydrophilic surface chemistry is incompatible with many commodity polymers [22].

Several review articles describe thus 'pretreatments' for plant fibers to improve their interaction with polymer matrices [23–25]. The effects of compounding on the morphology of composites have also been reviewed [26]. There are also reviews of composites with specific plant species, including bamboo [27], kenaf [28], and flax [29].

2.3. Moisture retention

Because they are hydrophobic, plant fibers absorb a significant amount of moisture. For instance, hemp fibers have been shown to retain more than 40% of their dry volume in water [30]. If fibers are not suitably dried prior to compounding, the moisture can form a barrier between fiber and matrix, thereby preventing effective adhesion between the two phases. Water droplets can also cause void spaces to form within the polymer which weaken the resulting material [31]. Composites produced with improperly dried fibers also have lower tensile strength and elastic modulus [32]. Fiber-reinforced composites are also sensitive to moisture after compounding; a flax–polyester composite which was stored in a humid environment had a lower elastic modulus and tensile strength, even after being dried [31].

2.4. Improving the performance of plant fibers

To summarize, plant fibers could be used in FRCs as a sustainable and biodegradable substitute for glass fibers. They can be harvested at low cost and have suitable mechanical properties for this application. However, their poor adhesion with conventional bulk polymers is a substantial barrier to their use in the manufacture of composite materials. The surface chemistry of the fibers can also cause them to absorb large quantities of water, which can be detrimental to FRC behavior.

To more effectively prepare plant fibers for use in FRCs, a process is needed which produces plant fibers of high aspect ratio with hydrophobic surface chemistry, without degrading the desirable tensile properties of the material. To understand how the fibers behave in response to proposed treatments, it is necessary to examine the structure and composition of the fibers.

3. Physicochemical and morphological characteristics of plant fibers

3.1. The structural approach

Apart from cotton, all intensively cultivated plant fibers are structural fibers from either the leaves of monocot plants, such as sisal or abaca, or from the bast of dicot plant stems. Hemp and flax, the principal textile fibers in Northern Europe, are bast fibers. In both cases, these structural fibers have a role in the plant which is analogous to that of the skeleton in vertebrates. The fibers are an aggregate of many long, thin, rigid cells called sclerenchyma cells, also called 'ultimate fibers' or 'elementary fibers'. Once they reach their final dimensions, mature sclerenchyma cells develop a thick, cellulose-rich secondary wall that greatly augments the mechanical properties of the fibers. Soon after the secondary wall is complete, the cell dies. Inside the secondary cell wall, the space formerly occupied by the cytoplasm becomes a hollow center cavity called the lumen. This hollow cavity reduces the overall density of the fibers and increases their capacity for water retention. The secondary wall is itself divided into three layers, denoted S_1, S_2, and S_3, with 'S' standing for secondary and the subscript referring to the order in which the layers develop [33], so that S_1 refers to the outermost layer and S_3 the innermost. S_2 makes up the majority of the thickness of the cell wall, contains more cellulose than the other two sublayers, and is structurally the most important segment of the cell wall.

Each layer of the cell wall contains an array of thin strands of semicrystalline cellulose called fibrils. The fibrils are coated with an amorphous layer of hemicellulose and pectin. This layer serves both to prevent the fibrils from aggregating and to connect cellulose to the complex web of

Table 1
Tensile strength, modulus, and density of selected fibers [18–21].

Fiber	Elastic modulus (GPa)	Tensile strength (MPa)	Density (g/ml)
E glass	73	2400	2.55
Kevlar 29	70.5	2920	1.44
1080 Steel	207	2550	7.9
Nylon 66	3.5	85	1.14
Hemp	70	550–900	1.48
Flax	60–80	800–1500	1.4
Sisal	38	600–700	1.33

lignin that fills in the spaces between fibrils [34,35]. The fibrils are in turn composed of many cellulose microfibrils running in parallel. Each microfibril is a semicrystalline cable of several dozen cellulose molecules.

