Chapter 3
Modification of the Interface/Interphase in Natural Fibre Reinforced Composites: Treatments and Processes

The modification of surface properties of synthetic reinforcement fibres to modify composite interphase performance is mostly achieved by chemical functionalization techniques in aqueous media, and in some cases in organic media. In particular, surface treatments of glass fibres are carried out by the use of complex aqueous chemical systems, known as sizings, including one or more organofunctional silane coupling agents, a film former and other additives, i.e. cationic or non-ionic lubricants, anti-static agents, surfactants, wetting agents, chopping aids, and antioxydants). Recent developments on sizing of glass and carbon fibres also include the use of physical methods, such as plasma, for the deposition of a sizing layer on fibre surface, and the addition of nanoparticles in sizings, such as carbon nanotubes (Bergeret and Krawczak 2006; Thomason 2013).

Natural fibres does not yet benefit from such a technological and scientific background. Thereby, many strategies of bulk and surface modifications are currently developed to implement natural fibres in composite materials applications (Belgacem and Gandini 2005; Bledzki and Gassan 1999; Faruk et al. 2012, 2014; George et al. 2001; John and Anandjiwala 2008; Kalia et al. 2009; Zafeiropoulos 2011). Natural fibre treatments can be classified in two distinct categories:

- The first category of treatments, often called "**pre-treatments**" in literature, is mostly intended to enhance the wetting and the mechanical interlocking between the fibres and the matrix. These pre-treatments can be enzymatic, chemical or thermal. They primarily modify the topography (roughness) and the surface physico-chemistry (surface free energy, polarity, chemical functionality) of fibres by the extraction of some non-cellulosic compounds from the middle lamellae and plant cell walls. Thereby, they can also affect the inter-cellular cohesion within the fibre bundles, and hence promote the dispersion of the fibres within the polymer matrix, resulting in an enhanced specific interfacial area. Pre-treatments are also used to prepare natural fibres for a subsequent functionalization treatment that is applied to improve their compatibility with a polymer matrix.

- The second category of treatments consists in the functionalization of natural fibres. **Functionalization** is carried out by chemical or physical treatments, and can be applied either directly to raw fibres or after a pre-treatment. It aims at achieving a chemical and/or physico-chemical coupling between the fibres and the matrix by means of reactive (polymerizable) molecules and/or grafted polymers that are intended to react directly with the fibres before composites processing or incorporated into the matrix during the processing.

In this chapter, the different pre-treatments and functionalization treatments and related processes developed to modify natural fibres and interfacial properties in biocomposites will be exposed.

3.1 Pre-treatments of Natural Fibres

The pre-treatments developed to prepare natural fibres for their use in composite applications are mainly based on retting, chemical and thermal processes. Most of these treatments originate from the textile and wood industries, and were developed since many years to improve the quality of biomass derived products.

3.1.1 Retting Treatments

Several retting techniques are reported in literature, named as (i) dew retting, (ii) water retting, (iii) enzymatic retting, (iv) chemical retting and (v) mechanical retting (Paridah et al. 2011). These retting processes are commonly used to ease the extraction of bast fibres from flax, hemp, jute and kenaf stems. It should be noticed that mechanical retting, better known as decortication,[1] takes place after harvesting, and consists of successive mechanical processes (rippling, drafting, breaking and threshing) intended to separate bast fibres, and usually carried out after a prior dew retting (Reux and Verpoest 2012).

Retting treatments act by degrading non-cellulosic biopolymers constituting the cell walls and the middle lamella which cements adjacent plant cells. This leads to the splitting of fibre bundles from the surrounding cortical tissues (Akin et al. 1996; Brown et al. 1986). The quality of the extracted fibrous material in terms of biochemical composition, fineness, cleanness and mechanical strength is greatly influenced by the type and conditions of retting as reviewed by Paridah et al. (2011).

During **dew retting**, indigenous soil fungi colonize the stems and secrete hydrolytic enzymes (polygalacturonase, pectin-lyase, xylanase) which metabolize the intercellular compounds from the middle lamellae and those present in the cell walls (pectins and hemicelluloses, especially xylan in the case of flax) (Brown et al. 1986). The efficiency of this retting technique is however highly dependent on

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[1]Commonly referred to as "defibring" in the case of hemp and "scutching" in the case of flax.

duration and pedoclimatic conditions (temperature, humidity). Hence, the resulting extracted fibres are of variable quality and fineness. Furthermore, the presence of highly cellulolytic fungi may cause the degradation of cellulose resulting in the production of poor quality fibres (Brown et al. 1986). Martin et al. (2013) studied the influence of the degree of dew retting of flax fibres on the mechanical properties of polypropylene PP/20% w/w flax composites. The mechanical characterization of the composites showed an increase of about 20% in Young's modulus accompanied by a 30% increase in tensile strength at the highest degree of retting (6 weeks of dew retting). This improvement in mechanical properties was primarily attributed to a more efficient separation of the retted fibre bundles during extrusion and injection that increased their aspect ratio (from 11 ± 8 to 14 ± 7 after 6 weeks of retting) and hence improved the load transfer efficiency from the matrix to the fibres. An increase in tensile modulus and strength of the retted fibres was also reported although its origin was not clearly identified.

