Chapter 1

Surface modification of natural fibers in polymer composites

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1.1 Introduction

Fibers are the basic building block of many materials and despite the fact that, for years, these structures have been mainly applied in textiles manufacturing, they have strong potential for widespread applications. The most common areas of applications are: in the automotive industry, medical field, civil

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engineering, aerospace industries, among others [1−5]. In the last few years, the development of new materials based on fibers revealed the huge potential of these materials to improve the quality of human life. The constituents of these fibrous materials may be of natural or synthetic origin. Natural fibers, including cellulosic, protein, and mineral fibers are collected directly from nature and are considered environmentally friendly materials. On the other hand, synthetic fibers are man-made and despite being the most used fiber for new materials development, they raise several environmental issues. These nonrenewable resources generate large amounts of waste at the end of the product lifecycle and require a long time for their complete degradation [6,7]. In the last few years, there is a great deal of concern about the replacement of synthetic materials by natural ones in order to reduce the cost, the production of CO_2 and oil dependence, as well as problems related to materials recycling. It is estimated that 20%−25% of the total greenhouse gas emissions in industrialized countries come from the transportation industry. Therefore, the challenge is to develop lightweight and low price composites based on natural fibers to be used in the automotive industry in order to turn automobiles more fuel efficient and environmentally friendly [8]. Many automotive components are already produced with natural composites based on fibers like flax, hemp, and sisal. Table 1.1 presents several automotive industries that are already using natural fibers in the automobile components [8].

Natural fibers have high strength, high modulus of elasticity, high moisture absorption, and low elongation and elasticity when compared to non-natural fibers [11,12]. Natural fibers can be classified according to their origin into animal, vegetable, or mineral. Animal fibers include fibers such as silk, hair, wool, and feather and are proteinaceous in nature [13]. Vegetable fibers, on the other hand, are generally based on arrangements of cellulose with lignin including cotton, hemp, jute, flax, kenaf, ramie, sisal, bagasse, abaca, pineapple, and banana [14]. Mineral fibers, unlike the animal and vegetable fibers of animal or plant origin, cannot be strictly defined as bio-based fibers. Nevertheless, as the previous ones, they are obtained from nature. Mineral origin fibers, consisting mainly of silicates, are not renewable and include materials based on clays, asbestos, and inosilicates [14].

Some advantages of natural fibers are: abundance, nontoxic nature, low density, low cost, biodegradability, high toughness, and reasonable specific strength properties [15]. However, they also possess some drawbacks when used in composites. For example, large variations in properties (like in wettability, mechanical behavior, tensile strength, etc.), flammability, poor moisture absorption, and swelling properties. These variations lead to formation of cracks and promote material defects [16,17].

The poor compatibility with different matrices especially with polymers is a major drawback due to the hydrophilic character of the fiber and the hydrophobic polymer in a natural fiber−reinforced composite [18,19]. As a result, numerous techniques have been tried till date to modify the surface of

TABLE 1.1 Automotive manufacturers and application areas of natural fibers [8–10].

Company/ manufacturer	Model applications	Automobile parts
Audi	A2, A3, A4, A6, A8, Roadster, Coupe	Seat backs, side and back door panels, boot lining, hat rack, spare tyre lining
BMW	3, 5,7 series, BMW I series	Door panels, headliner panel, boot lining, seat backs, noise insulation panels, door trim
Citroën	C5	Interior door panelling
Chrysler	A, C, E, and S-class models	Door panels, windshield, dashboard, business table, pillar cover panel
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156	Door cladding, seat-back linings, door panels, seat bottoms, head restraints, back cushions
Ford	Mondeo CD 162, Focus, Freestar	Door panels, boot liner, sliding door inserts
Lotus	Eco Elise	Body panels, spoiler, seats, interior carpets
Mercedes-Benz	Trucks, Mercedes A	Internal engine and roof cover, sun visor, interior insulation, bumper, wheel box
Opel	Vectra	Packing trays, panel inserts
Peugeot	406	Seat backs, parcel shelf
Renault	Clio, Twingo	Rear parcel shelf
Rover	2000	Insulation, rear storage shelf/panel
Saab	–	Door panels
Seat	–	Door panels, seat backs
Saturn	L300s	Packing trays, door panel inserts
Toyota	Brevis, Harrier, Celsior, Raum	Door panels, seat backs, spare tyre cover
Vauxhall	Corsa, Astra, Vectra, Zafira	Headliner panel, interior door panels, instrument panel
Volkswagen	Golf, Passat, Bora	Door panel, seat back, boot lid finish panel, boot liner
Volvo	C70, V70	Seat padding, natural foams, cargo floor tray

natural fibers, in order to reduce their water absorption and improve their adhesion with polymeric matrices. This chapter provides an overview of natural fiber properties and the functionalization techniques available to allow their surface modification for advanced applications in the field of green composites. Several examples of natural fiber composites utilized in the automotive industry will be described.

1.2 Properties of natural fibers

As shown in Table 1.2, natural fibers are mainly composed of cellulose, hemicellulose, lignin, pectin, waxes, and water-soluble substances [15,22]. The differences in the chemical composition, structural parameters, and properties of each fiber are related to the different modes of extraction, the origin of growth, the climatic conditions, and the age of the fiber plant [22].

Table 1.3 presents the mechanical properties of several natural fibers compared with synthetic ones such as e-glass, a very common inorganic synthetic fiber used in automobile parts.

The properties of each fiber depend on the chemical composition, chemical structure, and cellular arrangement of the fiber. Synthetic fibers like e-glass, aramid, or carbon are commonly used, due to their good mechanical properties, as fillers and reinforcements for door panels, seat backs, dashboards, and interior automobile parts. However, these fibers are abrasive and difficult to machine; they are obtained from nonrenewable resources and present potential health hazards caused by glass fiber particles [26]. Regarding the comparison between the natural fibers and the synthetic e-glass, it is expected that the natural fibers could replace glass fiber into biocomposites due to several properties, namely, their low density, comparable specific strength, favorable mechanical properties, weight reduction potential, high stability, and wide availability [15,22,27]. They also can be produced using ecologic and low-price methodologies contributing to the sustainability of the process.

1.3 Surface modification techniques

Due to the presence of amorphous regions, hydroxyl and other polar groups, natural fibers exhibit a high propensity to absorb moisture. The increased moisture at the surface of the fiber further leads to a decrease in the mechanical properties resulting in loss of dimensional stability and leading to biodegradation. This significantly reduces the potential application of natural fibers for reinforcing polymers, since the adhesion at the interface is not suitable for the development of composites. Thus, various treatments could be applied to modify the surface of the fibers in order to make them more suitable for such applications. In general, these surface-modifying treatments can be physical, chemical, or biological, and regardless the mechanism associated with each type of treatment; the goal is similar for all of them: break the atoms bonds of some fiber surface groups in order to enable their functionalization [28,29].

TABLE 1.2 Chemical composition in percentage of some natural fibers and the respective structural parameters [19–21].

Types of fiber	Cellulose	Lignin	Hemi-cellulose	Pectin	Wax	Microfibrillar spiral angle	Moisture content
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	8.0	12.6
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0	10.0
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0
Kenaf	31–39	15–19	21.5	–	–	–	–
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	20.0	11.0
Pineapple	70–82	5–12	–	–	–	14.0	11.8
Henequem	77.6	13.1	4–8	–	–	–	–
Cotton	82.7	–	5.7	–	0.6	–	–
Coir	36–43	41–45	0.15–0.25	3–4	–	41–45	8.0

TABLE 1.3 Properties of natural fibers compared with e-glass, s-glass, aramid, and carbon fibers [8,15,19,23–25].