The fibrils wind around the cell in a helix which climbs the major axis of the fiber cell like the thread of a screw (Fig 1). The pitch angle of this helix is the same for every fibril in a given cell wall, but this angle varies from layer to layer and from species to species. In other words, every organism has a distinct pitch angle for each layer of its sclerenchyma cells. This pitch angle is called the microfibrillar angle (or MFA) and determines the mechanical properties of the cell. A small MFA (for instance in hemp, jute, and flax) means that the helix is steep, so the orientation of the fibrils is closer to being parallel with the length of the cell, while high MFA (i.e., cotton, coir) indicates a flatter pitch angle [3,18,31,36–38]. As the fibrils become more aligned with the length of the cell, they increase the tensile modulus of the fiber along this axis. Consequently, a fiber composed of cells with low MFA will have higher axial tensile modulus than a fiber composed of cells with high MFA, all other things being equal.

Every species has a characteristic MFA, and each layer of the cell wall in a given species will also have its own MFA. Frequently, the MFA layer of the S_2 layer is the only one to be reported since this sublayer makes up the majority of the cell wall thickness and contains the majority of the cellulose. S_2 also tends to have a much lower MFA than the other layers of the cell wall, meaning that it plays a larger role in determining the tensile strength of the fiber. S_1 and S_3 tend to have relatively flat MFAs.

3.2. Cellulose crystallinity

The relationship between MFA and elastic modulus demonstrates the critical role of cellulose microfibrils in the structure of fiber cells and by extension of cellulose. The remarkable stiffness of cellulose microfibrils is in part due to their relatively high degree of crystallinity. Cellulose forms at least four different crystal structures. Biologically synthesized cellulose forms crystals of cellulose I, also called native cellulose. This is the stiffest cellulose crystal polymorph, with a theoretical modulus of 134 GPa, higher than that of aramid fiber [39,40]. Although cellulose II has a modulus of only 90 GPa, it is more thermodynamically stable than cellulose I. Consequently, when cellulose I
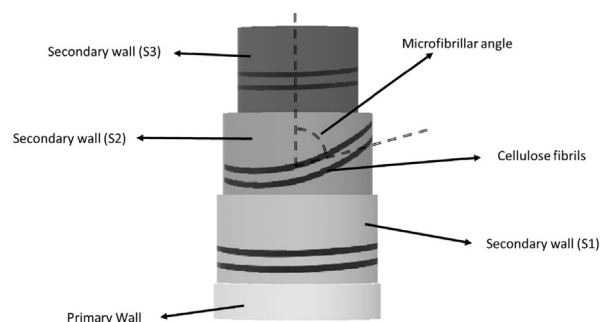
swells or dissociates in a solvent, it will recrystallize as cellulose II. Cellulose II is also formed after immersion in concentrated sodium hydroxide or nitric acid or through the action of certain bacteria. Its formation is irreversible [16,41,42]. Cellulose III and IV are not frequently encountered in practice. They are formed reversibly from either cellulose I or II under specific conditions. If cellulose is exposed to ammonia or certain other amines, it forms crystals of cellulose III upon drying. If cellulose III is then heated to 260 °C in glycerol, it then converts to cellulose IV. Both polymorphs return to the structure of the untreated cellulose when stored in a hot and humid environment [42].

The remarkable stiffness of cellulose crystals is derived from the number of hydrogen bonds that form both along a given chain and between neighboring chains. Each glucose unit in the molecule contains three hydroxy groups, so a typical cellulose chain will have tens of thousands of hydroxy groups, each of which represents a potential hydrogen bond. The effect of hydrogen bonding can be seen when comparing the lattice structure and modulus of different cellulose crystal structures [41].

3.3. Cellulose reactivity and degradation

As with all polymers, the tensile strength of cellulose fibrils increases with increasing molecular weight [43,44]. It is therefore important to consider how (pre)treatments on plant fibers affect the molecular weight of the cellulose they contain. If too much degradation occurs, the polymer becomes brittle. In the conditions under which the fibers are likely to be treated, cellulose is most likely to be degraded via hydrolysis of the glycosidic bond which links together the glucose molecules in the cellulose chain. Cellulose also degrades through oxidation when exposed to bleach, peroxide, or ozone or through pyrolysis at high temperature.

The study of cellulose degradation is most well developed in conditions which are relevant to specific industrial processes. For instance, since kraft paper is used as an electrical insulator in high-voltage electrical transformers, the kinetics of cellulose oxidation have been studied at the operating temperature of these transformers (approximately from 80 °C to 120 °C) in paraffin or naphthenic oil [17]. Cellulose is also digested to produce small molecules such as ethanol and glucose. Tremendous research efforts have been carried out by many researchers and research teams to identify the optimal conditions for hydrolysis [45,46]. By comparison, the study of plant fibers in structural applications contains relatively little study of cellulose degradation. It is much more common to evaluate treatments on plant fibers in terms of mechanical properties. Consequently, cellulose degradation during fiber treatment must be extrapolated from kinetic studies of hydrolysis which were intended to improve conversion of cellulose to small molecules.

