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Interfacial Modification of Hemp Fiber–Reinforced Composites

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Nesrin Sahbaz Karaduman and Gokce Ozdemir

Additional information is available at the end of the chapter

Abstract

Natural fiber–reinforced biocomposites are increasingly used in various industries such as automotive, construction, biomedical, and recreation, thanks to their distinctive advantages over traditional glass fiber–reinforced plastics. Natural fiber composites are sustainable, environmentally friendly, low cost, low density, and easy to process as well as have high mechanical properties. The quality of fiber-matrix interface is of critical importance since it determines the load distribution capability of the material. The interface between natural fibers and polymer resins has always been problematic because of the low compatibility between cellulose-based hydrophilic natural fibers and hydrophobic polymer resins, which leads to poor fiber-matrix adhesion and therefore inefficient load distribution between fibers and matrix. To date, several interfacial modification methods have been implemented to address this issue and improve the properties of the resulting composites. This chapter focuses on the interfacial modification of hemp fiber–based composites. First, hemp fiber structure and the nature of fiber-matrix interface were explained. Mechanisms of fiber/matrix adhesion as well as qualitative and quantitative methods for the determination of interface strength were outlined. Finally, the interface modification methods for hemp fiber–reinforced biocomposites were presented in the light of scientific literature.

Keywords: hemp fiber, natural fiber–reinforced biocomposites, fiber-matrix interface, interfacial modification, engineering applications

1. Introduction

Over the last few decades, the search for more eco-friendly and sustainable materials led to the use of natural fibers for composite reinforcement. Natural fibers are renewable, low cost, and readily available. They have low density when compared to commodity fibers such as glass,

carbon, and aramid. Composites reinforced with natural fibers have high specific mechanical properties comparable to those of glass fiber–reinforced plastics. Therefore, natural fiber–reinforced biocomposites provide a gateway toward more eco-friendly and sustainable economies [1, 2]. Some common applications of biocomposites include automotive, packaging, civil engineering, sports, and recreation [3, 4].

The overall performance of biocomposites depends on several factors such as fiber and resin type, fiber/matrix volume fraction, fiber architecture, and fiber-matrix interface quality. The interface between natural fibers and polymer resin has a large impact on the mechanical and degradation properties of biocomposites. In a composite structure, fibers are the main load-bearing component, whereas the matrix phase keeps the fibers together and protects them from external damage. A good bonding between fibers and matrix is necessary for the successful transfer of applied loads from weak matrix material to stiff and strong fibers. The fiber/matrix interface in these composites has always been problematic because of the incompatibility between the surface energies of hydrophilic natural fibers and hydrophobic polymer resins. Research efforts generally focused on enhancing the fiber-matrix bonding by using various chemical and physical modification techniques such as silane treatment, acetylation, use of coupling agents, and alkali treatment [5].

This chapter deals with the interfacial modification of hemp fiber–based composites. In this scope, first, the structure of hemp fiber was explained. Mechanisms of fiber/matrix bonding in composite materials were outlined. A range of available techniques for the determination of interfacial strength was presented. Finally, the interface modification methods used for hemp fiber–reinforced composites were introduced in the light of scientific work in this field.

2. Hemp fiber structure

Hemp is a member of bast fibers (**Figure 1**) [6] which are extracted from the phloem layer of plant stem. Like all bast fibers, hemp fiber has a multicellular structure (**Figure 2**) [7, 8]. A single hemp fiber is made up of lumen, primer wall, and seconder wall [9, 10]. Seconder wall can be further divided into three sub-layers such as S1, S2, and S3. S2 layer is particularly rich in cellulose microfibrils that are responsible for the fiber strength and stiffness [11, 12]. Physical properties of hemp fiber along with some other common natural fibers are given in **Table 1** [9, 13, 14]. **Table 2** shows the chemical composition of hemp and other natural fibers [15, 16].

The most important component of hemp fiber is cellulose. Cellulose is a linear polymer of glucose ($C_6H_{12}O_6$). Glucose molecules add on successively through β-1,4 linkages to form long cellulose chains (**Figure 3**) [17]. These cellulose chains form hydrogen bonds with one another through their pendant —OH or —CH_2OH groups to form microfibrils. Typical diameter and length of these microfibrils are 2–20 and 100–40,000 nm, respectively [18]. There are different regions in cellulose with respect to the arrangement of these microfibrils, i.e., crystalline regions where the microfibrils are well oriented and run parallel to each other creating ordered structures and amorphous regions, which have a more disordered and openly packed structure. Crystalline regions are so closely packed that they are hard to penetrate for the majority
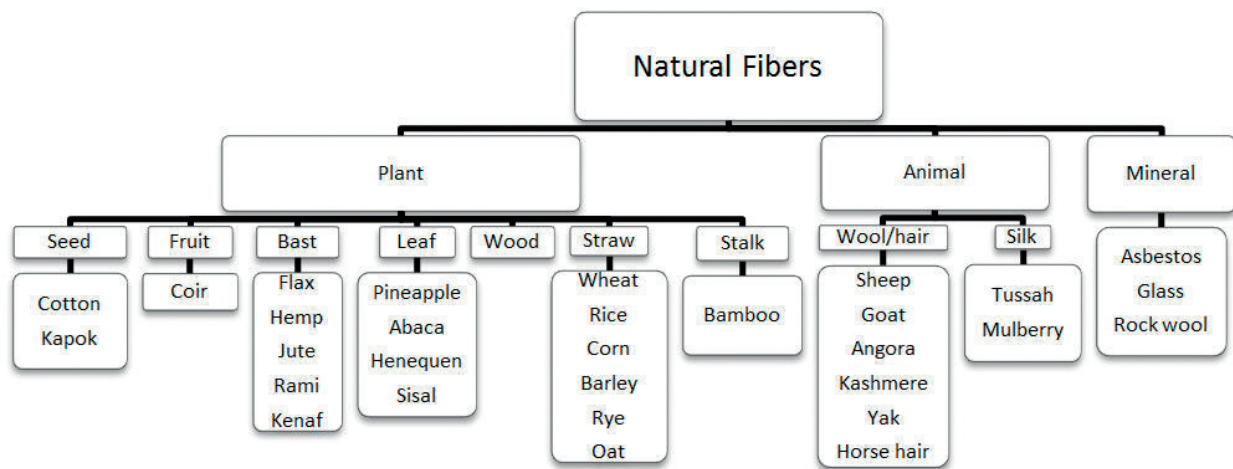
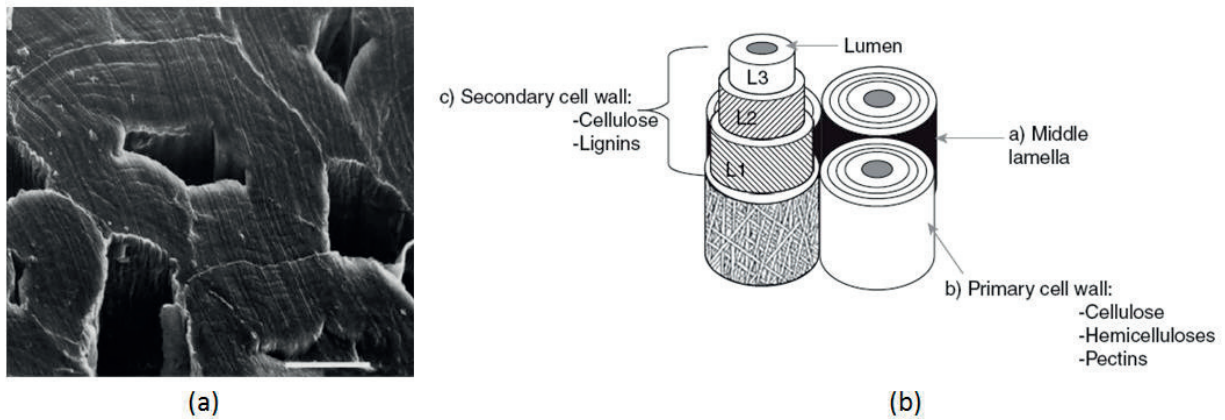**Figure 1.** Classification of natural fibers [6].