Fiber	Density (γ, g/cm^3)	Tensile strength (σ, MPa)	Stiffness/Young's modulus (ε, GPa)	Elongation at failure (%)	Specific tensile strength (σ/γ)	Specific Young's modulus (ε/γ)
Jute	1.3–1.5	393–800	10–55	1.5–1.8	300–610	7.1–39
	1.3–1.45	393–773	13–26.5	1.16–1.5	–	–
Flax	1.5	345–1100	27.6	2.7–3.2	571–1071	43
	1.4	800–1500	60.0–80.0	1.2–1.6	–	–
	1.5	345–1830	27–80	1.2–3.2	230–1220	18–53
Cotton	1.5–1.6	287–800	5.5–13	3.0–10	190–530	3.7–8.4
Kenaf	1.5	930	53.0	1.6	–	–
	1.45	930	53	1.6	641	36
Pineapple	–	413–1627	34.5–82.5	1.6	–	–
	1.4	1020	34.0–82.0	0.8–1.6	–	–
Sisal	1.5	468–640	9.4–22.0	3.0–7.0	–	–
	1.2–1.5	511–700	3.0–98.0	2.0–2.5	–	–
	1.3–1.5	507–855	9.4–28	2.0–2.5	362–610	6.7–20
Hemp	1.4	550–900	70	1.6	392–643	50
	1.5	550–1110	58–70	1.6	370–740	39–47

Abaca	1.5	12–980	–	–	–	–
Bagasse	0.5–1.2	290	–	–	–	–
Banana	0.75–1.3	180–914	–	–	–	–
Bamboo	1.5	575	27	–	–	18
Kapok	0.38	93.3	4	–	–	12.9
Ramie	1.5	400–938	44–128	1.2–3.8	270–620	29–85
Harakeke	1.3	440–990	14–33	4.2–5.8	338–761	11–25
Alfa	1.4	188–308	18–25	1.5–2.4	134–220	13–18
Coir	1.2	131–220	4–6	15–40	110–180	3.3–5
Silk	1.3	100–1500	5–25	15–60	100–1500	4–20
Feather	0.9	100–203	3–10	6.9	112–226	3.3–11
Wool	1.3	50–315	2.3–5	13.2–35	38–242	1.8–3.8
E-glass	2.5	2000–3500	70.0	2.5	1297	28
	2.6	2400	73.0	3.0	–	–
	2.5	2000–3000	70	2.5	800–1400	29
S-glass	2.5	4570	86	2.8	–	–
Aramid	1.4	3000–3150	63–67	3.3–3.7	–	–
Carbon	1.7	4000	230–240	1.4–1.8	–	–

1.3.1 Physical methods

Physical methods of processing natural fibers are mainly used to separate natural fiber bundles into individual filaments and to modify the fibers surface structure in order to improve its application on composites. Some examples of physical methods for natural fibers functionalization are related to the use of plasma, ultrasounds, and UV light.

1.3.1.1 Plasma treatment

Plasma treatments are among the most common physical surface modification processes used nowadays in the industry; they are very effective in substrate surface activation, especially when applied to natural fiber modification [30]. There are mainly two different types of plasma: thermal and nonthermal. However, due to the destructive character of the thermal plasma concerning fiber-based materials, just nonthermal plasma treatments will be addressed within this book, the ones at atmospheric pressure and at low pressure or vacuum [29,31].

Plasma treatment schematically represented in Fig. 1.1 is applied in order to remove surface contaminants (cleaning effect) which will induce changes in the surface properties like wettability, dyeability, flammability, etc. This treatment can also increase the surface roughness providing better mechanical binding to the polymers and improve the adhesion at the fiber–matrix interface. At the same time, the plasma can produce free radicals able to react with oxygen or other gases leading to the generation of surfaces with different hydrophilic/hydrophobic character [32,33].

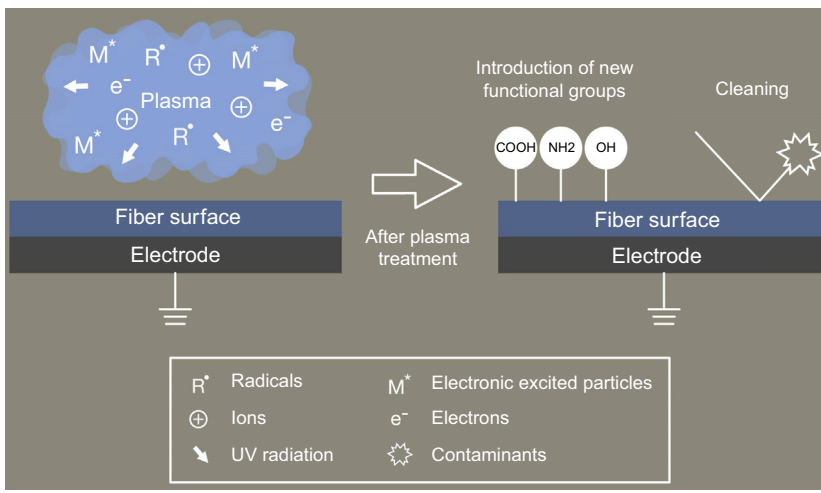


FIGURE 1.1 General scheme of the Plasma surface treatment.

Plasma is partially ionized gas, composed of highly excited atomic, molecular, ionic and radical species with free electrons and photons [34]. It is generated by applying an electric field over two electrodes with gas in between at atmospheric pressure or under vacuum [35]. In both cases, the properties of the plasma will be determined by the gases used to generate the plasma, as well as by the applied electrical power and the electrodes (material, geometry, size, etc.). The plasma treatment is an example of an electric discharge treatment which includes ions (10−30 eV), electrons (0−10 eV), and UV ($200 > \lambda < 400$ nm) and vacuum UV ($\lambda < 200$ nm) radiation (3−40 eV) [29].

Plasma vacuum requires that samples be treated in a low vacuum chamber in which a gas is introduced, causing ionization. Various gases have been used, including oxygen, nitrogen, helium, and air. The introduced gas ions strike the surface, causing chemical and topographical changes on the fiber surface. These chemical modifications are complex but generally involve removing atoms or breaking bonds that result in free radicals. However, this method is limited to the size of the vacuum chamber and is also a batch process [36].

The treatment with atmospheric plasma has attracted the researchers' attention due to the excellent results demonstrated by several works using this treatment applied to a wide variety of fibers, polymers, ceramics, and composites [37−40]. It is a very attractive technique because it allows the sample to be treated in situ rather than restricted to a vacuum chamber [29], allows a continuous and uniform treatment, is reliable, reproducible, and is not so expensive as the low-pressure treatments avoiding the use of expensive vacuum systems.

There are four main types of atmospheric plasma techniques which will be discussed in the following sections: corona treatment, dielectric barrier discharge technology (DBD), glow discharge (APGD), and atmospheric pressure plasma jet (APPJ).

Corona treatment

The corona treatment is one of the most interesting techniques for activating the surface oxidation of several materials and induces several changes in order to improve the compatibility between hydrophilic fibers and hydrophobic matrices [31]. Corona treatment is based on high-frequency discharges applied across electrodes and grounded metal roll as can be observed in the scheme of Fig. 1.2.

These discharges between electrodes induce ionization of the surrounding atmosphere creating plasma (ionized air) and the emission of blue color as can be observed (Fig. 1.2). The sample or the substrate is placed in the gap between the electrodes and is bombarded with high-speed electrons. The energy level of these electrons is high enough to break the molecule bonds of the most substrate surfaces [41]. This process will induce the surface oxidation

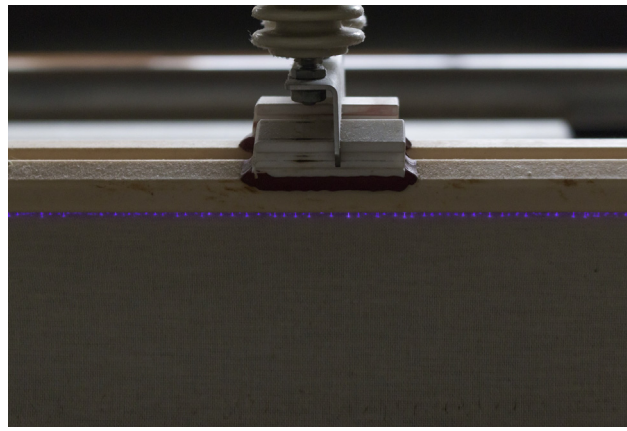


FIGURE 1.2 Corona treatment photography.

of the materials by the oxidants present in corona discharge like: ozone, atomic oxygen, and oxygen free radicals. These oxidants in combination with free radicals of the material surface will create oxidizing groups, for example, hydroxyl, carboxyl, carbonyl, or ester groups. The introduction of polar groups on the material surface will increase the surface energy improving the wettability and adhesion properties of the materials [42]. The corona process is very successful as a pretreatment for textiles. The treatment can be used for cleaning the surface of the material improving its roughness and adhesion properties. With this method it is possible to create better surfaces without changing the mechanical properties of the whole material [43]. One of the disadvantages of corona treatment is related to the penetration depth, in some cases, the corona systems have an effect only in loose fibers and cannot penetrate deeply into the yarn or woven fabric so that their effects on textiles are limited and short-lived [44]. Nevertheless, the corona treatment presents several advantages when compared with other plasma treatments and also with other surface modification techniques. There are no requirements regarding specific conditions during modification [45] (unlike the low-temperature plasma treatment, where vacuum chambers are used). It is a low-cost process and presents low energy consumption [46]. Finally, the process can be applied in large scale and directly in a high volume of material which is very important for the application in an industrial production line.