Cellulose hydrolysis has been studied in a variety of acids and bases for efficient production of glucose. Acid-catalyzed hydrolysis of cellulose has been modeled using a first-order unimolecular reaction equation whose rate increases exponentially with increasing proton activity as

Fig. 1. Cellulose fibrils wind in sclerenchyma cell walls.

described by the Hammett parameter. Using various glycosides as small-molecule analogs for cellulose, the activation energy for acid hydrolysis of the glycosidic bond has been estimated to be approximately 144 kJ/mol [47]. However, the hydrolysis of cellobiose (i.e., a glucose dimer connected through a (1−4)-B-D-Glucosidic bound) at 200 °C was found to be independent of acidity above pH 4 [48].

Cellobiose was also used as a small-molecule analog for cellulose to study base-mediated hydrolysis. The activation energy was found to be approximately 120 kJ/mol of cellobiose in 0.1 N and 0.01 N aqueous solutions of sodium hydroxide between 60 °C and 85 °C. At 85 °C and 0.01 N sodium hydroxide, the pH rapidly decreased during the reaction, indicating that the reaction yielded a significant quantity of acid products which curtailed the reaction. The same reaction at 66 °C did not experience such a precipitous change in pH [49]. Unlike in acids, however, cellulose crystallinity can change in alkaline media. Consequently, it is more difficult to extrapolate cellulose degradation from small-molecule experiments at high pH because steric factors are more difficult to predict [50]. In fact, an investigation of the degradation of cellulose under alkaline conditions found that below 170 °C, base-mediated hydrolysis of the glycosidic bond is essentially negligible. Instead, degradation principally occurs through a step-wise 'unzipping' or 'peeling' mechanism, in which the monomers at the end of the chain are cleaved one-by-one in a chain reaction [51]. This peeling reaction is observed in cotton fabrics during scouring, a chemical cleaning process that consists of boiling the fabric in aqueous sodium hydroxide [52]. At room temperature, alkaline hydrolysis of cellulose is marginal.

Cellulose can also degrade when exposed to oxidizing agents such as peroxide or bleach (which are frequently used to remove lignin). In the presence of oxidizing agents, degradation probably occurs as a result of the oxidation of hydroxy groups on the cellulose chain, yielding aldehydes or ketones. A number of subsequent elimination reactions are then possible, including elimination of the glycosidic bond, which results in bond scission [14].

3.4. Role of other biopolymers in plant fibers

Like cellulose, pectin and hemicellulose are polysaccharides, meaning they are chains of sugar molecules (and in the case of pectin sugar acids). As a class, polysaccharides are relatively hydrophilic by virtue of the alcohol and carboxylic acid functionality they contain. Unlike cellulose which is entirely composed of glucose, hemicellulose and pectin both contain many different sugars and so are more 'irregular'. Consequently, these polymers do not crystallize and are more highly branched than cellulose. Also, both polymers tend to have much lower average molecular weights than cellulose.

The principal role of hemicellulose in fiber cells is as a crosslinker between cellulose fibrils and the other components of the cell wall such as pectin and lignin. Because of its low molecular weight and irregular structure, hemicellulose typically does not have a high degree of crystallinity and therefore its mechanical properties are inferior to those of cellulose fibrils. Because they are polysaccharides, hemicellulose polymers also have a large number of hydroxy groups which render them hydrophilic. In combination with their low degree of crystallinity, this means that hemicellulose retains a significant degree of moisture, since water molecules can easily infiltrate the polymer's irregular structure. For the same reasons, hemicellulose can be hydrolyzed more easily than can cellulose because dissolved catalysts can permeate into the former more easily than the latter. In practice it is not difficult to extract hemicellulose, for instance, by using warm water and dilute acid or base, while leaving the cellulose fraction of the fiber more or less intact.