Water retting is carried out in an aqueous environment and occurs under anaerobic conditions. Pectic enzymes produced by bacteria are responsible for the decomposition of pectin substances from the middle lamella (Sharma 1987). Since retting conditions are more easily controllable, this leads to better fibre quality than dew retting. Good quality hemp fibres were also obtained by seawater retting due to the presence of specific strains *Stenotrophomnas maltophilia* and *Ochrobactrum anthropi* able of producing pectinases and degrading the middle lamella (Zhang et al. 2008). However, water retting is a polluting process due to the substances released in water by the anaerobic degradation of plants. For this reason, dew retting has superseded water retting in several countries. Meijer et al. (1995) studied the effect of dew and water retting on the properties of flax fibres. The authors highlighted the possibility of monitoring retting by a biochemical analysis method consisting in measuring the decrease in the amount of pectins over time. Nevertheless, the authors noted that there is no clear relationship between the evolution of the pectin content and the resulting fineness of extracted fibres. As reported in Martin et al. (2013), other techniques based on sugar analysis or indirect correlation based on thermogravimetric, near infrared spectroscopy (NIR) or Shirley analysis were developed to quantify the degree of retting of flax fibres. However, there is currently no standardized method.

Chemical retting consists in treating natural fibres in aqueous solutions of sodium hydroxide, sodium benzoate or hydrogen peroxide at low concentration (Paridah et al. 2011). In this regard, it is very similar to chemical pre-treatments (see Sect. 3.1.2). This retting technique is highly effective in removing components from the middle lamella, and allows obtaining well separated fibres. However, a reduction in the tensile strength and modulus of fibres is often reported even for low concentrations of chemicals due to degradation of cell walls components (Paridah and Khalina 2009; Paridah et al. 2011). In addition, processing costs are higher than water and dew retting techniques that do not require chemical inputs.

Enzymatic retting is based on the use of specific bacterial strains and/or fungi, and the controlled action of enzymes on the fibres. Indeed, even if indigenous microorganisms are present in large amounts on natural fibres, their action can be better controlled with a prior sterilization followed by inoculation of selected strains or

enzymes by direct spraying or immersion in aqueous media. Although enzymes secreted by microorganisms isolated from retted straw should be more effective in retting, the use of exogenous enzymatic cocktails is preferred due to high costs inherent to the screening of efficient indigenous microorganisms and production of specific enzymes. It should also be noted that enzymatic retting is a batch process that involves reprocessing of waste water and effluents (Van Sumere 1992). Li (2009) have treated hemp fibres by natural retting with indigenous microorganisms in sealed plastic bag and compared it with various enzymatic retting treatments, including inoculation of different white rot fungi (Li et al. 2009), *Phanerochaete sordida (D2B), Pycnoporus species (Pyc), Schizophyllum commune (S.com)*, and immersion in enzymatic solutions (Li and Pickering 2008) containing pectinase and laccase and chelators (sodium salt promoting solubilization of pectins). The authors studied the effect of these retting treatments on the mechanical properties of PP/maleic anhydride-grafted polypropylene (MAPP)/hemp fibres 57/3/40% w/w composites prepared by extrusion. The results demonstrated that these treatments significantly altered fibre roughness and eased the splitting of fibre bundles due to the partial removal of intercellular non-cellulosic components from the middle lamella. The highest increase in tensile strength was observed for composites reinforced with fibres retted with the lignivore fungus *S.com*. However, the authors showed that this enzymatic treatment reduced the tensile strength of the fibres by 38%, suggesting that the increase in the mechanical performances of the composites was mainly due to an improvement in the interfacial adhesion. This was confirmed on the one hand by the observation of fracture surfaces of the composites, which showed limited debonding of treated fibres from the matrix (Li and Pickering 2008) and, on the other hand, by the great increase in interfacial shear strength (IFSS) as measured by a pull-out test (Li 2009).

The use of retting treatments therefore appears to be beneficial to the quality and performances of natural fibres and their biocomposites. The main challenge lies in the determination of an optimal balance leading to an efficient separation of fibres bundles and enhanced fibre shape factors within the composite without impairing the intrinsic mechanical properties of the fibres. This requires an advanced control of the action of microorganisms and enzymatic degradation processes that should be targeted towards non-cellulosic components from the middle lamellae so as to preserve as much as possible the biopolymers constituting the cell walls.

3.1.2   Chemical Treatments

Considering the complex structure of natural fibres which is made of various biopolymers and oligomers of varying polarity, they are likely to be sensitive to aqueous and organic solvents. Indeed, changes in the biochemical composition and physico-chemical properties of natural fibres can be observed when they are treated with solvents due the solubilization and partial or total extraction of various intra and inter-cellular components. Even water treatments can induce significant chemical modifications in natural fibres. Bourmaud et al. (2010) studied the

influence of water pre-treatments at different temperatures onto flax fibres. The authors showed the extraction of several polysaccharides from the middle lamella even at ambient temperature for long treatment times (72 h). They also found that when the fibres are treated with water at high temperature (105 °C), pectins undergo partial hydrolysis. Based on these results, Le Duigou et al. (2012) showed that a water treatment at ambient temperature (72 h at 23 °C) results in small decrease of fibre properties but a significant improvement in interfacial shear strength (IFSS) with poly(acide L-lactique), due to the removal of weaky bonded components from the fibre surface. Truss et al. (2016) studied the impact of water washing on the evolution of biochemical composition of hemp fibres. The authors found a modification of the surface chemistry of the fibres due to the elimination of cuticle components loosely attached to the surface. Water washing also removed inorganic material and large amounts of nitrogen containing polymers, probably proteins. The analysis of the recovered washing water suggested that the water treatment also removed products from the bulk of the fibres that were not originally on the surface.