Figure 2. (a) Bundled hemp bast fibers [7]. (b) Schematic representation of hemp fiber structure [8].

Fiber	Length, l (mm)	Diameter, d (μm)	Aspect ratio (l/d)	Microfibril angle (°)	Density (kg/m³)	Moisture uptake (%)
Cotton	20–64	11.5–17	2752	20–30	1550	8.5
Flax	27–36	17.8–21.6	1258	5	1400–1500	12
Hemp	8.3–14	17–23	549	6.2	1400–1500	12
Jute	1.9–3.2	15.9–20.7	157	8.1	1300–1500	12
Kenaf	2–61	17.7–21.9	119	–	1220–1400	17
Ramie	60–250	28.1–35	4639	–	1550	8.5
Sisal	1.8–3.1	18.3–23.7	115	10–22	1300–1500	11
Coir	0.9–1.2	16.2–19.5	64	39–49	1150–1250	13

Table 1. Physical properties of natural fibers (single fiber) [9, 13, 14].

Fiber	Cellulose (% wt.)	Hemicellulose (% wt.)	Lignin (% wt.)	Pectin (% wt.)	Moisture (% wt.)	Wax/oil (% wt.)
Cotton	85–90	5.7	–	0–1	7.85–8.5	0.6
Jute	61–71.5	13.6–20.4	12–13	0.2	12.5–13.7	0.5
Flax	71	18.6–20.6	2.2	2.3	8–12	1.7
Hemp	70–74	17.9–22.4	3.7–5.7	0.9	6.2–12	0.8
Rami	68.6–76.2	13.1–16.7	0.6–0.7	1.9	7.5–17	0.3
Sisal	66–78	10–14	10–14	10	10–22	2
Pineapple	70–82	–	5–12.7	–	11.8	–
Coir	32–43	0.15–0.25	40–45	3–4	8	–

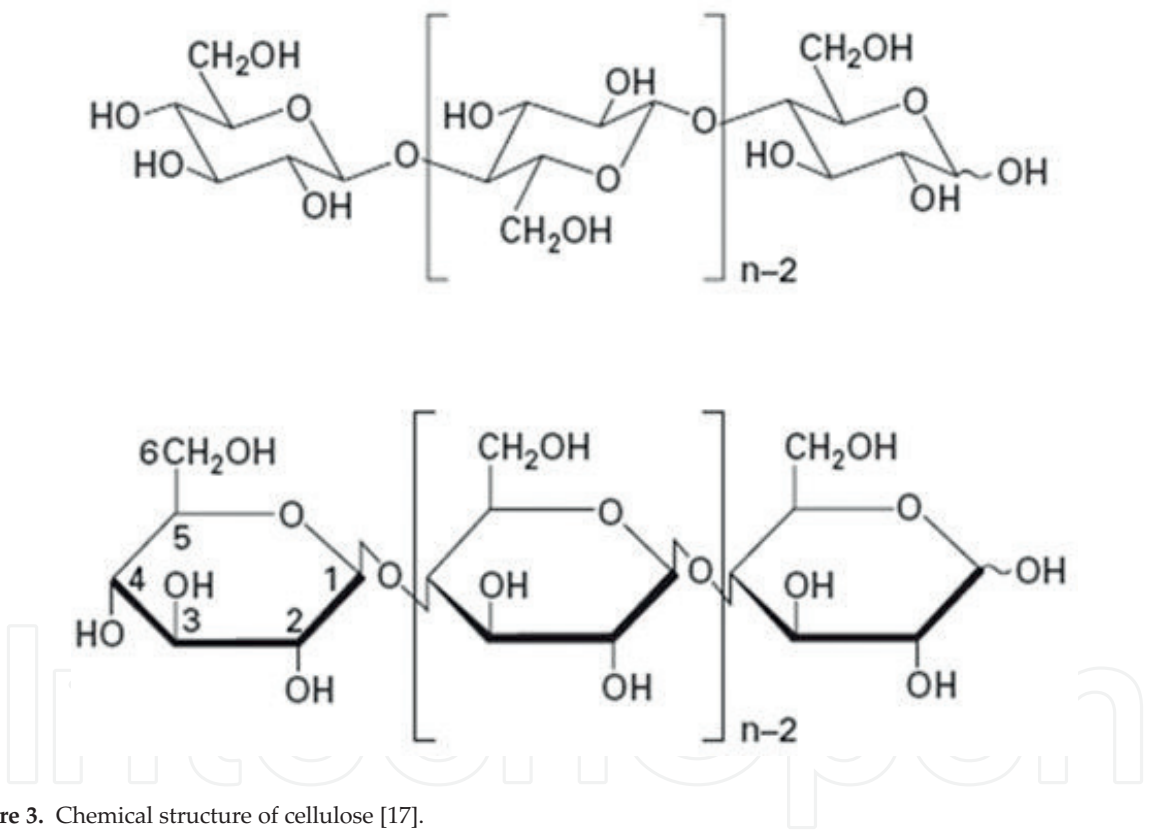Table 2. Chemical composition of plant fibers [15, 16].