Pectin is distinct from hemicellulose because unlike the latter it contains galacturonic acid. Pectin acts as a binding agent in the cell wall and in the amorphous layer which binds together adjacent fiber cells, called the middle lamella. It is this lamella which must first be degraded to break apart bundles of fiber cells into individual fibers. Like cellulose and hemicellulose, pectin forms hydrogen bonds as well as covalent ether and ester linkages and can also form a very specific type of ion bridge if calcium ions are present. This ion bridge can be formed by chains of galacturonic acid monomers, which are effective chelating agents. When neighboring pectin molecules contain long sequences composed purely of galacturonic acid, the acid monomers often form a series of parallel ion bridges, forming a structure which is frequently called the 'egg-box structure' [53–55].

On the other hand, lignin is a complex, branched network composed of phenylpropyl groups connected by ether bonds. Lignin is produced in mature sclerenchyma to fill the space between cellulose fibrils. Lignin is much more hydrophobic than any of the polysaccharides in the cell wall, so its accumulation is associated with increased hydrophobicity and reduced permeability. By filling the space between cellulose fibrils, lignin also serves to make the cell more rigid, although it does not appear to improve the tensile properties of the fiber [56]. Because it is aromatic, lignin reacts under ultraviolet light and in the presence of radicals. When exposed to heat and light, textiles containing lignin have reduced breaking tenacity and extension compared to textiles produced from lignin-free cotton [57]. The embrittlement of aging paper is attributed to the degradation of lignin, although recently it has been determined that the acidity of the manufacturing process plays a more important role in the aging of old books [58].

4. Fiber treatments

To convert plant fibers from raw plant material into effective reinforcement agents, it is necessary to reduce their hydrophilicity and water retention and to improve compatibility with a given polymer matrix. In addition, the treatment must not degrade the molecular weight of cellulose, reduce its degree of crystallinity, or convert it to a weaker crystal polymorph. A wide variety of treatments on plant fibers have been reported in literature, but at present, there does not seem to be a single treatment which accomplishes all of these objectives simultaneously.

4.1. Separation processes

4.1.1. Decortication

In this case, a fiber is separated from (mostly waste) biomass (referred to as 'shive') using a combination of shear stress and impact force, which breaks apart the relatively weak shive while leaving the fibers intact. This kind of decortication is typically used for hemp shives, side-products made from hemp.

Usually, industrial decortication is accomplished either using a hammermill to pulverize the shive or by feeding the plants through an array of blades which scrape off unwanted material. Because decortication processes tend to be proprietary, there is not very much publicly available literature on their operation.

Decorticated fibers still contain a large quantity of pulverized shive entrained in a tangled mass of fibers. The fibers must be cleaned by passing between opposing arrays of pins or blades and through the use of vibration to shake out particles bound to the fibers. Finer shearing arrays are also used to comb away additional shive and to separate fiber aggregates into finer strands. Ultimately, the process is intended to yield a mass of fine, clean technical fibers. In the textile industry, these fibers are separated into two broad categories, called 'tow' fibers and 'line' fibers, based on their response to carding—a process in which the fiber is embedded in a stationary bed of pins and sheared by a second moving set of pins. The shorter fibers which are entrained in the moving pins are designated tow fiber and are less valuable for textile applications, while the fibers which remain embedded in the stationary pins are the longer line fibers [59]. Recently, modern fiber processing plants have been reported by several different groups of inventors [59–61]. These processes demonstrate the potential in the near future for renewed industrial-scale production of plant fibers.

4.1.2. Retting

The effectiveness of decortication is predicated on poor bonding between fiber and shive. If the fibers are still tightly bound to the rest of the plant, then greater effort is needed to separate the fibers. Therefore, fiber plants are usually pretreated to selectively degrade binding agents prior to decortication. These pretreatments are collectively referred to as 'retting'. In practice, retting primarily consists of the removal of pectin from the fibers [62,63]. Conventional retting consists of exposing the plants to naturally occurring enzymes that digest the noncellulosic matrix which binds the fibers to the rest of the plant. Some nonenzymatic retting processes have also been explored. These are less well developed than the traditional enzymatic methods.

4.1.2.1. Water retting. Until the 1950s, the preferred method for retting flax was water retting—immersion of the fiber plant in a pool of water or a river to allow naturally occurring organisms to degrade the plant matrix. Water retting uses relatively little energy but it is labor-intensive and environmentally problematic. A significant volume of wastewater is produced from this process, so to reduce water pollution many countries have banned water retting in favor of dew retting, which is also sometimes called field retting [64]. However, water retting continues to be used in some jurisdictions including Hungary, Serbia, and China, since this process is more easily controlled than economically viable alternatives [30,65].