Lefeuvre et al. (2015) conducted a comprehensive study on the selective removal of non-cellulosic components from the middle lamella and matrix components from the cell walls. Scutched flax fibres were subjected to a successive sequence of extractions in boiling water, EDTA, HCl and NaOH aqueous solutions. Results highlight the important role of non-cellulosic components on the mechanical behaviour of the fibres. Tensile strength and stiffness of the fibres gradually decrease along the extraction treatments. Furthermore, the authors assumed that pectins extracted by weak acid, were more involved in the load transfer whereas hemicelluloses and pectins extracted by alkali, ensure the cohesion between cellulose microfibrils and contribute to the stiffness of the fibre. Acera et al. (2016) also described the influence of different chemical extraction treatments on the biochemical composition and physical chemical properties of flax tow fabrics and their composites. The pre-treatments by various aqueous and organic solvents with increasing solvation capacity resulted in a gradual extraction of cell walls components from the fibres. The authors observed a strong influence of these pre-treatments on the microstructure and mechanical properties of epoxy composites reinforced with the treated flax fabrics. This study demonstrates that the removal of non-cellulosic inter- and intra-cellular components can improve the fibre dispersion and promote their impregnation within the matrix. However, it may also result in a drastic decrease of the mechanical properties of the fibres and composites, hence highlighting the key role of non-cellulosic components in the stress transfer mechanisms from fibre to fibre and fibre to matrix.

Among all the chemical pre-treatments, the alkali pre-treatment, also called mercerization, is widely used in the textile industry and consists in treating natural fibres and man-made cellulosic fibres with basic aqueous solutions, generally NaOH. The study of the effect of alkali pre-treatments on natural fibres for polymer composite applications has been widely studied (Chandrasekar et al. 2017). Alkali pre-treatments modify the biochemical composition of natural fibres by the extraction of the different non-cellulosic components from the fibres, such as lignin, pectins or hemicelluloses. The extraction of these components can induce a separation of fibre bundles into elementary fibres or even promote the defibrillation of the latter into cellulose

microfibrils. The alkali treatment is also likely to modify the cellulose crystalline structure in natural fibres, depending on the alkali concentration but also on the duration of the treatment and the nature of the alkali reagent used. If the NaOH concentration is high enough (>15–20%w/w in water), the crystalline structure of native cellulose recombines from cellulose I to a more stable crystalline form, called cellulose II, in which the cellulose chains are organized anti-parallel involving changes in the inter- and intra-molecular hydrogen bonding network. This is accompagnied by a significant swelling of the fibres due the diffusion of water molecules into their crystalline structure. Altough being less pronounced as with ethanol or toluene (Acera Fernandez et al. 2016), the removal of some hydrophobic components (waxes, oils…) by alkali pre-treatments can also increase the hydrophylic character of the fibres. It should be pointed out that at very high alkali concentrations ($\sim$30%w/w in water), a decrease of the cellulose crystallinity and polymerization degrees for jute and flax fibres were observed (Gassan and Bledzki 2001).

The removal of non-cellulosic components from the fibres by alkali treatments is also likely to modify their surface morphology. In some cases, cellulose microfibrils are visible on the surface of the fibres after the treatment, with an increase of the surface roughness (Baley et al. 2006). For the production of composite materials, these morphological modifications are an opportunity for the creation of new available interfaces between reinforcements and polymer matrix. In this regard, Yan et al. (2012) observed the fracture surface of flax/epoxy composites and concluded that mercerization of flax fibres can improve the mechanical interlocking of the matrix onto the fibres by the increase in surface roughness. The authors also assumed that the removal of waxes from the fibres surface promotes the formation of hydrogen bonds with the matrix, and concluded that the interfacial adhesion in such composites was improved by the combination of mechanical and physico-chemical interactions. Van de Weyenberg et al. (2003, 2006) also reported an increase in mechanical properties due to an improvement of the fibre/matrix interface for flax fabrics/epoxy composites. Besides, alkali treatments can enhance the accessibility and reactivity of fibres towards grafting agents due to the increase in available hydroxyl groups and the removal of hydrophobic compounds. For this reason, alkaline treatments have been also used as pre-treatments for the surface functionalization of natural fibres and their further use in composite materials (Javadi et al. 2010, Le Moigne et al. 2014).

Beyond these morphological and physico-chemical changes, a softening phenomenon consecutive to the alkali pre-treatment has been reported and ascribed to the possible decrease in cellulose crystallinity or to the recombination of cellulose I into cellulose II. These structural evolutions tend to decrease the Young's modulus of cellulose (140 GPa for cellulose I and 90 GPa for cellulose II), and hence of natural fibres. Nevertherless, this softening cannot be generalized to all treatment conditions and with all natural fibres. Furthermore, this softening effect is not necessarily detrimental for the composite performances. Indeed, less fragile fibres can be particularly advantageous for better impact resistance of composites or for limiting fibre breakage during extrusion of thermoplastic composites.

Concluding, the alkali treatment is one of the most used chemical pre-treatments of natural fibres when used to reinforce thermoplastics and thermosets composites. This

pre-treatment has generally a positive effect on the final properties of composites (Chandrasekar et al. 2017), which is primarily attributed to an increase in surface roughness and specific surface area due to the cleaning and separation of natural fibre bundles into elementary fibres. These modifications result in a better interfacial adhesion by an enhanced mechanical interlocking. Furthermore, the partial removal of the non-cellulosic components (lignin, hemicelluloses, pectins, waxes, fats…) increases the concentration of cellulose hydroxyl groups at the fibres surface which can react with functionalizing molecules or interact with the matrix. However, as observed for all chemical pre-treatments, too concentrated alkali treatments can result in the removal of essential non-cellulosic matrix constituents that contribute to the structural properties of natural fibres, as well as the partial depolymerisation of cellulose. This can greatly weaken the fibres structure and lead to a drastic loss of their mechanical properties, hence reducing the properties of the composites.