Figure 3. Chemical structure of cellulose [17].

of chemical agents. Amorphous regions, on the other hand, are more accessible and easier to manipulate. Therefore, almost all fiber modifications aim at modifying the structure of amorphous regions as well as the surfaces of crystalline regions. Hemicelluloses refer to a group of polysaccharides which bind individual cellulose microfibrils in cell walls [18, 19]. They generally have amorphous structures and are easier to remove or manipulate by using chemical agents. Lignin is also an amorphous material with a branched structure. It typically consists of oxyphenyl propan units [9, 18, 20, 21]. Pectin is a common name representing a range of complex pectic polysaccharides [22]. Like hemicelluloses, pectin serves as a binding agent in

plant cell wall. There are various other aromatic compounds in plant cell wall such as condensed tannins [23] and low-molecular-weight phenolic acids, e.g., ferulic and *p*-coumaric acids. Other ingredients of lignocellulosic plant fibers include low (often negligible) amounts of fats, waxes, and lipids [24].

3. Fiber-matrix interface in composite materials

3.1. Mechanisms of fiber-matrix adhesion

3.1.1. The concept of wetting and intermolecular interactions

Wetting is the ability of a liquid to make and sustain contact with a solid surface, when the two phases are brought together. Fiber wetting occurs when intermolecular interactions between the fiber and resin molecules are greater than the cohesive forces between the resin molecules. There are various intermolecular interactions that may take part in the adhesion process such as ion-ion, ion-dipole, dipole-dipole, van der Waals interactions, and hydrogen bonding [25]. Fiber wetting is the first necessary step before any further interaction or bonding between fibers and matrix can occur. A successful wetting means that the resin spreads over the greatest possible surface area of the fibers (contact angle, $\theta = 0°$) (**Figure 4**) [26].

Wetting behavior of fibers can be fully described by determining four wetting parameters such as thermodynamic work of adhesion (W_a), interfacial energy (γ_{SL}), spreading coefficient (S), and wetting tension (ΔF_i) [27]. Thermodynamic work of adhesion W_a is the energy required to separate a unit area of interface and can be described with Dupré equation [26]:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{1}$$

Where γ stands for surface energy; subscripts S, L, and V indicate solid, liquid, and vapor phase, respectively. According to Dupré equation, wetting is favored if the surface energies of the two constituents are large, and their interfacial surface energy is small.

The interfacial energy is defined as the work necessary to increase the interfacial surface area by unit area [27]. Hence, a small value of interfacial energy indicates a good wetting.

The spreading coefficient is the ability of a liquid to spontaneously spread over a solid. A positive value of the spreading coefficient indicates instantaneous spreading.
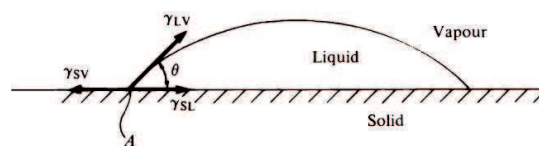
$$S = \gamma_{SV} - \left(\gamma_{SL} + \gamma_{LV} \right) \tag{2}$$

Figure 4. Contact angle, θ and surface energies, γ for a liquid drop on a solid surface [26].

Finally, the wetting tension can be defined as the work needed against wetting a porous network by eliminating a unit area of the solid-liquid interface while exposing a unit area of the solid vacuum interface. A positive value of wetting tension is an indication of good wetting [27].

$$\Delta F_i = \gamma_{SV} - \gamma_{SL} \tag{3}$$

In general, wetting is strongly favored when the surface energy of the fiber greatly exceeds that of the resin. For instance, glass fibers (γ_{SV} = 560 mJ m^{-2}) are easily wetted by polyester resin (γ_{LV} = 35 mJ m^{-2}), whereas polyethylene fibers (γ_{SV} = 31 mJ m^{-2}) are not [26].

3.1.2. Chemical bonds

Chemical bonds include ionic, covalent, and metallic bonds. Covalent bonds are the most common form of chemical bonding in the case of natural fiber composites and are much stronger compared with intermolecular interactions. These bonds generally form between the hydroxyl groups of natural fibers and the functional groups of the polymer resin. Coupling agents with these functional groups can also be used to improve fiber/matrix bonding.

3.1.3. Coulombic interactions

Coulombic interactions can occur when the surfaces of fibers and resin have charges of opposite signs. Coulombic forces are weaker when compared to other forms of interactions and are not stable due to the fact that they can change with humidity, pH, and temperature.

3.1.4. Mechanical interlocking

Another important mechanism for interface adhesion for natural fiber composites is mechanical interlocking. In this case, the resin in liquid form penetrates into the surface cavities of fibers during composite production and is locked inside these cavities upon curing/hardening. It is noteworthy that this mechanism works only for fibers with a rough surface. As the surface roughness of the natural fiber increases, so does the effectiveness of mechanical interlocking. Thus, some fiber modification techniques such as alkali treatment are employed to increase the surface roughness of natural fibers and promote the mechanical locking between fibers and resin.

3.2. Interfacial bond strength measurement

Single-fiber or bulk laminate methods can be employed to determine the interfacial bonding strength of composite materials. The most common single-fiber tests are pull-out, microbond, and full fragmentation tests. These test methods use a single fiber embedded in a matrix. The interfacial shear strength (IFSS) is correlated with the shear debonding stress of the single fiber. One major limitation of single-fiber tests is that the shear behavior of fibers in real composite material may be different from that of the single fiber because of the effect of neighboring fibers. Yet, single-fiber tests yield a reasonable quantification of interfacial bond strength under tensile loading. Bulk laminate experiments, on the other hand, include transverse tensile and bending tests, short beam shear test and Iosipescu shear test. Complementary methods used
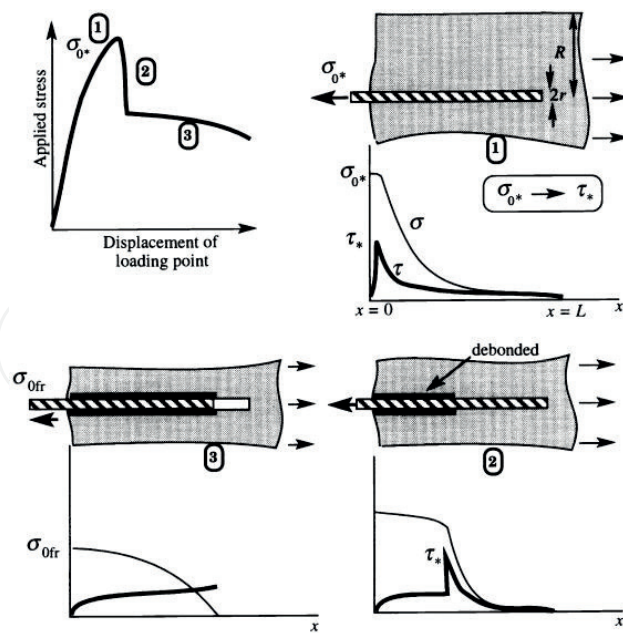
Figure 5. Schematic stress distributions and load-displacement plot during the single-fiber pull-out test [26].

for the assessment of interfacial adhesion include X-ray photoelectron spectroscopy (XPS), ToF-SIMS, SEM, and surface energy analysis. Only single-fiber test methods which are the most common are explained in this section, since the full discussion of all the available techniques goes beyond the scope of this chapter.