4.1.2.2. Dew retting. Dew retting, the principal alternative to water retting, is not much more sophisticated than its predecessor; the stalks are cut and pressed to remove the seeds and then left on the ground to decay. The process is difficult to control because the rate at which retting proceeds is governed by meteorological conditions and the soil on which the retting occurs. A relatively large degree of variance is observed in dew-retted stocks, so naturally a greater proportion of the stalks will either be over-retted, meaning that the cellulose fibers have degraded, or under-retted, meaning that the gums which bind fiber to shive are not completely removed [66]. Under-retted fibers tend to be stiffer and lighter in color, while over-retted fibers take on a darker color, eventually turning black. The diminished control of the extent of retting of dew-retted fibers means that these tend to yield more tow fiber than water-retted fiber. To improve the reliability of the retting process, more sophisticated retting processes began to be explored from the beginning of the 1980s [67].

4.1.2.3. Stand retting. Stand retting is a potential improvement on dew retting which was explored by researchers in Northern Ireland in the 1980s. It consists of spraying the still-standing plants with a water-borne desiccant a few weeks after mean peak flowering. The desiccant dries out the plant tissues and degrades the noncellulosic tissues, effectively retting the still-standing plant. The fibers recovered from stand-retted plants are more uniform than those recovered from dew-retting [66]. However, the literature on stand-retting appears only to have studied the effect of one desiccant, namely the trimesium salt of the glyphosate [64,66–70]. The use of the trimesium salt apparently stems from the degree of wetting which is achieved—similar experiments using other formulations of glyphosate had uneven results because the compounds were not able to evenly coat the plants [68]. Recently, the International Agency for Research on Cancer classified glyphosate as 'probably carcinogenic to humans' [71], and there is some concern that stand retting will increase dietary exposure to the herbicide because glyphosate must be applied for a relatively short time before harvest [72].

There do not appear to have been stand-retting trials with other desiccants. It may be possible that the researchers decided that the treatment was too costly relative to dew retting or that it produced too much pollution in water runoff.

4.1.2.4. Controlled enzymatic retting. Another improved retting process is so-called enzymatic retting, in which the cut stalks are mixed with a specially composed enzyme mixtures tailor-made to attack specific components of the plant to more efficiently separate fibers from shive [73]. These enzyme mixtures usually contain chelators (often

ethylenediaminetetraacetic acid) to extract calcium ions from plant cell walls to facilitate pectin extraction. One characteristic of pectin networks is that they contain ionic crosslinks (also called ion bridges) using calcium ions [54]. In the absence of calcium ions, the bonding between neighboring pectin molecules is weakened, and they are more easily dissociated [74]. This is especially important in species such as flax or hemp, where the lignin content is very low and pectin is the principal member of the noncellulosic matrix in the primary cell wall and middle lamella. These mixtures tend to be expensive, so there is a strong incentive to reduce the quantity of enzyme required per unit mass of retted fiber. It has been demonstrated that the volume of retting solution could be significantly reduced by spraying stalks with enzyme solution instead of immersing them in a tank and by crimping stalks with a fluted roller so that the solution could more easily permeate through the protective skin of the plant [75]. In an improved configuration of their process, the stalks are sprayed to soaking, placed in a rotating drum for 2 min to distribute the enzyme solution and then incubated under damp burlap at 40 °C for 24 h, after which the fibers were rinsed in water and then dried at 50 °C [76]. The process yielded slightly finer fibers that could be produced through dew retting of the same flax in higher yields. Micrographs of flax stalks in cross sections also showed the fibers to have been loosened by the process.

4.1.2.5. Retting by heat-treatment: the Duralin process.
Yet another alternative to retting is the Duralin process, a nonenzymatic process which can be used instead of retting to debond fibers from shive. Stalks are pressure-cooked in water at temperatures ranging from 160 °C to 180 °C for about 15 min, causing the noncellulosic polymers to hydrolyze to low molecular weight. The stalks are then dried and then re-heated to between 150 °C and 180 °C either in air or dry steam, at which temperature they are held for anywhere from half an hour to several hours to cure the fibers [77,78]. During the curing process, the degraded noncellulosic molecules condense as a layer on the surface of the fibers. Because of this surface layer, the fibers absorb less moisture and do not swell when wet, unlike retted fibers [78]. Duralin fibers were found to separate from shive more easily than dew-retted fibers, reducing the cost of mechanical separation processes [77].