3.1.3 Thermal Treatments

Heat treatments of lignocellulosic biomass, also called torrefaction or retification, were mainly developed for the wood industry. They basically consist in a series of heating cycles at high temperature to produce heat-treated wood with improved durability. Indeed, heat treatments significantly reduce water uptake and swelling of wood, and make it more resistance to fungal attack and decay. Moreover, from an environmental point of view, heat treatments are an interesting alternative to commonly used biocidal treatments. Several heat-treatment processes for wood have been patented, especially in Europe: retification® (New Option Wood, France), ThermoWood® (VTT, Finland), Plato® (Plato International BV, the Netherlands), OHT (Oil Heat treatment, Menz Holz GmbH, Germany), etc. These processes primarily differ by their operating conditions, i.e. heating temperature (from 180 to 280 °C) and heating rate, residence time, atmosphere (relative humidity, oxidizing or inert), and optional use of oils (Hill 2006; Nguila-Inari 2008).

Heat treatments induce a chemical modification of the biopolymers constituting wood cell walls. In particular, hemicelluloses, which are amorphous and of low molecular weights, undergo a severe hydrolytic depolymerization (Yildiz and Gümüskaya 2007). Furthermore, this process can be catalysed by the degradation products formed (acetic acid or heterocyclic aldehydes as furfural). At higher temperatures (around 220 °C), lignins are also modified with the release of various molecules (vanillin, eugenol, guaiacol…) (Hakkou et al. 2005a, b, c; Yildiz 2002). This can be associated with crosslinking phenomena with aldehydes (furfural) formed during the degradation of hemicelluloses (Hakkou et al. 2005b). To a lesser extent, an increase in the degree of crystallinity of cellulose can be observed due to a more rapid degradation of the amorphous zones, crystalline cellulose degrading above 300 °C (Sivonen et al. 2002). All these chemical and structural modifications give the wood fibres greater dimensional stability in humid atmosphere, as a consequence of the degradation of hemicelluloses that are highly hygroscopic.

Studies have also been carried out on the potential of controlled heat-treatments of natural fibres for their use in composite materials. By analogy with heat-treated wood, this could effectively eliminate low molecular weight compounds, most hygroscopic ones and those weakly bounded to the cell walls, and thus modify surface physico-chemistry of natural fibres by making them more hydrophobic. Such modifications are likely to improve the fibre/matrix interfacial adhesion and limit water uptake and swelling of fibres within the composite. Finally, it should be noted that heat treatments have the advantage of not requiring the use of solvents, and therefore constitute an interesting alternative to chemical treatments. In this regard, Ayrilmis et al. (2011a) have shown that thermal cycles applied to *Eucalyptus camaldulensis* fibres at moderate temperatures (120 to 180 °C) during 20 to 40 min can significantly reduce water uptake, and hence improve the dimensional stability of polypropylene based composite panels (50/50% w/w) prepared by dry-blending and thermocompression. Berthet et al. (2016) studied the effect of heat-treatments (torrefaction) on milled fractions of wheat straw in an inert atmosphere (N_2) at temperatures ranging from 180 to 280 °C and cycle times from 15 min to 90 min for their further incorporation in biopolyester matrix, i.e. poly(hydroxybutyrate-co-valerate) (PHBV). The authors showed in particular that the heating temperature has a significant impact on the biochemical composition, the colour, the morphology and the hydrophobicity of the wheat straw fractions. Heat-treatments conducted at 180 and 230 °C degrade some of the hemicelluloses, lignins and other non-cellulosic compounds such as proteins, waxes and fatty acids. The authors assumed that a combustion of the finest particles could occur, thereby explaining the larger median size and shape factor obtained with the treated wheat straw fractions. Moreover, the results show a significant increase in the hydrophobicity of heat-treated wheat straw, characterized by water contact angles of about 115° and a significant decrease in the polar component of their surface energy. The physico-chemical and morphological modifications of the heat-treated wheat straw fractions led to an improved interfacial adhesion with the PHBV matrix and a reduction by about 30% of water vapor permeability for PHBV/wheat straw 80/20% w/w composites. However, the presence of microscopic defects, i.e. porosities, within the microstructure of the composites did not allow an improvement of the mechanical properties as compared to the neat matrix.

Nevertheless, it should be pointed out that excessive thermal cycles can irreversibly damage the microstructure of natural fibres and reduce their mechanical properties. Gourier et al. (2014) have shown that heat-treatment of flax fibres at moderate temperatures between 140 and 190 °C during a short cycle (8 min) representative of an extrusion and injection process does not affect their tensile strength and even increases their Young's modulus by about 10%. In contrast, when exposing flax fibres to temperatures above 250 °C, a drop of more than 30% of their modulus and nearly 70% of their strength was observed. Van de Velde and Baetens (2001) also reported significant degradation of the tensile properties of flax fibres above 180 °C. Gassan and Bledzki (2001) and Placet (2009) found a significant decrease in the tensile properties of jute, flax and hemp fibres (*Cannabis sativa* L.) for heating temperatures above 150–170 °C. In all these studies, the loss in mechanical properties following heat-treatments was explained by structural modifications occurring within natural fibres, especially in the secondary cell wall

S2. The authors assumed a degradation of cellulose and non-cellulosic components (hemicelluloses, pectins, lignins) of the cell walls, as well as a rearrangement of cellulose microfibrils and modification of the behaviour under mechanical stress.