3.2.1. Single-fiber pull-out test

Single-fiber pull-out is among the most common testing methods for interface characterization of natural fiber composites [28, 29]. In this method, a single fiber that is half embedded in a matrix is pulled out of the matrix under a tensile load. The apparent interfacial shear strength (IFSS, τ_{app}) is determined using the peak force (F_{max}):

$$\tau_{app} = F_{max}/\pi dL \tag{4}$$

in which d is the fiber diameter and L is the embedded fiber length. The apparent IFSS provides an approximate value for the interface bonding.

More sophisticated treatment of single-fiber pull-out test requires calculating the debonding shear stress by using shear lag theory [30, 31]. **Figure 5** shows axial distributions of the normal stress in the fiber and shear stress at the interface [26]. There are three stages for the complete pulling out of the fiber, i.e., elastic loading up to debonding, propagation of the debonding front, and pull-out by frictional sliding. Shear lag theory assumes that there is no shear strain in the fiber and no transfer of normal stress across the fiber ends [26].

The peak in the load-displacement curve (σ_{0*}) is indicative of the debonding event. The debonding shear stress τ_* can be determined using σ_{0*} with the following relation [31]:

$$\tau_* = \frac{n\sigma_{0*}\coth\left(\frac{nL}{r}\right)}{2} \qquad (5)$$

Where r is the fiber radius; n is a dimensionless constant; n is given by

$$n = \left[\frac{2E_m}{E_f(1+v_m)\ln(1/f)}\right]^{1/2} \qquad (6)$$

in which E_m and E_f are the matrix and fiber modulus, respectively; f is the fiber volume fraction; v_m is the matrix Poisson's ratio.

3.2.2. Microbond test

Microbond test is generally used for fibers with small diameter and is similar to the fiber pull-out test. In this method, a small droplet of resin is applied to the fiber and the specimen is positioned between two knife edge–shaped plates (**Figure 6**) [32]. A tensile force is then applied to the free end of the fiber to pull the resin droplet against the knife edges so that the load is transferred to the fiber-matrix interface. The same equation as in the pull-out method is used to calculate the IFSS. This technique requires very small droplets and is suitable for very soft matrix materials [33].

3.2.3. Full-fragmentation test

In the full-fragmentation test, a single fiber is fully embedded in a matrix, and the matrix is elongated in tension parallel to the fiber axis (**Figure 7**) [34]. Eventually, the fiber breaks into a number of fragments with varying lengths. The shortest fiber length obtained in this way is referred to as the critical fiber length, L_c. Shear strength, τ, is determined by using the aspect ratios of the fiber fragments considering Weibull modulus of the fiber [26]. Fiber fragmentation test gives the best approximation to real composite material compared with other single-fiber tests. Another advantage of this method is that it also takes the heterogeneity of natural fibers into consideration [33].
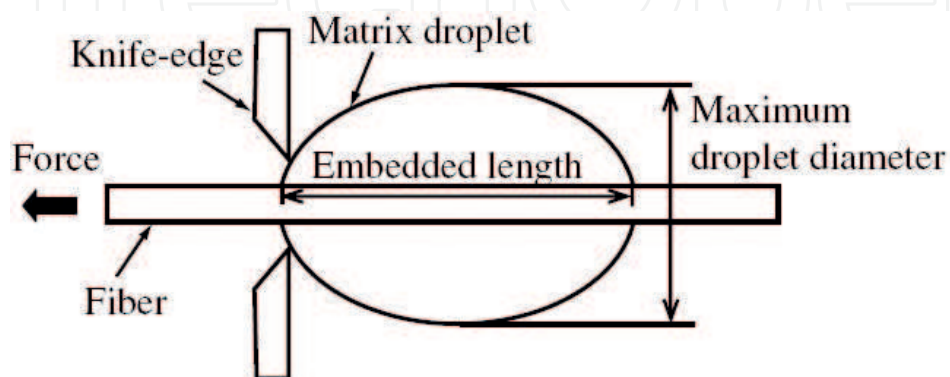

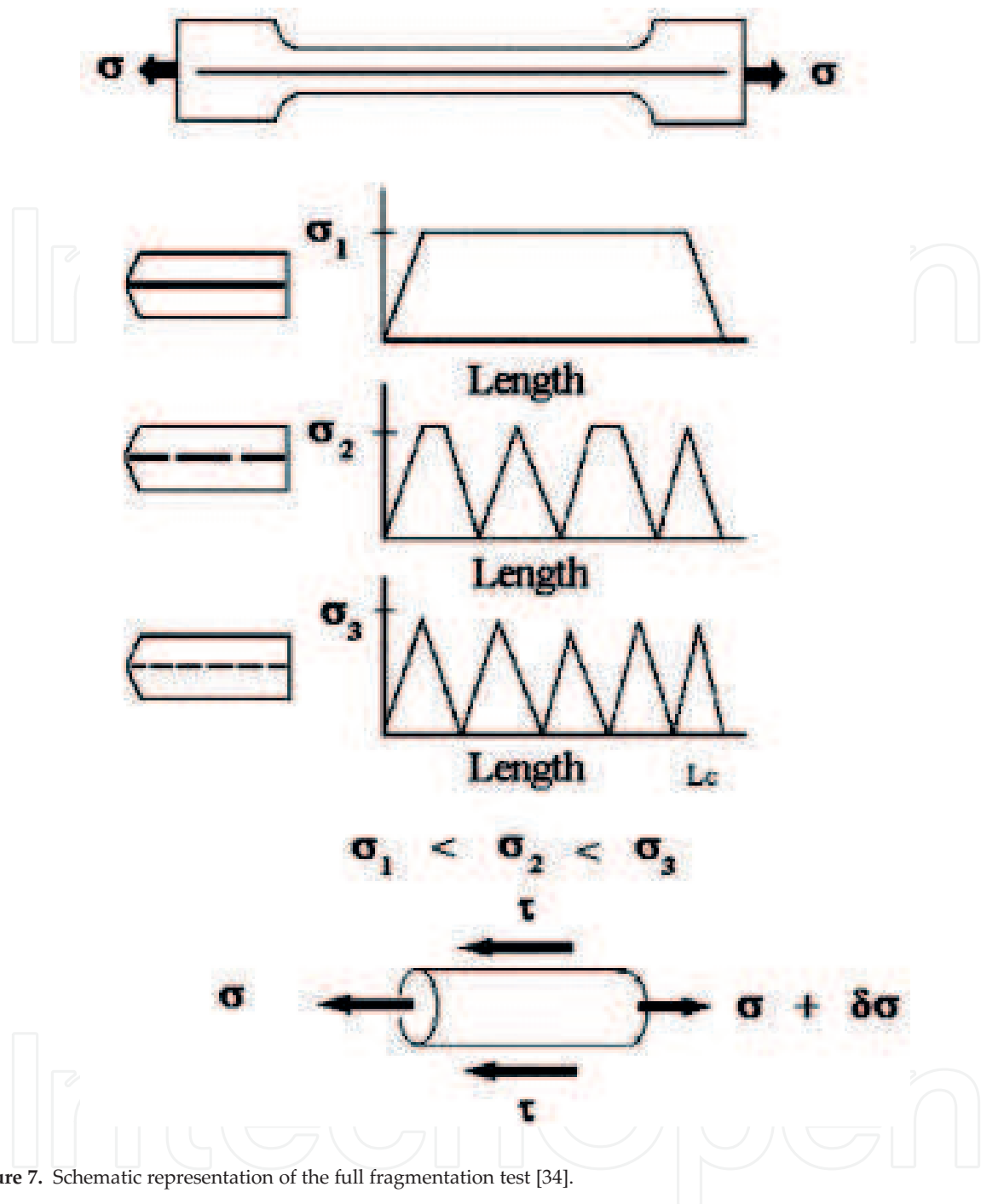**Figure 6.** Schematic representation of the microbond test [32].