The resin layer that cures on the surface of Duralin fibers is an important difference between these fibers and those produced by retting. Most importantly, the reduced moisture uptake of the fibers causes them to be more resistant to enzymatic degradation and to swelling [77]. Electrokinetic studies have also demonstrated that Duralin fibers are significantly more hydrophobic than retted fibers [79]. It is possible that increased hydrophobicity might improve the compatibility of these fibers with some polymer matrices, although it has been shown that Duralin-treated flax fibers may actually have a weaker interfacial bond with unsaturated polyester and low-density polyethylene than do dew-retted flax fibers [80]. However, Duralin fibers do have a higher elastic modulus than dew-retted fibers [81], probably due to the increase in crystallinity which was observed in fibers after Duralin treatment [77].

4.1.3. Steam explosion
Finally, steam explosion has been explored as a substitute for retting [82–85]. As the name suggests, steam explosion is a process through which lignocellulose can be degraded by the action of saturated steam at high pressure and temperature as well as by the shear forces incurred by rapid depressurization and expansion of the steam. The process is more frequently discussed as a way to facilitate conversion of lignocellulose to glucose [46], but there is no reason why the process cannot be used to separate fibers from shive. Depolymerization of cellulose fibers during steam explosion may be a concern because at sufficiently high temperature, the steam can convert some components of hemicellulose into weak acids which catalyze hydrolysis of cellulose chains [86]. However, under conditions which are not sufficiently severe, the shive is not completely disaggregated thereby requiring further separation. Despite these constraints, steam explosion of flax is reported to have been successfully optimized for the separation of fibers. These fibers were found to be more tenacious, have better elongation and homogeneity, and produce fewer spinning breaks than so-called 'cottonized' (i.e., mechanically separated) fibers [84].

4.1.4. Other literature on retting
Academic discussion of retting appears to be almost entirely based on the study of flax and hemp. There is almost no study of the response of hard fibers (i.e., monocot leaf fibers) to retting, and what little literature exists is of dubious quality [87–90]. Otherwise, studies of the mechanical properties, industrial processing, or harvesting of hard fibers tend either to use very rudimentary retting apparatus or none at all, and the retting process is only mentioned briefly [8,91,92]. This may be in part because hard fibers are significantly more rigid than soft fibers (i.e., bast fibers), so accordingly they can tolerate much more severe mechanical separation processes [93]. One can presume some similarities between retting of hard fibers and soft fibers, but it is likely that the chemical composition and architecture of each species of plant is sufficiently different from others that many of the techniques which have found success with flax and hemp will need significant modification to be effective in retting fibers from other species of plants.

4.2. Fiber refining

4.2.1. Mercerization
Mercerization was originally developed to improve the tenacity of cotton [15] but has since been used extensively on fibers from many species of plants [25,94,95]. The process consists of immersing the fibers in an alkaline bath, usually aqueous sodium hydroxide, for several hours then washing the fibers to neutral pH and drying them. The process is intended to improve the extension-to-break and tensile strength of the fibers and is also an efficient way to remove hemicellulose from fibers. The removal of hemicellulose may improve fiber−composite interactions because mercerized fibers have increased surface roughness and greater cellulose exposure (meaning more potential fiber−matrix bonding sites) [96].

During mercerization, alkaline solution reduces the number of protons available for hydrogen bonding and also mediates hydrolysis. The diminution of hydrogen bonding weakens the forces holding cellulose fibrils together. As the binding forces weaken, individual cellulose molecules begin to dissociate, the fibril is permeated by the solvent, and the fibril swells significantly. This permits a greater surface of the fiber to be accessed by solvent but also disrupts naturally occurring crystallinity; an irreversible transition in cellulose crystal structure is reported for mercerization treatments above a critical alkali concentration, reportedly 6 wt.% for sodium hydroxide [97,98].

After mercerization, the cellulose chains which had become disordered in alkaline solution recrystallize as cellulose II, which is more thermodynamically stable than the cellulose I allomorph which naturally occurs in plant fibers. This conversion has a significant influence on the mechanical properties of the mercerized fiber, since cellulose II crystals have a Young's modulus of 90 GPa, while that of cellulose I crystals is 140 GPa [40,99,100]. It is supposedly possible to mercerize fibers with only a very dilute solution of sodium hydroxide to avoid producing cellulose II, but this phenomenon has only been reported in one experiment, so it may be premature to make definitive conclusions about the phenomenon [101].