Concluding, heat-treatments can have positive effects on the physico-chemical and morphological properties of natural fibres, and the final performances of composites. However, tailoring the heating conditions (temperature, time, and atmosphere) according to natural fibres characteristics, i.e. their biochemical composition, the structure of their cell walls, is critical to control the thermal degradation of biopolymers and limit the resulting loss in mechanical properties.

3.2 Functionalization of Natural Fibres

Functionalization treatments are primarily achieved through chemical reactions intended to compatibilize natural fibres with polymer matrices and improve performances of the final composite materials. Functionalization of natural fibres consists in modifying their surface chemistry by grafting molecules bearing functional groups having a particular affinity or being able to react with the macromolecules of the matrix. These functionalizing molecules that are polymerizable molecules or low molecular weight polymers, are therefore selected according to their chemical structure and reactivity towards the matrix. Physical treatments or physical-activated chemical functionalization are also considered for the modification of fibre surface properties and compatibilization with the matrix. Conversely, it is also possible to modify the reactivity of the matrix through chemical modifications or incorporation of additives that can react with the fibres during composite processing. These different approaches will be detailed in the next paragraphs.

3.2.1 Chemical Functionalization

Grafting of coupling agents on the surface of lignocellulosic fibres is commonly used to develop a less polar and/or reactive surface that would favour the compatibility and chemical coupling with the matrix. Such a process is often called surface finishing or sizing, and has been initially developed for modifying synthetic fibres as carbon and glass. Coupling agents are molecules possessing two functions. The first is to react with hydroxyl groups (or others functional groups) of natural fibres while the second is intended to react with functional groups of the matrix, thus forming a bridge of chemical bonds between the fibre and the matrix (George et al. 2001). So far, over 40 coupling agents have been tested and used in research and production (Lu et al. 2000). These agents are classified as organic, inorganic, and organic-inorganic groups, among which organic agents are better than inorganic agents because of stronger interfacial adhesion. The most popular coupling agents currently being used include anhydrides, fatty acids, isocyanates, organosilanes and all kinds of short-chains chemicals.

Esterification with anhydrides. Anhydrides can be classified into two major groups: non-cyclic anhydrides (i.e. acetic) and cyclic anhydrides (i.e. maleic). Of the non-cyclic anhydrides, acetylation with acetic anhydride (Fig. 3.1), which consists in substituting hydroxyl groups with acetyl moieties, is the most widely reported to reduce the hydrophilic character of lignocellulosic fibres (Hil et al. 1998; Baiardo et al. 2002), thus resulting in a surface free energy and polarity similar to the one of low-polar polymer matrices (Zafeiropoulos et al. 2002a, b). The reaction involves the formation of ester bond by esterification of carboxylic groups of the anhydride with the free hydroxyl groups of lignocellulosic fibres. Such treatment requires several steps, and the use of strong bases or catalysts to ease the reaction. Because the substitution of hydroxyl groups with acetyl moieties occurs primarily on lignin and hemicelluloses, fibres that contain greater amounts of these components generally show greater degrees of esterification. Acetylation is also known to result in smoother surfaces, due to the removal of waxy substances. Surface acetylation was found to promote the adhesion between flax fibres and P(3HB-co-3HH) (Zini et al. 2007) or Bionolle (Baiardo et al. 2004; Zini et al. 2004), but not so much with PLA (Zini et al. 2004) or PHB (Lee and Wang 2006) (Table 3.1). Significant improvement of mechanical properties was mainly due to transcrystallization phenomena (Zini et al. 2004, 2007). The limitation of this kind of treatment is that the acetylation reaction can lead to a decrease of fibre intrinsic strength and tenacity, as observed for flax fibres (Zini et al. 2004, 2007). This implies a lower reinforcing capacity which is likely to counterbalance the improvement in mechanical properties related to the enhanced interfacial adhesion. The use of acetic anhydride treatment on natural fibres proved to be not as effective compared with other techniques (Tserki et al. 2006).

Baiardo et al. (2004) studied the impact of two types of fibre modification (either acetylated or valerylated fibres) on the mechanical properties of Bionolle®/flax fibres composites. In spite of achievement of similar surface tension values for the two kinds of modified fibres, the reinforcing effect of the two considered modified fibres was different. These results highlight that similar surface tensions for matrix and fibres is not a sufficient condition to obtain a strength improvement. Another important parameter is the fibre tenacity that is likely to change depending on the reaction conditions used to modify the fibre surface. A decrease in fibre tenacity would be detrimental to reinforcement of the composites.

Reactions of lignocellulosic fibres with cyclic anhydrides such as maleic anhydride have also been performed. The fundamental difference with other chemical treatments is that maleic anhydride is not only used to modify fibre surface but also to functionalize polymer chains of matrix, as largely exploited to achieve better interfacial
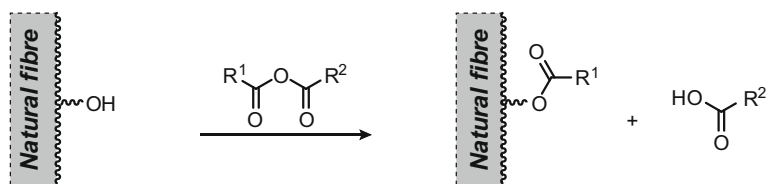

Fig. 3.1 Esterification reaction of lignocellulosic fibres with anhydride

bonding in natural fibre based polyolefins (Mohanty et al. 2004). In this case, maleic anhydride grafted polypropylene or polyethylene are directly incorporated during composite processing by reactive extrusion (see Sect. 3.3.2).