Dielectric barrier treatment

The plasma dielectric-barrier discharge (DBD) technique is similar to corona treatment process, however, in the corona, the discharges are between bare metal electrodes without dielectric. The DBD plasma technique consists of two plane parallel metal electrodes with at least one of the electrodes covered by a dielectric layer which accumulates the transported charge on its surface

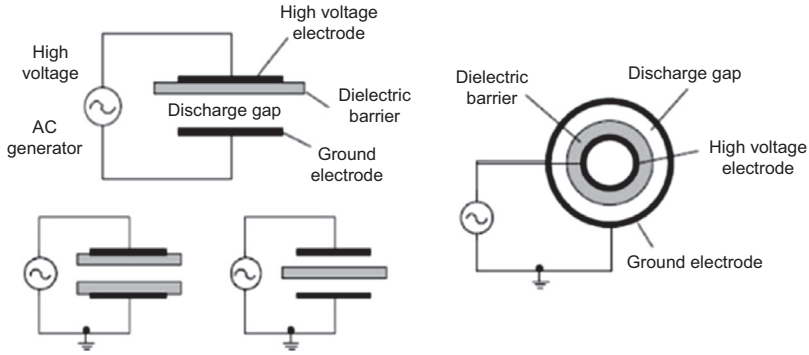


FIGURE 1.3 Scheme of a general dielectric barrier discharge apparatus [29].

and distributes the charge over the entire area of the electrode (Fig. 1.3) [30,47,48]. The preferred materials for the application as dielectric barriers are glass or silica glass or, in special cases, ceramics and polymer layers or thin enamel [49]. If an alternating voltage ranging from low-frequency AC to 100 kHz is applied to the electrodes, breakdown processes are initiated in the gas gap and transient microdischarges are established with duration of nanoseconds and distributed over the dielectric surface [50,51]. Discharges of this type are well-known for the treatment of surfaces for the production of ozone [52].

Regarding the surface treatment, the dielectric barrier discharges provide high-energy electrons (generated through collisions during discharge), which are able to produce radicals and electronically excited particles efficiently. The DBD can trigger different reaction paths that can lead to the production of reactive intermediates, which, in turn, will promote the surface activation of the materials [29,49].

This technology is commonly used for the treatment of textiles, polymers, plastic foils, metal surfaces, and also in the sterilization of surfaces, deposition of films, removal of components from flue gases, and conversion of greenhouse gases [53]. The major disadvantage of DBD is that the treatment or the discharge is not completely uniform and has a short duration.

Atmospheric pressure glow discharge

Compared with the DBD technique, the atmospheric pressure glow discharge (APGD) is very suitable for a more uniform surface treatment. Glow discharge is characterized as a uniform, homogeneous, and stable discharge usually generated in helium (sometimes argon and nitrogen can be used, but helium is the preferred gas) as we can see in Fig. 1.4 [44].

APGD is generated by applying relatively low voltages (when compared with DBD) across symmetrical conductive electrodes at higher frequencies (MHz). Plasma is homogenous across the electrodes and gives one current pulse for every half cycle [54]. The APGD plasma is characterized by high

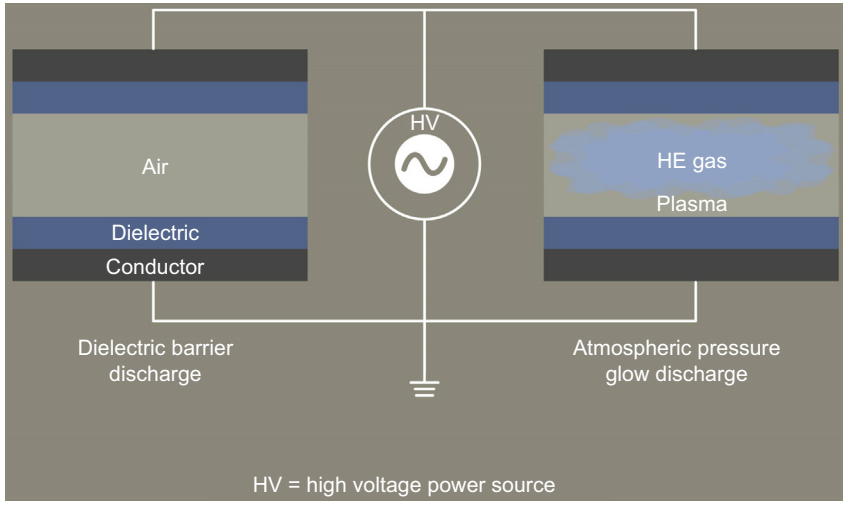


FIGURE 1.4 Scheme of atmospheric pressure glow discharge (APGD) compared with dielectric barrier discharge (DBD).

electron energy and high densities of excited and charged particles at low gas temperature. Nonequilibrium glow discharge plasma provides active species that can be used for surface treatment without material overheat [55]. This treatment is used in several applications such as: surface modification, etching, thin-film deposition, ozone generation, degradation of organic compounds, sterilization, disinfection, biological and chemical decontamination, surface cleaning, food safety, and waste treatment [56].

Atmospheric pressure plasma jet (APPJ)

In general, the APPJ source can contain two tubular metal electrodes separated by a gap through which a discharge current occurs as shown in Fig. 1.5. Inside the

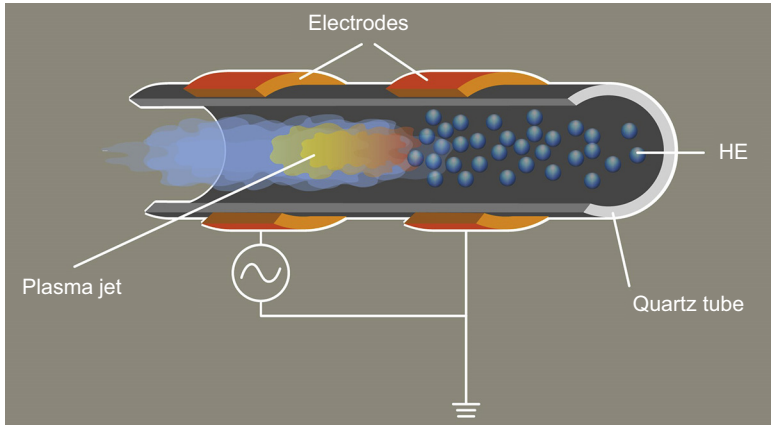


FIGURE 1.5 Schematic view of one of the possible experimental set-ups of APPJ.

electrodes lies a quartz cylindrical tube through which helium (or other gases) flows. To generate the plasma, several parameters can be optimized like wave pulse, the frequency of pulse, and rate of gas flow. The plasma is launched through the open end of the quartz cylindrical tube directly into the sample [57].

An APPJ can provide a local treatment with a relatively high density of charged particles, reactive oxygen and nitrogen species since the length of the plasma plume (bright region) from the opening of the APPJ can be of several centimeters. Short lifetime species such as atomic oxygen can, therefore, be involved in reactions with the target. Furthermore, a very precise treatment is possible and owing to the high gas velocity, penetration of the plasma components into small cavities can be achieved. The APPJ is suitable for industrial and research applications, such as surface modification, biological material sterilization, biomedical applications (dermatological, dental, etc.), ozone formation, and treatment of heat-sensitive materials [58].

1.3.1.2 Ultrasound and ultraviolet treatments

Ultrasound treatments are not so used as the previously described plasma treatments. However, they are also effective in the rising of different substances and pollutants from the surfaces even without the use of surfactants in the rinsing bath. This effect could be attributed to the acoustic cavitation, known as the process of bubble formation and collapse, responsible for most of ultrasound's physical and chemical effects observed in solid/liquid or liquid/liquid systems [59]. Effects of ultrasonic treatment on natural cellulosic fibers, such as cotton, have been extensively studied and changes were found, the ultrasonic treatment can alter the crystalline morphology of cotton and subsequent mechanical and chemical properties of the fiber and fabric [60].

The ultraviolet (UV) light is an electromagnetic radiation ranging from 10 to 400 nm which can cause chemical reactions with several organic molecules, leading to effects greater than simple heating effects. The UV radiation is a potential energy source able to promote photochemical reactions in the molecular structures of natural fibers changing its mechanical properties, and simultaneously, acts as a clean method to modify the surface of natural fibers [61,62]. UV radiation has proved to be a clean and cost-effective method and is also a very promising technique to be used in industrial applications due to the economic construction and simplicity.

Some examples regarding the use of these techniques for the surface modification of natural fibers in polymer composites will be shown later in this chapter.