The loss of elastic modulus is offset by increased tensile strength and extensibility after mercerization, probably because of the dissociation–recrystallization process that occurs as a result of mercerization. This phenomenon may eliminate naturally occurring defects in the fiber, thereby improving its strength and extensibility in a manner somewhat analogous to an annealing process. This explanation is consistent with the marked increase in crystallinity which is observed in mercerized fibers [102].

In alkaline solution, pectin and hemicellulose undergo base-mediated hydrolysis and dissolve. As they dissolve, more of cellulose fibrils become exposed. Hemicellulose and pectin are strongly hydrophilic, so their removal can also reduce the water retention of mercerized fibers. Finally, the removal of these polymers also increases the porosity of the fibers. The alkaline solution also hydrolyzes some lignin bonds but is unable to extract lignin from fibers at anywhere near the extent that it extracts polysaccharides [30].

The scientific literature reports mercerization of a wide variety of plant fibers, principally in sodium hydroxide solutions. The majority of these experiments were performed between room temperature and 30 °C using alkali concentrations of up to 20% and reaction times of between 30 min and 48 h. Mercerized fibers have also been compounded with a variety of polymer matrices [95]. Mercerization tends to improve flexural strength and tensile strength, and impact resistance tends to be improved.

While mercerization removes some lignin, it is not an effective method for the removal of this component [103]. More complete delignification can be accomplished through a variety of methods, but these methods are outside the scope of this article, which is interested primarily in mechanical and structural application of cellulose fibers because additional delignification has not been demonstrated to lead to a substantial improvement of the mechanical properties of the fibers. On the contrary, some authors suggest that plant fibers may in fact be weakened by excessive removal of lignin because the integrity of the plant cell wall is compromised [104].

4.2.2. Bleaching

In the textile and paper industries, bleaching is frequently used to remove lignin and to improve the dyeability of a pulp or fiber. Bleaching can also oxidize alcohols to aldehydes, so bleaching can be used to alter the surface chemistry of cellulose fibers or to activate them for reaction with compatibilizers. Chlorine-containing bleaches were once very common—principally sodium hypochlorite—but environmental concerns have precipitated a transition toward elemental chlorine-free and total chlorine-free processes which include the use of peroxides, ozone, and strong acids.

A composite of sisal fibers and BAK 1095, a biodegradable polyesteramide, had higher flexural strength and lower stiffness and tensile strength for bleached fibers relative to unbleached fibers [105]. In another experiment, coconut fibers were effectively broken into finer strands by a combination of sodium hypochlorite and sodium hydroxide. The treated fibers also had reduced water retention [106].

By removing lignin, bleaching can also expose more of the cellulose fibril surface for bonding with a resin or compatibilizing agent. However, cellulose can also be degraded in the process, so the quantity of bleach should be modulated as a function of lignin content. When biomass samples with a range of lignin contents were exposed to acid chlorite bleach, the samples with high lignin content were delignified with relatively little cellulose degradation while samples that were already lignin-free experienced significant cellulose degradation [107].

4.3. Compatibilization

To improve bonding between fiber and matrix, a number of different molecules have been bonded either to the polymer or to cellulose to alter the surface chemistry of the material or to provide reactive functional groups which can form covalent or electrostatic bonds between fiber and matrix. In general, these molecules have the ability to bond with the hydroxy groups functionality on cellulose, as well as functionality which permits bonding with a given polymer matrix. The most common compatibilizing treatments are addition of silanes, acetylation, and grafting with maleic anhydride.

4.3.1. Silanes

Silanes are a versatile compatibilizers that can be synthesized with a wide variety of appended functionality. Silane coatings can therefore be tuned to suit the characteristics of a wide range of polymer matrices. Generally, silanes take the form R-Si-(OR')$_3$, where R is a functional group selected for compatibility with the matrix, while OR' is an alkoxy group which is intended eventually to be replaced with cellulose. Silanes tend to be soluble in ethanol, so fiber coating often takes place in this solvent to permit more even deposition of silanes on the fiber surface.

Another method to use silanes to compatibilize fiber and matrix is to graft silanes onto the matrix and compound a small quantity of this silane-grafted polymer with the fibers to produce a masterbatch.