Esterification with saturated and insaturated fatty acids. Numerous studies are focusing on the grafting of fatty acids in order to decrease the hydrophilicity of lignocellulosic fibres and thus increase their resistance towards water (Zafeiropoulos et al. 2002a). As an example, it was shown that the grafting of stearic acid (stearation) on flax fibres allows increasing the theoretical work of adhesion with PP (Zafeiropoulos et al. 2002b). However, it is worth noting that this treatment was less efficient than acetylation (Zafeiropoulos et al. 2002b). Similar effect was observed for PE/sisal fibres composites, with an increase of the interfacial shear strength qualitatively confirmed with observations from SEM fractographs (Torres and Cubillas 2005). Stearation has been tested for various types of lignocellulosic biomass, including flax (Zafeiropoulos et al. 2002b), jute (Dogan et al. 2016) or sisal (Torres and Cubillas 2005).

Some works are also devoted to the use of fatty acid amide, the amide being a reactive site able to form hydrogen bonding with hydroxyl groups of natural fibres. This coupling agent can be potentially derived from waste oil fatty acids (Chun et al. 2016). Fatty acyl chlorides (acylation) are also often used, requiring the presence of a catalyst such as pyridine (Freire et al. 2006, 2008). The influence of the fatty acid chain length (from hexonoic to docosanoic acids) on the esterification efficiency of bleached kraft pulp fibers obtained from *Eucalyptus globulus* has been studied by Freire et al. (2006). It was shown that for a same reaction time, degree of substitution (DS) of cellulose hydroxyl groups decreased significantly when increasing the fatty acid chain length. The increase in the DS of cellulose esters promoted the extensive decrystallization of cellulose, but did not enhance any further the hydrophobic character of fibres surface. Besides, these acylation reactions reduced somewhat the thermal stability of the fibres (Freire et al. 2006). Improved interfacial adhesion with LDPE was achieved with treated cellulose fibres, resulting in enhanced mechanical properties (Table 3.1), as well as better water resistance (Freire et al. 2008). The results obtained clearly demonstrate the importance of a strict DS control in order to achieve better composite performances (Freire et al. 2008).

Treatment with isocyanates. Isocyanates have a functional group –N=C=O, which is highly reactive towards hydroxyl groups of cellulose and phenolic groups of lignin, and can form a stable urethane bond (Fig. 3.2). In the case of diisocyanates, the remaining moiety is able to react with the polymer matrix during composite processing to provide a covalent linkage between the matrix and the fillers (Ohkita and Lee 2004; Ly et al. 2008; Petinakis et al. 2009). When using stiff and small bifunctional monomers such as methylene-bis-diphenyl diisocyanate (MDI) or 1,4-phenylene diisocyanate (PPDI), the bridging of two fibres or the reaction of both functions at the surface of the same fibre are excluded (Ly et al. 2008). The main interest of treatment with isocyanates is the absence of reaction by-products such as water that could damage the composite. Grafting reactions can be conducted in solution, by immersion of lignocellulosic particles in the presence of a catalyst and during quite long reaction durations (around 72 h) (Rozman et al. 2001; Ly et al. 2008), or directly during the

Table 3.1 Effect of fibre surface chemical functionalization on the evolution of mechanical properties of treated fibre/polymer composites, as compared to the respective untreated fibre/polymer composites—Some examples

Chemical treatment	Matrix	Fibre type	Fibre content	Young's modulus	Tensile strength	Elongation at break	References
Acetylation	PLA	Flax	16 vol.%	+18%	Not affected	−11%	Zini et al. (2004)
	PBSA	Flax	16 vol.%	Not affected	+15%	Not affected	Zini et al. (2004)
	PHBHH	Flax	25 vol.%	Not affected	+30%	–	Zini et al. (2007)
Fatty acids (various chain length and treatment conditions)	LDPE	Cellulose	30 wt%	From −55% to +144%	Up to +68%	From −70% up to +170%	Freire et al. (2008)
Fatty acid	PP	Cocoa pod husk	40 wt%	+12%	Not affected	+90%	Chun et al. (2016)
Isocyanate (MDI)	PLA	Wood flour	20 wt%	Not affected	+6%	Not affected	Petinakis et al. (2009)
			40 wt%	+20%	+9%	Not affected	Petinakis et al. (2009)
	PP	Pine	30 wt%	+30%	+35%	–	Girones et al. (2008)
Isocyanate (PMDI)	PBS	Lignin and switchgrass	50 wt%	Not affected	+28%	+30%	Sahoo et al. (2013)
Silane	PLA	Ramie	30 wt%	–	+13%	+28%	Yu et al. (2010)
	PLA	Flax	20 wt%	+5%	+20%	–	Le Moigne et al. (2014)
	TPU/DAPA blend (50/50)	Cellulose	10 wt%	−14%	Not affected	Not affected	Reulier et al. (2016)
	TPU/DAPA blend (80/20)		10 wt%	+16%	Not affected	Not affected	Reulier et al. (2016)
	PHBV	Oak wood flour	20 wt%	+16%	+6%	Not affected	Scrubar et al. (2012)
	PHBV	Coir	10 wt%	Not affected	−6%	+6%	Javadi et al. (2010)

(continued)

Table 3.1 (continued)

Chemical treatment	Matrix	Fibre type	Fibre content	Young's modulus	Tensile strength	Elongation at break	References
Silane (TMOS)	PHBV	Olive husk flour	20 wt%	+34%	+25%	−31%	Hassaini et al. (2017)
Alkali +Silane	PHBV	Coir	10 wt%	Not affected	−6%	Not affected	Javadi et al. (2010)
	PLA	Flax	20 wt%	+6%	+25%	–	Le Moigne et al. (2014)
PEG (350)–grafting	PBSA	Flax	25 vol.%	Not affected	+6%	+7%	Baiardo et al. (2004)
	PLA	Flax	21 vol.%	Not affected	+52%	–	Zini et al. (2004)

processing of composite materials (Lee et Wang 2006; Petinakis et al. 2009; Sahoo et al. 2011, 2014).