Figure 7. Schematic representation of the full fragmentation test [34].

In a real composite structure, the interface is usually subject to various loads, and its failure may comprise different modes such as debonding, cracking, and sliding, most of which involve plastic deformation of the matrix. Single-fiber experiments generally consider shear debonding and sliding as the failure mechanisms with no regard to normal stress across the interface because of the difficulty in applying such stresses to a cylindrical interface. The basic assumption in all these tests is that the tensile load applied to the fiber end is transferred as a shear load across the fiber/matrix interface. Thus, higher tensile loads indicate better fiber/matrix adhesion at the interface. It is important to bear in mind that the single-fiber tests yield

only approximate values, and the real-life structure can be subjected to different distribution of loads and may show very complex interface failure mechanisms.

4. Interfacial modification methods for hemp fiber composites

4.1. Physical modification methods

4.1.1. Corona treatment

This method is based on "corona discharge", i.e., an electrical discharge appearing around the surface of charged conductors, caused by ionization of the surrounding fluid. This ionization creates radicals on the surface of the fibers and promotes fiber-matrix bonding. Ragoubi et al. [35] investigated the mechanical properties of composites obtained from different combinations of untreated and corona-treated hemp fibers and PP matrix. The corona treatment resulted in a significant increase in tensile strength with 30% enhancement in Young's modulus. Authors reported that the etching effect generated by corona treatment which is evidenced by microscopy increased the mechanical locking between fibers and the matrix and therefore resulted in enhanced mechanical properties.

4.1.2. Plasma treatment

In plasma treatment, plasma of different gases is used to modify the surface of natural fibers. It is similar to corona treatment in that an ionized region including excited species such as ions and radicals is formed around the fiber surface. This technique requires a vacuum chamber and gas feed to maintain the desired pressure and composition of the gas mixture. Jimenez et al. [36] studied the impact of atmospheric air pressure plasma (AAPP) treatment on the mechanical properties and interfacial behavior of hemp fiber–reinforced cellulose-acetate-butyrate (CAB) biocomposites. During testing, the untreated and AAPP-treated fibers exhibited a linear region and then exhibited a sharp drop in strength after reaching ultimate failure stress. After the treatment, the tensile strength, Young's modulus, and elongation at break of hemp fibers reduced dramatically. However, the heat generated during the plasma treatment causes dehydration of the fibers and the etching effect of plasma results in rougher fiber surfaces. It was shown that the interfacial shear strength (IFSS) increases after 1-min AAPP treatment due to enhanced surface roughness and accompanying increment in fiber/matrix mechanical locking. The introduction of functional groups and cleaning of contaminant substances were other factors that enhanced fiber/matrix bonding efficiency.

4.1.3. Alkali treatment

Alkali treatment is among the most popular fiber modification methods for its simplicity, low cost, and effectiveness. This technique involves using a dilute solution of sodium hydroxide (NaOH) or other bases to modify the fiber surface. Alkali treatment creates a rougher fiber surface by removing hemicelluloses polymers and other polymeric materials from the fiber surface thus improving mechanical locking between fibers and resin. Alkali treatment also separates fiber bundles by removing pectin and hemicellulose polymers that bind the individual

fibers together resulting in an increased effective fiber surface area for resin adherence. Mwaik-ambo and Ansell [37] treated hemp fibers with different concentrations of NaOH. After the treatment, the surfaces of hemp fibers were cleaner and rougher. X-ray diffraction and thermal analysis indicated that the crystallinity index of the fibers slight increased at low NaOH concentration but reduced at higher concentrations of NaOH. Alkalization increased the surface roughness and resulted in better mechanical locking between fibers and the matrix, thus improving the composite mechanical properties (**Figure 8**) [37]. In another study [38], the same research group treated hemp fibers with NaOH and reported that alkalization caused a rapid degradation of the cellulose between 0.8 and 8% NaOH concentrations. At higher concentrations, the degradation was reported to be marginal. Similarly, there was a marginal decrease in the crystallinity index at NaOH concentrations between 0.8 and 30%. SEM study indicated that alkalization resulted in rougher fiber surface, favoring fiber-matrix interlocking and adhesion.