Silane deposition in an aqueous ethanol solution begins with acid- or base-catalyzed hydrolysis of the alkoxysilyl ethers, yielding silanol (i.e., Si–O–H). Two competing reactions then occur; the silanol either forms hydrogen bonds with the fiber surface or undergoes condensation reactions with other silanols to produce silicate gels. However, silanols will not undergo condensation reactions with the hydroxy groups on cellulose except at high temperature. Silanol only begins to bond with cellulose when heated above 100 °C. At lower temperatures, silanes will adsorb on the surface of fibers but will not form covalent bonds [108].

Silane coating yields a more hydrophobic fiber surface [109] and reduces the rate of water absorption but does not significantly diminish the water retention capacity of the fiber [110]. Silanes can also improve the flexural strength of composites; by using a silane with acrylate functionality, it was possible to improve the flexural strength of an alfa grass–polyester composite [111]. Silane-coated hemp fibers were also determined to have greater tensile strength and Young's modulus than untreated fibers [112].

4.3.2. Esterification

Plant fibers can also be compatibilized through conversion of the hydroxy groups on cellulose chains to esters. In general, esters tend to be less hydrophilic than hydroxy groups, and many esters can also react with specific polymer matrices to improve interfacial bonding. Acetic anhydride is frequently used in this role, but a wide range of molecules could potentially be used in this role. Alternately, it is possible to graft anhydride functionality onto polymers. These grafted molecules have activated carbon electrophiles which are intended to bond with the hydroxyl groups on cellulose, thereby forming covalent networks between fiber and matrix. Maleic anhydride is often used in this role because it can be easily grafted to unsaturated polyolefins such as polypropylene through the use of radical initiators (e.g., dicumyl peroxide) [113].

When wood fibers were acetylated (i.e., cellulose hydroxy groups were esterified as acetyl esters) and then dispersed in a polylactic acid matrix, the resulting composite material had improved dimensional stability and strength and lost less of its strength after being immersed in water [114]. In another experiment, the equilibrium moisture content of composites reinforced with cellulose fibers originating from pine, aspen, bamboo, or jute diminished with increasing acetyl ester content [31]. Acetylation has also been used to disperse cellulose microfibrils because the elimination of alcohol functionality results in a commensurate elimination of sites for hydrogen bonding which permitted microfibrils to be more separated [115].

As previously stated, it is also possible to graft acid anhydrides onto polymer matrices to form covalent linkages between polymer and fiber. Polypropylene with grafted maleic anhydride (referred to as PP-g-MA) is probably the most frequently used of these polymers in academic literature. Cellulose bonds spontaneously to maleic anhydride in the molten polymer, which permits bonding to occur during blending without the addition of a catalyst.

Composites of PP-g-MA with both hemp and jute fibers were found to have improved interfacial shear strength compared to composites which did not contain the anhydride [116]. When wood flour and rice husk flour were separately compounded at 30% by weight in five different varieties of PP-g-MA, the resulting composites all had improved tensile, flexural, and impact strength relative to composites in unmodified polypropylene. In fact, the filler was found to weaken the unmodified polypropylene. Micrographs of fracture surfaces showed that the PP-g-MA showed better adhesion between filler and polymer [117]. Flax–polypropylene composites were found to be more hydrophobic when PP-g-MA was used, with the Wilhelmy contact angle of water rising from roughly 45° for a composite with unmodified polypropylene to more than 80° for a composite using polypropylene with 10% by weight maleic anhydride, while the contact angle in ethylene glycol rose from approximately 50° to 70° for two composites already mentioned. This was attributed to a large diminution of the polar surface interaction parameter of the composite [118].

5. Conclusion

Plant fibers can be treated in a number of ways to improve their performance in FRC materials. These treatments alter the fibers in a number of ways. It is possible to treat fibers to remove unwanted components including lignin, pectin, and hemicellulose, to alter the surface chemistry and morphology of the fiber, to reduce the moisture retention of the fiber, and to graft different functional groups or some combination of these alterations. Many of these treatments come from the paper and textile industries, and their effect on plant fiber behavior in composite materials remains relatively unexplored. It is thought that, with suitable treatment, plant fibers could perform as well or better than synthetic alternatives such as glass or carbon fibers, thereby providing a biodegradable, sustainable material that might be economically competitive.

Acknowledgments

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