As an example, Lee and Wang (2006) reported the use of isocyanates as a coupling agent in PLA or poly(butylene succinate) (PBS)/bamboo fibres systems, leading to a slight improvement of tensile properties (Table 3.1) and water resistance. The slight positive effect of grafting with diisocyanate on the interfacial fibre/matrix adhesion was also evidenced by Petinakis et al. (2009) on PLA/wood flour micro-composites, with an increase of the tensile strength from 60.24 to 65.68 MPa for a filler content of 40 wt%. In the case of PBS/(25 wt% of lignin and 25% of switchgrass fibres) hybrid composites, the 28% improve in tensile strength induced by the incorporation of 1% PDMI was ascribed to the better mechanical interlocking between the polymer and the fillers (Sahoo et al. 2013). The same tendencies were observed for PP/wood fibres composites, with an increase in the tensile strength up to 30% but also in the tensile modulus (Table 3.1) (Gironès et al. 2008). Authors highlighted the importance of polyreactivity for the coupling agents' efficiency. However, ecotoxicity is an important factor to consider when developing polymer composites from renewable resources, especially for food packaging applications. Isocyanates may not be regarded as viable treatment compounds for natural fibres since the decomposition of certain isocyanates in water can result in the formation of heterocyclic diamines that are suspected to be carcinogenic substances.

Treatment with organosilanes. Organosilanes are widely used for the coupling of glass fibres with polymers. They have also been adopted for improving the interface in lignocellulosic fibres/polymer systems (Pickering et al. 2003; Xie et al. 2010). The general chemical formula of silane is $X_3Si–R$ (Fig. 3.3), where R is a functional group able to react with the polymer matrix, and X is an alkoxy group (usually methoxy or ethoxy) that can hydrolyse in aqueous solution to form silanols. Silanols can be adsorbed on fibre surface and condense with hydroxyl groups of the fibre to a measurable extent after an appropriate heat treatment. Besides, silanols can themselves condense into stable siloxane linkages –Si–O–Si–, thereby forming a polysiloxane network on the fibre surface that gives molecular continuity across the composite interphase (Belgacem and Gandini 2005; Xie et al. 2010). FTIR and wettability measurements are two complementary methods that can be successfully used to characterize the efficiency of the treatment on natural fibres (Le Moigne et al. 2014).

Silanization has been successfully applied to different types of lignocellulosic fibres, including pure cellulose (Reulier et al. 2016), ramie (Yu et al. 2010), sisal (Li et al.
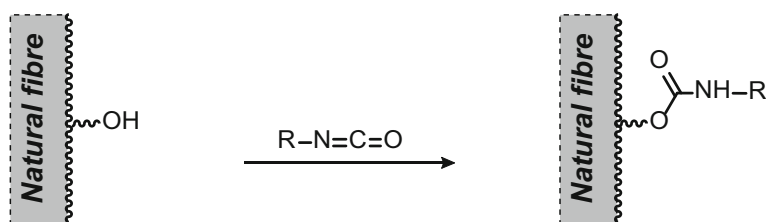

Fig. 3.2 Chemical reaction of isocyanates with hydroxyl groups of natural fibres

2008), coir (Javadi et al. 2010), spent kraft (González et al. 2012), sisal (González et al. 2012), cotton (Calabia et al. 2013), bamboo cellulose (Lu et al. 2014) or flax fibres (Le Moigne et al. 2014), oak wood (Scrubar et al. 2012) and olive husk (Hassaini et al. 2017) flours, to improve the interfacial adhesion in polymer-based composites. The type of organosilane should be appropriately chosen according to the targeted polymer matrix. For example, in the case of HDPE/sisal fibres composites, it was shown that Van der Waals forces can be set up between γ-methacryloxypropyl trimethoxy silane (MPS) treated sisal fibers and the HDPE matrix, inducing a great improvement of the interfacial shear strength (IFSS). On the other hand, γ-aminopropyl triethoxy silane (APS) can only react with the sisal fibres but does not interact with HDPE, resulting in a similar IFSS to that obtained with the untreated fibres (Li et al. 2008). When organosilanes are properly adapted to the fibres/matrix system, the resulting mechanical properties of composites can be significantly improved (Table 3.1), especially their tensile strength (González et al. 2012; Le Moigne et al. 2014). It is worth noting that an alkaline pre-treatment can be done prior to the organosilane treatment, to take benefits of the two treatments (Javadi et al. 2010, Le Moigne et al. 2014), even if the effects are not always really significant (Javadi et al. 2010) (Table 3.1).

Short-chains chemical grafting. Such reactions also involve the substitution of hydroxyl groups of lignocellulosic fibres with less polar groups such as acetate, valerate or short poly(ethylene glycol) (Zini et al. 2004). As compared to acylation, the PEG grafting procedure does not significantly alter the tensile strength of flax fibres, thus leading to an even more improvement of PLA-based material mechanical properties (Zini et al. 2004) (Table 3.1).