1.3.2 Chemical methods

Alternatively to the physical methods, natural fibers can also be treated with several chemical methods such as alkali treatment (mercerization), silane treatment, maleated coupling, acetylation, permanganate and peroxide treatment,

benzoylation, graft polymerization, etherification, isocyanate treatment, etc. These chemical processes for modification of natural fibers are used in order to improve their surface and mechanical characteristics. These chemical modifications consist of chemical reactions between the reactive constituents of the natural fibers (hydroxyl groups, for example) and a chemical reagent forming a covalent bond between the two [19]. It has been observed that some of these chemical treatments (for example, alkali treatment) can significantly improve the mechanical properties of natural fibers by modifying their crystalline structure, as well as by removing weak components like hemicellulose and lignin from the fiber structure [63]. Also, moisture absorption and subsequent swelling of natural fibers can also be reduced through selective chemical treatments (e.g., water repelling agents). Moreover, silane coupling agent treatment can also improve the fiber/matrix interface interactions through the formation of strong chemical bonding and therefore, result in considerable improvement in the mechanical performance of composites [64]. Some of the existent chemical treatments will be briefly described in the following sections.

1.3.2.1 Alkali treatment

The alkali treatment also known as mercerization is one of the oldest and most used chemical treatments for natural fibers. This method consists of treating the fibers with sodium hydroxide (NaOH) in order to remove from the surface certain amounts of lignin and hemicellulose and completely remove pectin, wax, oils, and other organic compounds [65]. After this removal, it is supposed to have more cellulose molecules exposed at the surface, improving the adhesion of fibers to the polymeric matrix due to the higher number of possible reactions sites (Gandini A, 2009). In this way, the treatment influences the chemical composition of the fibers and the molecular orientation of the cellulose crystallites. The surface roughness is also increased enhancing the mechanical properties and adhesion [63]. The following Fig. 1.6 exhibits, in a general way, the alkali treatment reaction where the addition of sodium hydroxide promotes the ionization of the natural fibers hydroxyl groups to alkoxides.

1.3.2.2 Silane treatment

Silanes are very promising and versatile coupling agents to be used in the treatment of natural fibers in order to improve the chemical interactions between the fiber and the polymeric matrix [66]. The silane molecule should have bifunctional groups which may respectively react with the two phases thereby forming a bridge in between them [64]. As we can see in Fig. 1.7,

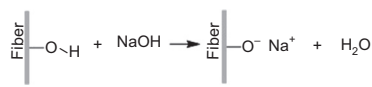


FIGURE 1.6 Mechanism of the alkali treatment of natural fibers.

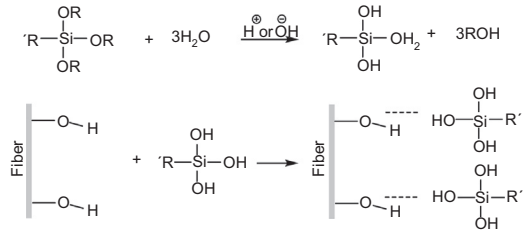


FIGURE 1.7 Mechanism of the reaction between the silane groups and the functional groups of the natural fibers.

the first step of the reaction mechanism is the silane coupling agent hydrolysis. The alkoxy groups from the coupling agent under use are firstly hydrolyzed in order to generate reactive silanol groups. After this, the hydrolyzed silane solution is mixed with natural fibers. The reactive silanol groups of the silane molecule allow the silane to bind to the OH groups of the fiber surface by hydrogen bonds. On the other side, the alkyl groups connect the silicon atom to the organofunctionality of the polymer functional groups forming a siloxane bridge between the fiber and the polymer. This phenomenon increases the compatibility with organic compounds and the hydrophobic character of the surface, thus leading to an increase in the strength of the interface in the polymer matrix [67,68].

Coupling agents are normally used to improve the degree of cross-linking in the fiber/polymer interface by providing a perfect connection between the silane groups. Among the various existing coupling agents, silane is one of the most reported as more effective in modifying the fiber/matrix interface. Moreover, it has been demonstrated that the efficiency of the silane treatment can be higher when the samples are subjected to an alkali treatment before the silane one. The generation of reactive sites in the molecule increases leading to a more successful reaction with silanes. Furthermore, both treatments can be combined improving the properties of the fibers and enhancing the fiber-matrix bonding in composites [69].

1.3.2.3 Acetylation

The acetylation method is very effective in modifying the surface of natural fibers in order to increase their hydrophobicity [70]. Generally, the treatment consists of applying acetic anhydride and acetic acid for plasticizing the cellulosic fibers (esterification method). The esterification occurs by reaction of acetyl groups (CH_3CO-) with hydroxyl groups ($-OH$) on the fibers as shown in Fig. 1.8 [25].

This chemical modification promotes the substitution of polar hydroxyl groups found on fiber cell wall by the less polar acetyl groups [71]. As a result, the hydrophilic nature of the fiber decreases leading to a better compatibility

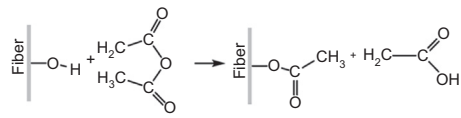


FIGURE 1.8 Reaction of the acetic anhydride with the functional groups of natural fibers.

with the nonpolar matrix. The acetylation treatments are effective in reducing the moisture absorption of natural fibers and also in improving the mechanical properties of composites, such as the interfacial shear and tensile and flexural strength [72]. In some cases, the acetylation can be preceded by alkali pretreatment for better results [24].

1.3.2.4 Benzoylation

Like acetylation treatment, the principal purpose of the benzoylation method also decreases the fibers' hydrophobicity. Firstly, as Fig. 1.9 presents, the alkali pretreatment is normally used to activate the hydroxyl groups of the fiber. Secondly, the benzoylation is performed by the reaction of benzoyl chloride with the cellulosic OH groups of the natural fibers [73]. This reaction leads to the introduction of functional benzoyl groups (C_6H_5CO) into the fibers, improving the possible adhesion with the matrix [74].

Although there is improvement of the fiber/polymer interaction, the benzoylation process increases the thermal stability of the fibers and the strength of the generated composite [63].

1.3.2.5 Maleated coupling treatment

Maleated coupling method is widely used to strengthen composites based on natural fibers. The fundamental difference from other chemical treatments is that maleic anhydride (MA) is not only used to modify the fiber surface, but also the polymeric matrix, in order to achieve better interfacial bonding between them and improved mechanical properties [75]. Maleic anhydride is commonly grafted to the polymers that are used to produce the final matrix to ensure a great compatibility between the matrix and the coupling agent. One of

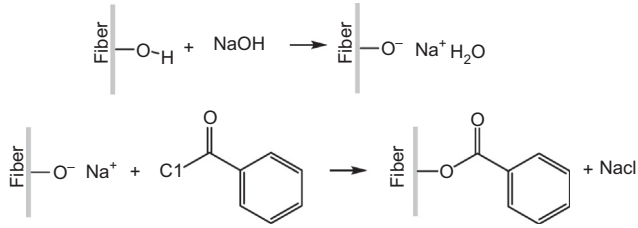


FIGURE 1.9 Reaction of the alkali treatment followed by the reaction between the fiber and benzoyl chloride.

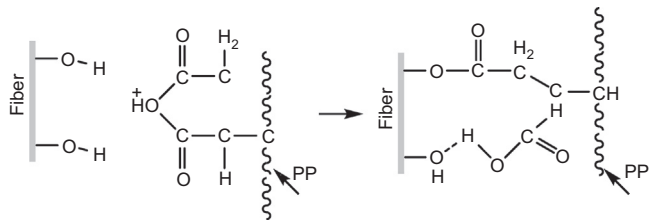


FIGURE 1.10 Reaction of maleic anhydride polypropylene with natural fibers.

the most common polymers used is polypropylene (PP), which in the presence of the maleic anhydride results in the grafted maleic anhydride polypropylene (MAPP) [25].

In this treatment, MAPP can react with the hydroxyl groups (OH) in the amorphous region of cellulose structure leading to the formation of hydrogen or covalent bonds between them [76]. The maleic anhydride could form carbon−carbon covalent bond with the polymeric matrix and also combine with hydroxyl groups of the fiber forming an efficient bridge interface. In Fig. 1.10 an example is shown of the possible reaction mechanism of MAPP with fibers [77].

1.3.2.6 Graft copolymerization

The graft copolymerization of many monomers onto a cellulose backbone is a very effective method used for their surface chemical modification [78]. Due to its abundance in nature, the vinyl monomers are the most utilized for graft copolymerization. In order to graft vinyl monomers onto natural fibers, redox initiators can be used such as: ceric (IV) ion (ceric ammonium nitrate (CAN)) or cerium (IV) sulfate. However, free radical initiators such as azobisisobutyronitrile ($C_8H_{12}N_4$: AIBN), potassium persulfate ($K_2S_2O_8$: KPS), or ammonium persulfate ($(NH_4)_2S_2O_8$: APS) has also been used for the grafting of the different monomer onto natural fibers [79]. The use of microwave radiation to induce multicomponent polymerization reactions is also a very used technique with increasing interest [80]. Several works showed that the physicochemical properties such as chemical resistance, moisture absorption, water uptake behavior, etc., of natural fibers (jute, hemp, flax, ramie, sisal, pinus, oil palm, coir, bamboo, okra, agave, *Grewia optiva*, *Cannabis indica*, *Hibiscus sabdariffa*, etc.) have been improved by graft copolymerization [81].