Aziz and Ansell [39] investigated the effect of alkalization and fiber alignment on the performance of hemp fiber composites. Alkali-treated fiber composites possessed higher flexural strength and modulus compared with untreated fiber composites. SEM micrographs indicated that the surfaces of hemp fibers were cleaner after the treatment. Dynamic mechanical analysis showed that the alkalized fiber composites have higher storage modulus values corresponding to higher flexural moduli. Ouajai and Shanks [40] investigated the properties of hemp fibers after mercerization with NaOH solution. The greater activation energy of treated hemp fiber compared with untreated fiber suggested an increase of purity and improvement in structural order. FTIR study indicated that mercerization removed noncellulosic substances from the fiber. However, NaOH treatment caused structural degradation of fibers especially at higher concentrations and longer treatment times as evidenced by X-ray measurements. Park et al. [41] investigated the interfacial properties of PP composites reinforced with as-received and alkaline and silane treated hemp fibers by using acoustic emission (AE) and dynamic contact angle measurement. Surface energy of the fibers was increased after alkaline treatment due to the removal of the weak boundary layers and resulting increase in surface area. The IFSS also increased after alkali treatment. Islam et al. [42] produced short and long hemp fiber reinforced polylactic acid (PLA) composites by film stacking method. Interfacial shear strength (IFSS) measurements proved that the interfacial bonding was favored by alkali treatment of hemp fibers which also led to improved composite mechanical properties. In another study [43],
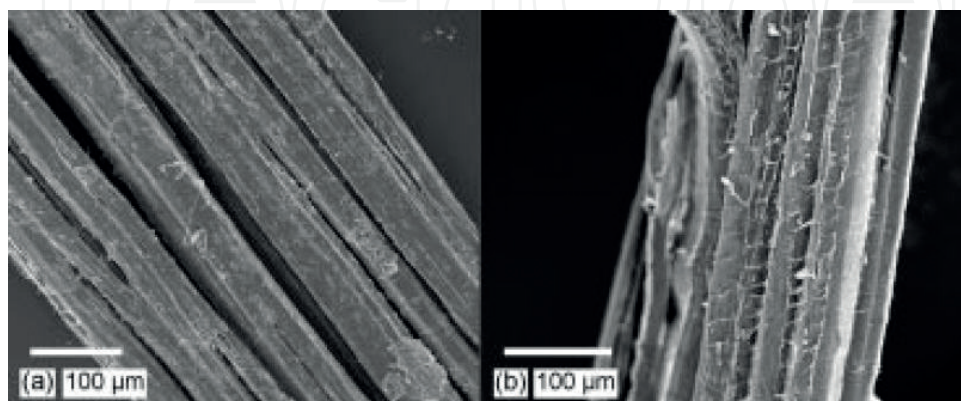

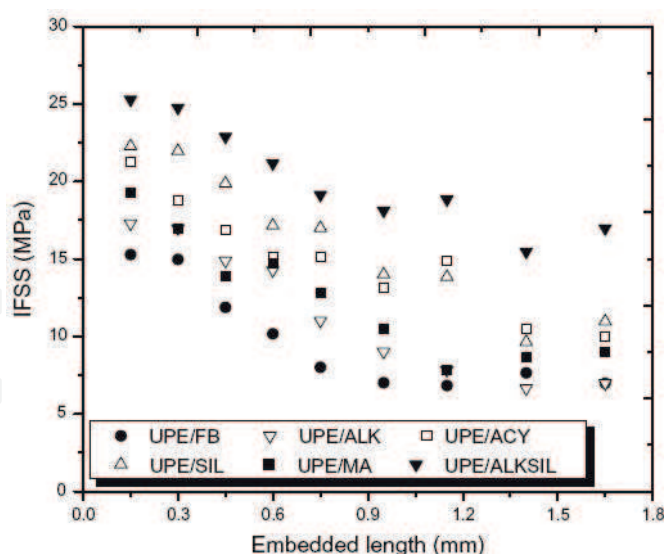**Figure 8.** (a) Untreated hemp fiber and (b) alkali treated hemp fiber [37].

Figure 9. IFSS as a function of embedded length for UPE/hemp fiber (untreated and treated) samples [44].

industrial hemp fibers were treated with a 5-wt% NaOH solution at 120°C for 60 min to remove noncellulosic fiber components. The results showed that alkali treatment removed lignin, separated fiber bundles, exposed cellulose hydroxyl groups, and enhanced thermal stability of the fibers by increasing cellulose crystallinity via better packing of cellulose chains. Alkali treatment also improved the strength and stiffness of resulting hemp/epoxy composites. Sawpan et al. [44] treated hemp fibers with a range of chemicals including NaOH, acetic anhydride, maleic anhydride and silane in an attempt to improve interfacial shear strength (IFSS) of hemp fiber–reinforced polylactide (PLA) and unsaturated polyester (UPE) composites. **Figure 9** shows IFSS as a function of embedded length for UPE/hemp fiber (untreated and treated) samples [44]. IFSS of alkali-treated hemp fiber composites (UPE/ALK) generally increased when compared to untreated samples (UPE/FB), which was attributed to better fiber/matrix bonding, increased matrix transcrystallinity, and increased chemical bonding as evidenced by FTIR results. In a recent work, Dayo et al. [45] prepared bisphenol A-aniline–based benzoxazine (BA-a) composites reinforced with 5% NaOH-treated short hemp fibers. The study showed that the rich —OH groups in treated fibers can promote the ring opening of oxazines at lower curing temperature and improve the adhesion between fiber and matrix. Considerable improvements were recorded in mechanical properties of the composites by using treated fibers.

4.2. Chemical modification methods

4.2.1. Esterification-based treatments

An ester refers to the product of the reaction between a carboxylic acid and an alcohol. In esterification technique, carboxyl groups, —COOH, in carboxylic acids react with hydroxyl groups, —OH, in cellulose macromolecules. After the reaction, —OH groups are eliminated resulting in more hydrophobic fibers making them more compatible with polymer matrix. Esterification techniques include acetylation, benzylation, propionylation and treatment with stearates [33]. Acetylation is the most popular and effective esterification technique for the

treatment of natural fibers. Tserki et al. [46] investigated the effect of acetylation and propionylation on various natural fibers including hemp. It was shown that ester bonds formed on the fiber surface and noncrystalline substances were removed, hence changing the surface topography. The moisture absorption of the fibers reduced after the treatment. **Figure 10** shows ester content versus reaction time plots of various treated fibers [46].

Mwaikambo and Ansell [37] applied acetylation treatment to hemp and other natural fibers. Acetylation was carried out using acetic anhydride with and without an acid catalyst to graft acetyl groups onto the cellulose structure (**Figure 11**) [37]. The surface of treated fibers was
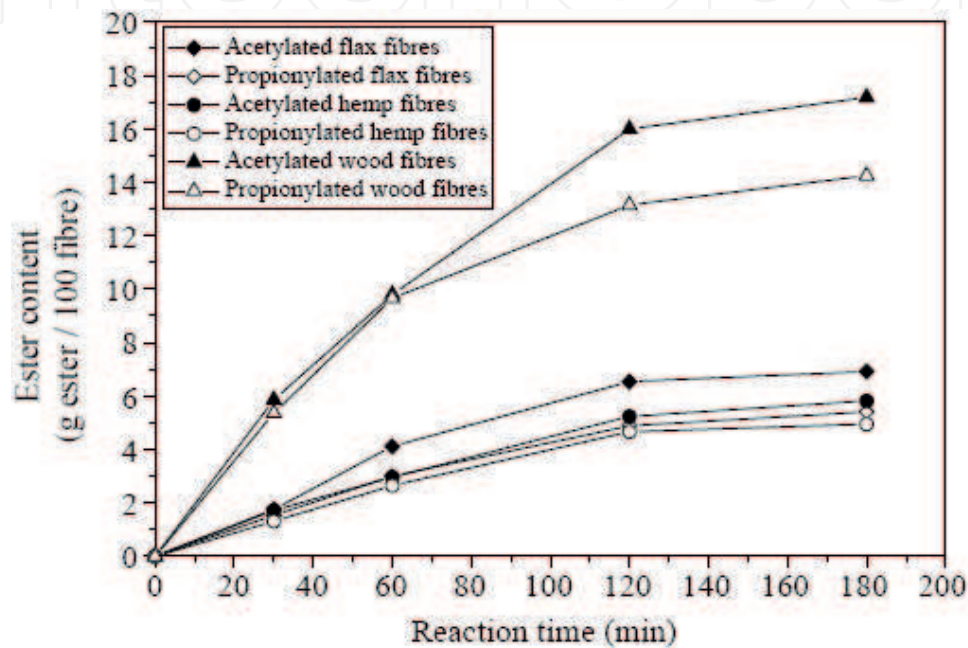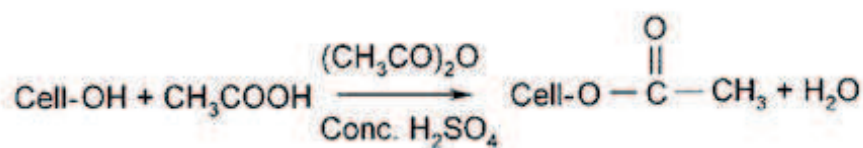

Figure 10. Ester content of chemically treated fibers [46].

Figure 11. Acetylation process [37].

rougher compared with untreated fibers. Acetylation significantly enhanced the performance of natural fiber composites by promoting better fiber to resin bonding. Gulati and Sain [47] examined the effect of acetylation on acid–base characteristics of hemp fibers by using inverse gas chromatography. The results suggested that acetylation caused hemp fibers to be more basic due to esterification of hydroxyl groups. Composites manufactured with acetylated fibers showed improved flexural properties.

4.2.2. Silane coupling agents

Traditionally, organosilanes are used in glass fiber–reinforced composites in order to enhance their strength and durability, and they are still the largest group of coupling agents used in composite industry today. A silane that contains at least one carbon-silicon bond (Si—C) structure is referred to as an organosilane. The organosilane molecule can be represented by the formula R—$(CH_2)_n$—Si(OR$'$)$_3$, where n = 0–3; R is a nonhydrolyzable functional organic group that is reactive toward various groups such as amino, epoxy, vinyl, methacrylate, sulfur; OR$'$ is a hydrolyzable group like an alkoxy group that can react with hydroxyl groups present in inorganic or organic substrates such as natural fibers. Organosilanes can significantly improve fiber/matrix bonding by serving as bridges between them. **Figure 12** shows the general mechanism of alkoxysilane reaction with the fiber surface [5].

Panaitescu [48] investigated the combined effect of 3-aminopropyl triethoxy silane and MAPP treatments on the morphology, thermal, and mechanical properties of hemp fiber–reinforced high-flow PP modified with poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS). Thermal stability of hemp fibers enhanced after silane treatment. Better dispersion of fibers and enhanced static and dynamic mechanical properties of their composites were observed with treated fibers compared with untreated fibers and their composites. In another study [49], the impact of silane treatment on the properties of nonwoven hemp fabric–reinforced unsaturated polyester resin (UPE) composites was investigated. The silane treatment resulted in a better interface adhesion and mechanical and thermal properties of the composites. Rachini et al. [50] reported that silane treatment of hemp fibers increased their hydrophobic character through a condensation reaction between hydrolyzed silane and hydroxyl groups of hemp fibers. Recently, Panaitescu et al. [51] treated hemp fibers with various silane coupling agents to improve the mechanical properties of hemp fiber/PP composites for automotive parts. The silane treatment resulted in bundle splitting and separation of elementary fibers. All the silane treatments were shown to increase the mechanical and thermal properties of the resulting hemp fiber/PP composites.

4.2.3. Graft copolymerization

In graft copolymerization, the cellulosic fiber is treated with an aqueous solution of selected ions and is then exposed to high energy radiation. As a result, the cleavage of cellulose macromolecules takes place, and radical groups are formed. Then, the cellulose material is grafted using a suitable polymer that is compatible with polymer matrix such as acrylonitrile, vinyl monomers, polystyrene, and methyl methacrylate. The most popular and efficient grafting method is the treatment of natural fibers with maleic anhydride grafted polypropylene (MAPP) copolymers.
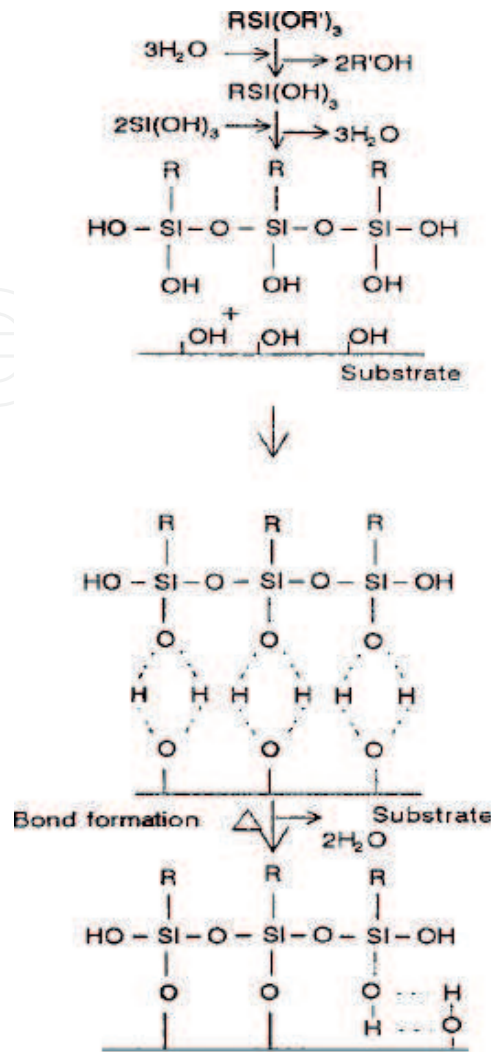
Figure 12. The general mechanism of alkoxysilane reaction with fiber surface [5].

This process results in the formation of covalent bonds across fiber-matrix interface. The reaction takes place in two steps as shown in **Figure 13** [5].