1.3.2.7 Other chemical treatments

Many other chemical compounds could be used in order to reduce the number of hydroxyl groups and also to improve the interfacial adhesion between the fiber and polymer. The permanganate treatment leads to the development of cellulose radical through MnO_3^- ion formation. The peroxide functional groups could initiate free radical reactions between the matrix and the

cellulose fiber. The isocyanate is highly susceptible to the reaction with OH groups. Stearic acid ($CH_3(CH_2)_{16}COOH$) and acrylic acid ($CH_2CHCOOH$) are also employed for altering the surface topography, and sodium chlorite ($NaClO_2$) is usually used for fibers bleaching [82].

1.4 Physical and chemical methods as treatments for natural fiber polymer composites (NFPCs)

As mentioned before, in the automotive industry natural fibers are replacing the glass and other nonrecyclable fibers in many components. Their biodegradability, low cost, low weight, ecological sustainability, low energy requirements for production, end of life disposal and carbon dioxide neutrality [28] have made them particularly attractive for developing green composites in the automotive sector. However, the adhesion between the natural fibers and the polymers used in the final composites remains as a problem. All the described physical and chemical methods for treating the natural fibers' surface could be the strategy to overcome this issue regarding the compatibility fiber/matrix and improving at the same time the mechanical properties.

Among all the natural fibers, flax, hemp, jute, kenaf, sisal, oil palm, pineapple, banana, and bamboo have received a great importance for developing NFPCs with potential application in the automotive industry [83,84].

In this section, several examples will be provided regarding these fibers treatment with chemical and physical methods to be applied as reinforcements in polymer composites.

1.4.1 Effects of plasma treatment on NFPCs

Recent research on banana fibers [85] demonstrated that atmospheric DBD plasma treatment represented in Fig. 1.11 effectively modified the surface of the fibers leading to the increase of tensile strength, elastic modulus, and adhesive properties of the treated banana fibers. Simultaneously, the fibers' hydrophilicity was improved and the cross-section images of the untreated and treated fibers revealed several changes introduced by the plasma treatment as we can see in Fig. 1.11.

Atmospheric glow discharge plasma was used by Ebru Bozaci et al. for **jute** treatment [86]. The jute fibers were pretreated by alkali treatment followed by the plasma one, exhibiting several morphological changes. The surface roughness increased, as well as wickability, with increasing plasma power and treatment time. These changes on surface properties could be very important for improving the polymer/matrix compatibility in composites production like was found by Gibeop et al. when they studied the effect of plasma treatment on mechanical properties of **jute fiber/polylactic acid** (PLA) composites [87]. The tensile, modulus, and flexural strength of the plasma-treated fibers increased due to the surface roughness improvement enabling a good compatibility with PLA matrix.

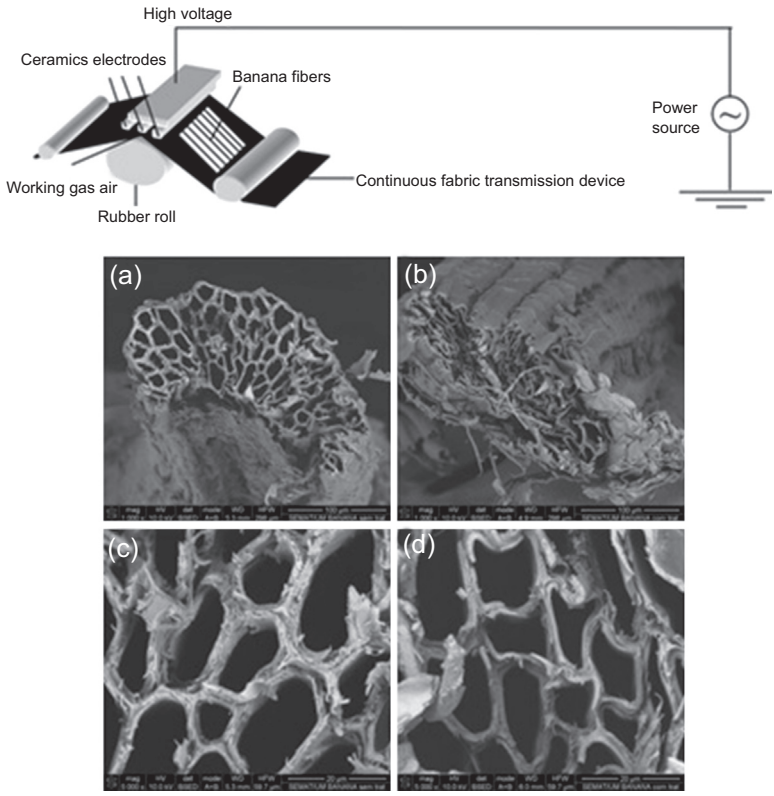


FIGURE 1.11 Schematic apparatus of DBD treatment and images of cross-section of banana fibers untreated (a, c) and plasma treated (b, d).

Ragoubi et al. studied the effect of corona plasma treatment in **hemp** fibers for the combination with **polypropylene** [26]. The treated fibers increased the strength at break of the composites hemp/polypropylene (TF/PP) from 28.6 to 37.8 MPa as shown in Fig. 1.12.

The corona treatment also improved the young modulus, stiffness, and elastic density energy properties of the composites produced with treated fibers. Furthermore, the surface modification with corona allowed a better surface contact with the polymeric matrix under study.

The study performed by Seki et al. revealed interfacial adhesion fiber/matrix improvement by using low temperature oxygen plasma in **jute** fibers treatment for the fabrication of high-density **polyethylene** (HDPE) composites. Composites with treated and untreated fibers were produced, and several properties were evaluated. The interlaminar shear strength of the oxygen plasma−treated jute fiber/HDPE composite increased 47% (plasma power 60W) when compared with the untreated jute/HDPE composite. The flexural

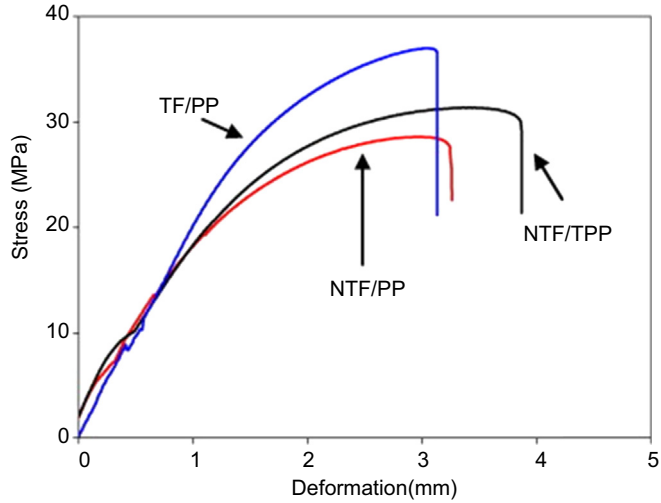


FIGURE 1.12 Tensile curves for the different composites TF/PP (corona-treated hemp in polypropylene), NTF/PP (untreated hemp with polypropylene), and NTF/TPP (untreated hemp with corona-treated polypropylene).

TABLE 1.4 Flexural strength and flexural modulus of the developed composites.

Composite	Flexural strength (MPa)	Flexural modulus (MPa)
Untreated jute/HDPE	31.4 ± 1.4	823.6 ± 12.7
Oxygen plasma-treated (at 30 W) jute/HDPE	39.7 ± 1.5	965.8 ± 13.2
Oxygen plasma-treated (at 60 W) jute/HDPE	45.6 ± 1.8	1244.5 ± 18.5

strength and flexural modulus also increased with plasma treatment with plasma power of 30 and 60W as can be observed in Table 1.4 [88].

Marais et al. utilized helium cold plasma treatment in reinforcing **flax** fibers for increasing moisture resistance and improving adhesion with the matrix. The analysis of **polyester** composites reinforced by flax fibers submitted to helium cold plasma revealed a reduction of water permeability of the composites and improved mechanical properties. In summary, plasma treatment of flax fibers resulted in a composite material with improved mechanical properties [89,90].

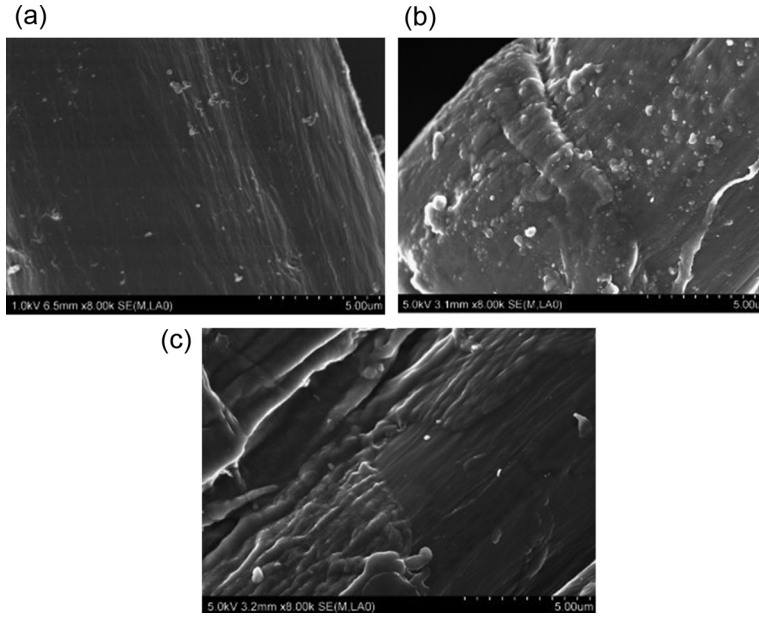


FIGURE 1.13 Scanning electron microscope images at 8000 magnification of (a) untreated flax fibers, (b) flax fibers after 15 min corona treatment, and (c) flax fibers after 30 min corona treatment.

Pizzi et al. employed corona discharge treatment on **flax** fibers impregnated with natural resins matrices with possible application as back rebatable flap in cars. Treated nonwoven flax fiber mats significantly improved the tensile and flexural properties of the **mimosa tannin–hexamine biocomposites**. Such as the scanning electron microscope images of Fig. 1.13 exhibit, the corona treatment turned the surface rougher which probably could increase the surface area of the substrate resulting in improved adhesion of the natural resin on the fiber substrate [91].

1.4.2 Natural fibers—chemical treatments and their influence on NFPCs

The influence of alkali treatment on **hemp** fibers was analyzed by [92] in a study where the hemp fibers were alkali treated with NaOH and Na_2SO_3 solution, while the polymer used in the final composite **(polypropylene)** was also modified with **MAPP**. The fiber–matrix interfacial adhesion is usually characterized by the interfacial shear strength (IFSS) of a composite. In this investigation, the composite formed by the NaOH/Na_2SO_3-treated hemp fiber with polypropylene/MAPP presented an IFSS equal to 15.4 MPa, which indicates a relatively high level of interfacial bonding when compared with other literature examples.

Xia et al. performed the modification of **flax** fiber surface by alkali, corona discharge, maleic anhydride (MA) grafting, and aminopropyl triethoxysilane treatment for the combination with **PLA** [93,94]. The alkali treatment successfully removed hemicelluloses, lignins, waxes, and oils from the fiber surface. At the same time, maleic anhydride and the silanes reacted with fiber to form $-OCO-CH=CH-COOH$ and $-(CH_2)_3-NH_2$ groups increasing the hydrophobic character of the fiber surface. Fig. 1.14 shows the morphology changes with the several treatments used. By analyzing the SEM images, it is clear that the surface roughness increased with alkali treatment (a) giving rise to more contacting points and improving the mechanical interlocking between

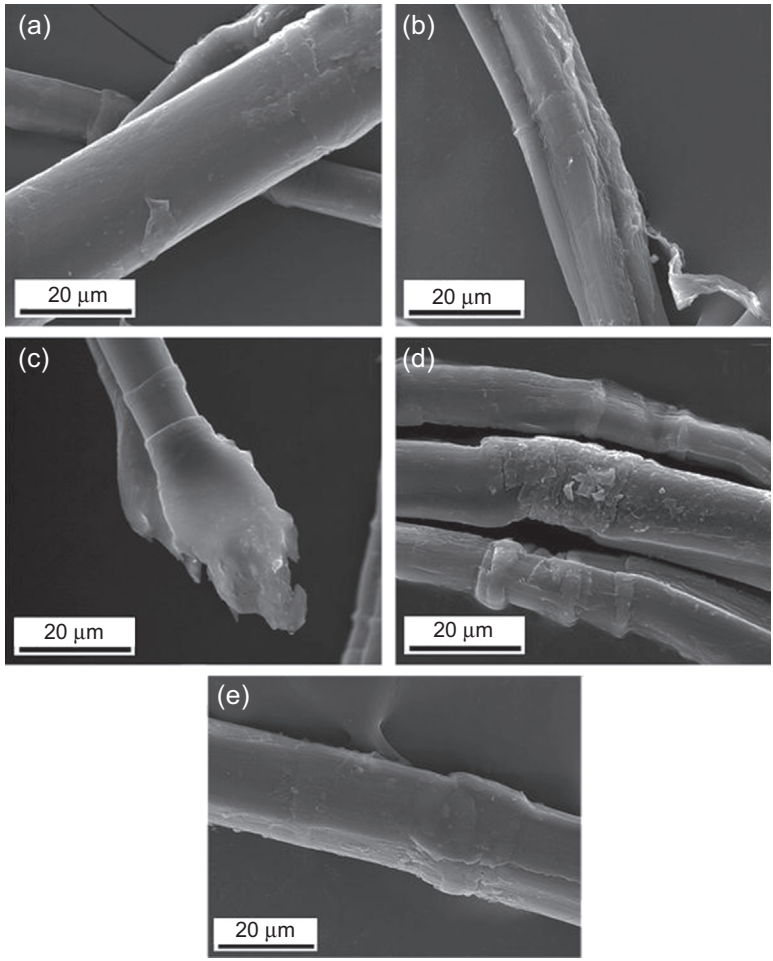


FIGURE 1.14 SEM images of (a) Untreated fiber, (b) alkali-treated fiber, (c) corona-treated fiber, (d) MA-grafted flax fiber, and (e) silane-treated flax fiber.

PLA and fiber. Images (d) and (e) show the fibers' surface covered by a coating layer promoted by MA and silane treatment acting as adhesive agents to increase the fiber−matrix interaction.

In a study performed by Annie Paul et al., **banana** fibers were subjected to different surface treatments such as: alkali, benzoylation, $KMnO_4$, and triethoxy octyl silane (TEOS). The influence of these chemical treatments was investigated in **PP** composites regarding several thermophysical properties [95]. All the chemical methods enhanced both thermal conductivity and diffusivity of the composite banana fibers/PP improving the contact between the fiber and the matrix.

Pineapple leaves (PALF) and Kenaf fibers were modified by alkali, silane, and combined alkali and silane treatments by Asim et al. regarding the compatibility improvement with polymer matrices. Table 1.5 summarizes several properties of untreated and treated fibers [96].

As can be observed in Table 1.5, diameters of chemically treated fibers were more uniform and smaller than untreated fibers due to the impurities removal. Tensile properties of silane-treated PALF and KF are enhanced as compared with the untreated, alkali-treated and NaOH-silane−treated fibers. Silane-treated PALF and KF have the highest IFSS.

The acetylation, isocyanate, maleic anhydride, and potassium permanganate treatments were used in **kenaf** fibers in order to improve the adhesion of the fibers to the polyurethane matrix by Datta and Kopczynska [97]. Once again, the mechanical properties of the **polyurethane/kenaf** composites were influenced with the chemical modification of kenaf fibers. As an example, the tensile strength of all the produced composites when compared with untreated fibers increased except with maleic anhydride treatment.

Kushwaha and Kumar modified **bamboo** fibers with alkali, maleic anhydride, permanganate, benzoyl chloride, and benzyl chloride treatments for their use as reinforcements in **epoxy and polyester** matrices [98]. All the mentioned chemical treatments improved the mechanical as well as water-resistant properties of bamboo-epoxy composites. The tensile strength improved 25% with MA and 54% with permanganate method. Benzoylation treatment decreased the water absorption from 41% (untreated fibers) to 16% (treated fibers).

As Fig. 1.15 exhibits, the combination of alkali with high intensity ultrasound (HIU) treatment was studied in **sisal** fibers by Krishnaiah et al. [99].

In this investigation, the effects on the morphology, thermal properties of fibers, and mechanical properties of their reinforced **PP** composites were studied. By the FE-SEM images presented in Fig. 1.16, it was possible to analyze the influence of each treatment on the fiber surface. The alkali treatment, as usual, removed the wax, oil, and other impurities present on the surface fibers while the ultrasounds removed the amorphous materials and also promoted the cellulose separation. This synergetic effect is very important to enhance adhesion or mechanical interlocking between the sisal fibers and the PP matrix.