Vignon et al. [52] studied the properties of hemp bast fibers purified by steam treatment compounded with polypropylene (PP), either directly or after surface treatment with polypropylene-maleic anhydride co-polymer. The treatment increased the mechanical properties, tensile modulus, and tensile strength at yield of the resulting PP composites due to a better adhesion between the matrix and the fibers. Mishra et al. [53] investigated the effect of maleic anhydride treatment on the mechanical properties of hemp/novolac resin composites. The treatment resulted in more hydrophobic character in hemp fibers. The impact strength, Young's modulus, flexural modulus, and Shore-D hardness were reported to be higher in maleic anhydride–treated fiber composites compared with as-received hemp fiber composites. Wielage et al. [54] investigated the influence of MAH-PP on storage modulus and loss factor of hemp fiber polypropylene composites. SEM analysis confirmed that the coupling agent causes a significantly better wetting of the natural fibers when compared to untreated composites.

- activation of the copolymer by heating ($t = 170°C$) (before fibre treatment) and
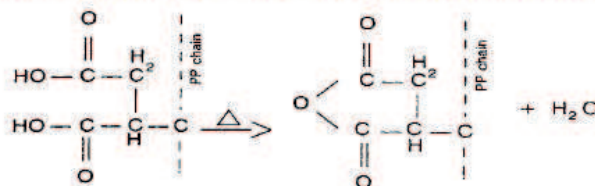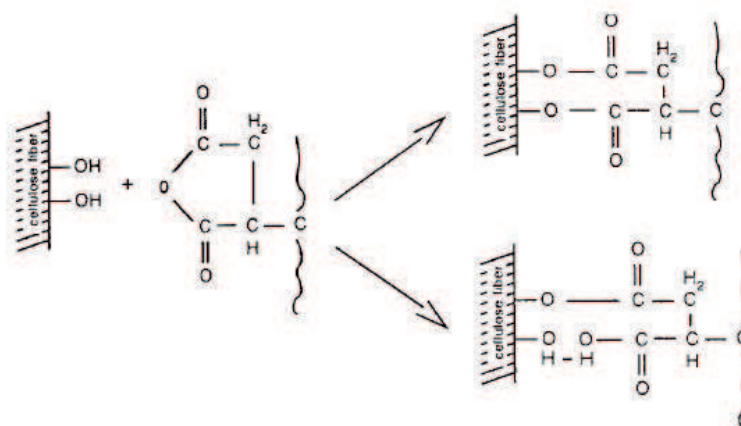

- esterification of cellulose.

Figure 13. The reaction between natural fibers and maleic anhydride grafted polypropylene (MAPP) copolymers [5].

Some researchers combined MAH-PP treatment with mercerization to obtain a synergistic effect. Bledzki et al. [55] modified hemp fibers by mercerization and MAH-PP coupling agent and used for the production of epoxy and PP composites. The tensile modulus increased after the chemical treatments. Mishra and Naik [56] treated hemp fibers with maleic anhydride and fabricated their polystyrene composites. They reported that maleic anhydride treatment resulted in significant enhancement in Young's modulus, flexural modulus, impact strength, and Shore-D hardness of the composites when compared to the untreated fiber composites. Wang et al. [57] investigated the effect of maleic anhydride-grafted polyethylene (MAPE) on the compressive dynamic behavior and flammability of short hemp fibers/high-density poly-ethylene (HDPE) composites. The compressive modulus and yield stress increased with MAPE treatment. Etaati et al. [58] investigated the static and dynamic mechanical and viscoelastic properties of short hemp fiber polypropylene composites. The maleic anhydride–grafted poly-propylene (MAPP) and maleic anhydride–grafted poly(ethylene octane) (MAPOE) were used as coupling agents for modifying the matrices. The damping ratio analysis suggested that the bonding between fibers and resin was improved by MAPP. This was also evidenced by tensile strength experiments and scanning electron microscope (SEM) observations. Recently, Sullins et al. [59] studied the impact of NaOH and maleic anhydride–grafted polypropylene (MAPP) on the properties of hemp fiber/PP composites. It was reported that the treatments resulted in composites with better mechanical properties. The composites with 5 wt% MAPP displayed the highest mechanical properties.

4.2.4. Treatment with isocyanates

Polymethylene-polyphenyl isocyanates (PMPPIC) can make strong covalent bonds with —OH groups of cellulose through their –N=C=O functional groups. The isocyanate treatment is very effective and can be used to modify both fibers and the polymer matrix. The reaction of isocyanates depends upon the catalysts and temperature. The main disadvantage of this method is the toxicity of the chemicals used. Hemp fiber were modified with 3-isopropenyl-dimethylbenzyl isocyanate (TMI), using dibutyltin dilaurate (DBT) as a catalyst and then used to reinforce unsaturated polyester (UPE) composites [60]. The treatment significantly increased the tensile strength, flexural strength, and water resistance of the resulting composites. SEM study of the fractured surfaces confirmed that the pretreatment significantly improved the interfacial adhesion between hemp fibers and UPE resins. FT-IR spectra and X-ray photoelectron spectroscopy (XPS) analysis indicated that the treated fibers made covalent bonds with the resin. In a recent study, Liu et al. [61] prepared an environmentally friendly composite from hemp fibers and acrylated epoxidized soybean oil (AESO) and N-vinyl-2-pyrrolidone copolymer. The properties of the composites were enhanced through the incorporation of isophorone diisocyanate (IPDI). The FTIR and ^{13}C NMR spectra reveal that IPDI could react with the —OH groups of both hemp fibers and AESO by forming urethane connections thus acting as a bridge between the fibers and matrix. As a result, the tensile and flexural properties, storage modulus, and glass transition temperature of the composites were significantly increased.

5. Conclusions and future trends

Natural fiber–reinforced composites have a growing popularity in various industries such as automotive, construction, recreation, sports, and biomedical due to their high mechanical properties and environmentally friendly nature. However, these composites suffer from problems related to weak interfacial bonding between natural fibers and polymer resins as well as the hydrophilic nature of plant fibers. Over the last few decades, studies mostly concentrated on improving fiber/matrix bonding in natural fiber composites in an attempt to enhance their mechanical properties and at the same time reduce their vulnerability to moisture. Several physical and chemical modification methods have been implemented such as corona, plasma, and alkali treatment, esterification-based treatments, silane coupling agents, graft copolymerization, and isocyanate treatment. Significant improvements have been recorded in the mechanical, thermal, and moisture absorption properties of biocomposites by applying these modification methods. Alkali treatment and graft copolymerization stand out among other treatments for their low cost and efficiency. Interface modification efforts are likely to continue in the future with the implementation of new physical and chemical methods. It is expected that more sophisticated techniques will come into play with an effective use of nanotechnology in the field. It is expected that, with the use of cellulose nanofibrils together with advanced nano-modification methods, stronger, more durable, and cost-effective natural fiber composites will dominate the composite industry in the near future.

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