TABLE 1.5 Values of diameter, tensile strength, tensile modulus, and IFSS of PALF and kenaf fibers.

Testing	Fibers	Untreated	NaOH-silane	NaOH	Silane
Fiber diameter (μm)	PALF	78.8	50.6	47.8	42.4
	KF	83.5	52	46.4	39.4
Tensile strength (MPa)	PALF	290.61	424.63	432.01	629.90
	KF	282.60	247.81	455.74	551.23
Tensile modulus (MPa)	PALF	5,381.59	6,599.71	8,396.76	10,998.39
	KF	7,132.65	11,867.02	15,247.35	19,707.86
IFSS (MPa)	PALF	1.70	1.93	1.81	2.35
	KF	1.27	1.71	2.89	4.54

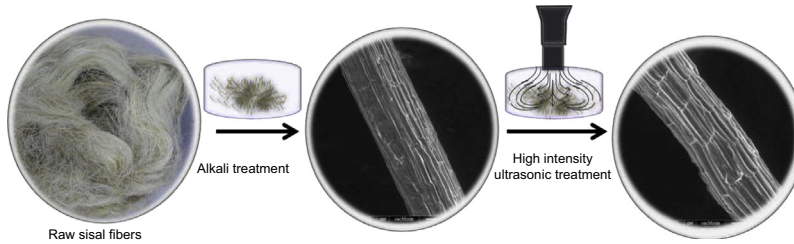


FIGURE 1.15 Alkali and HIU treatments on the sisal fibers.

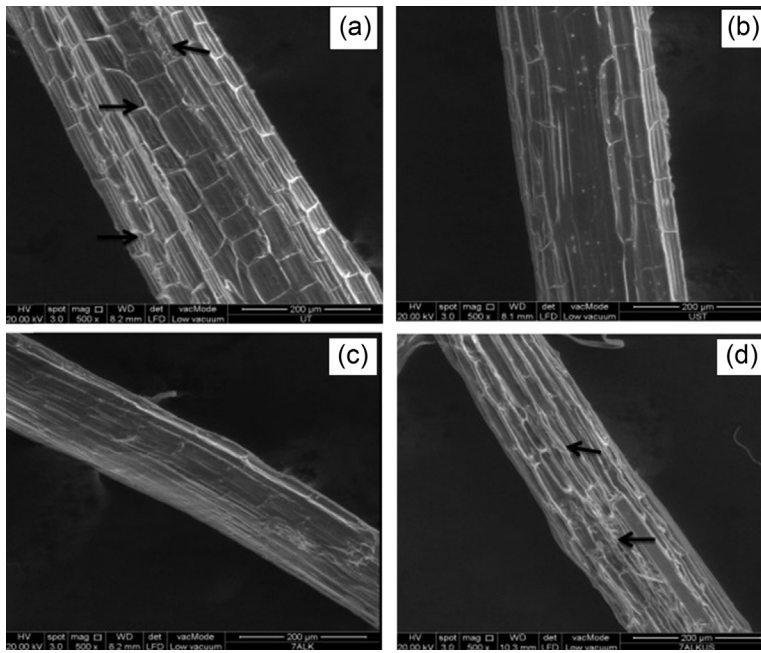


FIGURE 1.16 FE-SEM micrographs of sisal fibers: (a) Untreated, (b) Ultrasound treated, (c) Alkali treated, and (d) the combination of alkali and ultrasound treated.

Orue et al. [66] also studied the effect of chemical treatments on **sisal** fibers, the combination of alkali and silane treatment was used for improving the connection with **poly(lactic acid)** composites. As expected, the treated sisal/PLA composites showed better mechanical properties than untreated ones because the adhesion between fibers and PLA matrix was improved.

The influence of fibers alkali treatment in reinforced **oil palm fiber epoxy** composites was investigated by Muhammad Khusairy Bin Bakri et al. [100]. Fig. 1.17 shows microscope images of oil palm epoxy composites. The composites with untreated fibers showed lower absorption of epoxy in the fibers, while the composites with treated ones showed higher absorption of

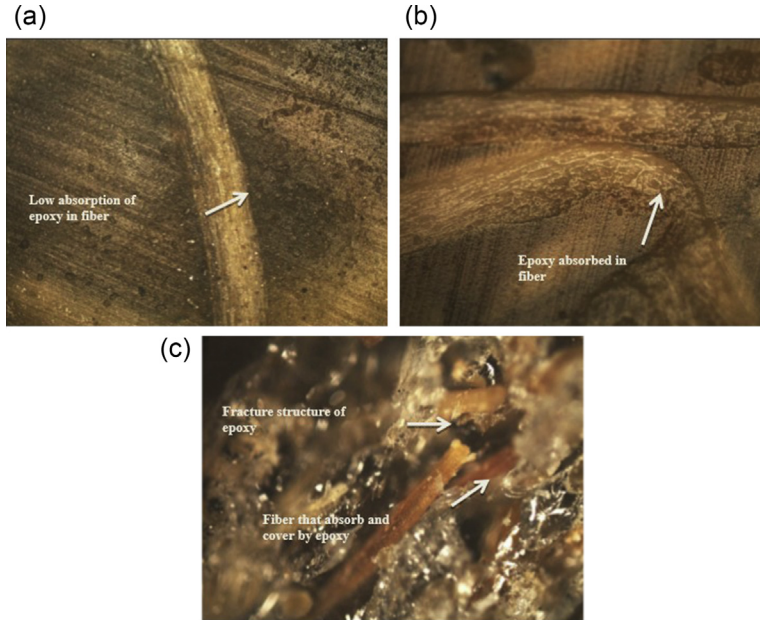


FIGURE 1.17 Light/optical microscope images of oil palm epoxy composites; (a) untreated, (b) treated, and (c) fracture part of oil palm fiber-epoxy.

epoxy in the fibers due to alkaline treatment. In Fig. 1.17(c) we can observe the fracture surface of oil palm fiber epoxy. The traces of epoxy on the fiber proved that fiber itself absorbed an amount of epoxy that changed its structure to become brittle. Therefore, the alkali treatment changed the structure of oil palm fiber inducing better compatibility with the matrix.

1.5 Biological methods as an alternative to chemical/physical treatments

Nowadays, chemical or physical modifications are among the most common type of surface treatments. Nevertheless, they present some disadvantages like: use of large amounts of solvents and hazardous chemicals, waste generation, pollution, high energy use, and high cost of some chemicals and equipment. Microorganisms such as fungi, bacteria, and enzymes could be used in order to overcome this issue; they can modify the natural fibers' surface with lower energy input. Thus, greener surface treatments could be developed for the extraction and surface treatment of raw fibers or natural fibers. Enzymatic, fungal, and bacterial treatments are described in the following sections.

1.5.1 Enzymatic treatment

The enzymatic treatment is an environmental friendly and very specific technique used nowadays in the development of natural fiber/polymer composites. The process consists in using enzymes for selectively removing hydrophilic pectin, lignin, and hemicellulosic components from the fibers [101], reducing the natural cellulosic fibers' hydrophilicity.

The principal enzymes applied in this catalytic process (enzymatic hydrolysis) are hydrolases and oxidoreductases [102]. The hydrolases include amylases, cellulases, proteases, pectinases, and lipases/esterases. From the class of the oxidoreductases the tyrosinase, laccase, or peroxidase was already studied for polymer modification [19]. Enzymatic catalysis differs from chemical catalysis due to the higher velocity of the reaction; the more delicate conditions of action (temperatures below 100°C, atmospheric pressure, and pH of 4−8); and the higher specificity of the reaction [103]. It was observed in several research works that the enzymatic treatment facilitates better fiber−matrix adhesion and improved mechanical properties of the composites [101,104−106]. For example, Laccase showed high selectivity to remove lignin efficiently without damaging the fiber's surface. Novamix, a mixture of lipase, protease, and amylase−xylanase, was used to separate microfibers from wheat husks and remove unwanted materials on the fiber surfaces without causing damage [107]. Abaca fibers, modified with commercial fungamix, exhibited smoother surfaces as Fig. 1.18 shows [108].

Beyond all these advantages, the cost of using enzymes is still the most important problem and the probable reason for its limited use. However, the possibility of recycling enzymes after each use could be one the chances of reducing the associated cost.

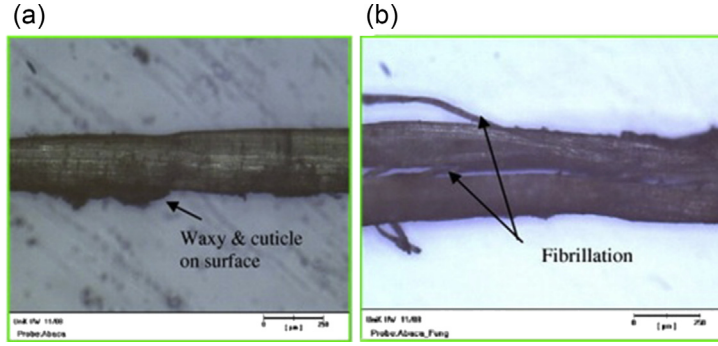


FIGURE 1.18 Micrograph of Abaca fiber surface morphology: (a) unmodified, (b) fungamix modified.

1.5.2 Fungal treatment

As the enzyme treatment, the fungal treatment is also an environment friendly and efficient alternative to the chemical methods. It is used to remove noncellulosic components (such as wax, lignin, or pectin) from the fiber surface by the action of specific enzymes [76]. The white-rot fungus *Schizophyllum commune* produces extracellular oxidases, enzymes that react with lignin constituents (lignin peroxidase). These enzymes are responsible for the lignin removal from the natural fiber surface increasing its roughness [109]. At the same time, the fungi are capable of producing *hyphae* which creates fine holes in the fiber surface providing roughness to the fiber surface and ultimately increases the interfacial adhesion with the matrix [110]. Hemp fibers treated with fungi *Ophiostoma ulmi* revealed lower percentages of impurities compared with untreated ones, due to water-soluble compounds' removal and due to the action of fungus on the hemp fiber as SEM images of Fig. 1.19 show [111].

Another study regarding the hemp fibers showed that after fungi treatment the composite strength is 22% higher in comparison to the untreated fiber. Moreover, for hemp polypropylene thermoplastics, fungi over alkali treatment showed a 32% improvement in composite strength [111].

Fungal treatment is a low cost method and green treatment that is poised to move the composite industry from conventional synthetic materials to green and environmentally friendly products [112].

1.5.3 Bacterial cellulose coating

Several methods were described in the previous sections taking into account the treatment of natural fibers by removing substances from their surface.

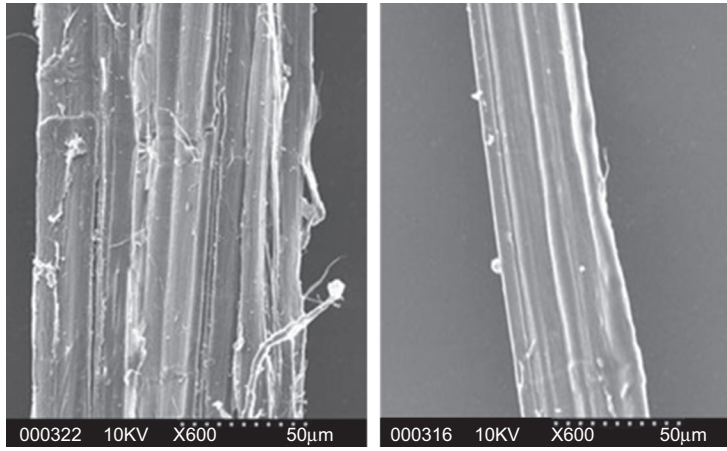


FIGURE 1.19 SEM picture of an untreated hemp fiber bundle (*left*) and *Ophiostoma ulmi* treated hemp fiber bundle (*right*).

The surface coating with bacterial cellulose is a recent modification technique which involves the addition of a new material onto the surface of natural fibers rather than removing.

Cellulose can be synthesized by various species of bacteria, such as those of the genera *Gluconacetobacter* (*Acetobacter*), *Agrobacterium*, *Aerobacter*, *Azotobacter*, *Rhizobium*, *Salmonella*, *Escherichia*, and *Sarcina* [113]. When that kind of bacteria are added to an appropriate culture medium in the presence of natural fibers, they produce bacterial cellulose which is preferentially deposited in situ onto natural fibers [114]. Bacterial cellulose (BC) exhibits unique properties when compared with plant cellulose, such as: high purity, high crystallinity, excellent biodegradability, large water-holding ability, and excellent biological affinity [115]. The goal of coating natural fibers with BC is to improve interfacial adhesion between fibers and polymers and also to develop green fiber−reinforced hierarchical nanocomposites with enhanced properties and much better durability [106,116].

Several methods were reported for coating natural fibers with BC, one of them regards the coating of sisal and hemp fibers with layers of BC by culturing *Acetobacter xylinum*. This method led to improved interfacial adhesion between the polymer PLLA and BC-coated natural sisal and hemp [117].

1.6 Nanoparticles deposition/functionalization

One of the most recent strategies for the natural fibers surface treatment is the incorporation of nanoparticles. Several types of nanoparticles can be used to enhance the interaction between the natural fibers and the matrix, to improve several characteristics of the fibers, and also to introduce new properties into the fibers.

As a promising surface treatment method, inorganic nanoparticles such as $CaCO_3$ can be employed as a filler to reduce the voids in the micropore fiber cell structure and as an adhesive between the fibers and the polymer matrix [118]. The nanoparticles on the fiber surface can provide nucleation sites to initiate the crystalline formation of the polymers, which will improve the compatibility between the fiber and the polymer matrix. Generally, the fibers are impregnated with Na_2CO_3 and $CaCl_2$ salts at a certain pressure and temperature and the inorganic nanoparticles of $CaCO_3$ are formed directly. This process compared to several chemical ones, is a simple, low-cost, and environmental friendly method which improves the mechanical characteristics of the fibers [119]. In addition to the filling and compatibility properties, the incorporation of nanoparticles can reduce the air bubble formation during the composite fabrication process improving the quality of the final product. Liang et al. reported that the mechanical properties of both kenaf fibers and kenaf fiber/polymer composites were increased by impregnating calcium carbonate nanoparticles into kenaf fibers. The tensile strength of the kenaf fibers increased more than 20% after the treatment, and also the tensile

modulus and strength of the composite composed of polypropylene matrix and treated kenaf fibers [120].

Besides $CaCO_3$, other types of nanoparticles can be used for functionalizing the natural fiber surface and introduce new properties, based on the type of nanoparticle used, magnetic and electrical conductivity; UV protection; self-cleaning; fire retardant; and other special properties can be achieved. Very promising results were obtained utilizing gold (Au), silver (Ag), Cu (copper), Pd (palladium), Pt (platinum), Co (cobalt), titanium dioxide (TiO_2) nanoparticles in fibers [121,122]. Cellulosic fibers with incorporated Au and Ag nanoparticles are used in homogeneous and heterogeneous catalysis, biosensors, protein delivery, and optical applications. Besides these applications, the Ag nanoparticles are also used in antimicrobial systems and also in the development of conductive structures [123,124]. The titanium dioxide incorporation allows extending the cellulose fiber applications to photocatalysis, stain-proofing, and self-cleaning; gas and humidity sensors; photovoltaics; photocleavage of water; photodegradation of organic pollutants; etc [125]. Zinc oxide (ZnO) nanoparticles have excellent ultraviolet protective properties and also conductive and fire retardant characteristics which can be incorporated into the composites [126,127]. Natural fibers with magnetic properties can be obtained by introducing, for example, iron oxide nanoparticles into the structure [128].

Several other examples could be presented; however, the goal is always the same, the combination of nanoparticles with natural fibers as an emerging strategy to produce a range of multifunctional cellulosic composites.

1.7 Concluding remarks and future trends

Currently, the application of natural fibers in several industrial fields is in full growth due to its environmental and economic benefits compared to synthetic materials. Natural fibers are recyclable, biodegradable, safe to use, and present high specific strength-to-weight ratio. This last parameter is of particular importance when we are dealing with automotive applications, the high specific strength-to-weight ratio of the fibers used in composites manufacturing leads to the automobile parts weight reduction, which is reflected directly in the fuel consumption reduction. However, one of the problems related to the use of natural fibers in polymeric composites is the low compatibility between the fibers and the polymeric matrix. Therefore, several fibers surface functionalization methods were described in this chapter including chemical, physical, biological, and with nanoparticles.

All the examples described herein reveal that the natural fibers surface treatment is essential to reduce the hydrophilicity of the fibers, to remove surface contaminants, and to increase the surface roughness improving the fiber surface properties and providing a better mechanical bonding between the fiber and polymer.

In conclusion, the natural fibers are very promising materials to be used in polymer composites development using different fiber surface modification methods. The chemical treatment is still the most frequently used method followed by the physical methods which are attracting more and more attention.

In the near future, we hope it will be possible to use biological methods and nanoparticles treatment to achieve better results and improve the sustainability of the processes involved in the manufacturing of natural fiber polymer composites.

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