Finally, other approaches include the use of **bio-based coupling agents** such as lysine-diisocyanate in bamboo fibres/PLA (Lee and Wang 2006), dopamine in hemp fibres/PLA (Bourmaud et al. 2009) or ramie fibres/PBS (Zhou et al. 2014), eucalyptus lignin in Lyocell cellulose fibres/(PLA, PP, MAPP) (Graupner et al. 2014), or the use of xyloglucan as an initiator for the synthesis of polymers from cellulose surfaces (Zhou et al. 2005). Attempts to produce **hybrid biocomposite systems** reinforced with natural fibres and nanoparticules such as organoclays (Majeed et al. 2013; Saba et al. 2014) were also conducted. However, the localization of these nanoparticles at the fibre/matrix interface was not well controlled.
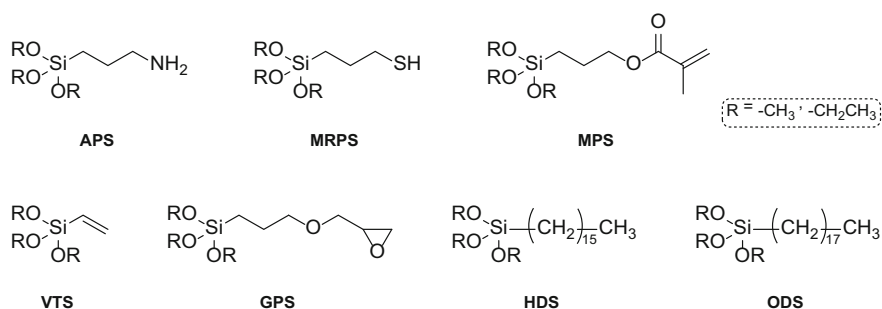

Fig. 3.3 Chemical structure of various organosilanes. APS: γ-aminopropyl trialkoxy silane; MRPS: γ-mercaptopropyl trialkoxy silane; MPS: γ-methacryloxypropyl trialkoxy silane; VTS: vinyl trialkoxy silane; GPS: γ-glycidylpropyl trialkoxy silane; HDS: hexadecyl trialkoxy silane; ODS: octadecyl trialkoxy silane

3.2.2 Physical Treatments and Physical–Activated Chemical Functionalization

Physical treatments are used to modify the topography and/or the surface physico-chemistry of natural fibres, or even to graft functionalizing molecules at their surface. These treatments do not require the use of solvents and are therefore considered for the development of eco-friendly processes. Another advantage is the high reactivity and fast reaction that can be achieved thanks to physical activation. Plasma and irradiation are currently the most studied physical treatment approaches to modify natural fibres.

Plasma treatment consists in creating in a chamber an ionized gaseous medium able to react with natural fibres. Thereby, plasma can modify the physico-chemistry and the surface topography of the fibres (Faruk et al. 2012). This process offers numerous possibilities for revealing or grafting functional groups (amine, carboxylic acid…) according to the carrier gas (nitrogen, helium, argon, air, fluorinated gas…) and the operating conditions. It can make a surface more hydrophobic (case of fluorinated gases) but also more hydrophilic by oxydation (case of air). The energy supplied by the plasma also makes it possible to cleave chemical bonds (C–C and C–H) and to create free radicals thus increasing the surface reactivity of the substrate. When coupled to a chemical treatment, the use of plasma can therefore efficiently activate the grafting of functionalizing molecules carrying C=C unsaturations or able to form free radicals under ionization (Kuzuya et al. 1993, 1997, 1998). In this regard, Gaiolas et al. (2012) and Popescu et al. (2011) have used cold plasma to graft acrylic monomers onto cellulose filters and fatty acids onto softwood kraft pulps. Gaiolas et al. (2012) obtained a pronounced hydrophobization of cellulosic substrates but no composite materials were prepared in these studies. It is worth mentioning that most of the studies dealing with the use of plasma to modify natural fibres for composite applications are more focused on surface activation of fibres than their functionalization under plasma.

Gassan and Gutowski (2000) studied the possibility to increase the polarity of jute fibres by corona treatment (sometimes referred to as air plasma), so as to improve the interfacial adhesion with epoxy matrices. The authors showed that a balance must be found between the increased polarity and the inherent degradation of the fibres under corona discharge. Indeed, corona proved to considerably improve the polar component of the surface tension of jute fibres, but a gradual decrease of their toughness was measured according to the duration and the power corona discharge. Kafi et al. (2011) also showed that an optimal treatment time can be determined for jute fibres treated by atmospheric plasma under helium and mixtures of helium/nitrogen and helium/acetylene. Indeed, the authors showed that the removal of waxes and pectins at the fibre surface by plasma treatment can increase their hydrophilicity and kinetics of water absorption up to 10 s of exposure, longer exposure times having no more effect due to the total removal of waxes. Flexural strength and modulus as well as interfacial laminar shear strength (ILSS) of polyester/jute composite laminates were also significantly improved due to changes in the surface chemistry and roughness of the fibres. According to Pizzi et al. (2009), the mechanical properties of lignin-based matrices

reinforced by non-woven flax and hemp fabrics can be significantly enhanced if exposing the fabrics to corona treatments during 5 to 15 min. This was explained by the increased roughness of the fibres, and so enhanced mechanical interlocking with the matrix. However, longer treatment times led to a severe degradation of the fibres and a reduction in tensile strength of the composites. Bozaci et al. (2013) modified flax fabrics by plasma treatments under air and argon. The authors also observed changes in surface physico-chemistry as well as an increased fibre surface roughness after treatment. Despite a gradual decrease of fabric strength related to an etching effect with increasing plasma power, the interfacial adhesion with high density polyethylene (HDPE) and an unsaturated polyester resin was improved as demonstrated by micromechanical pull-out tests. An increase in IFSS of 26 and 40% with HDPE and 47 and 30% with unsaturated polyester was obtained for plasma treatments under air and argon, respectively. This highlights the critical role of processing gases that should be tailored according to the matrix. In this study, the modification of O/C ratio resulting from the oxydation of the fibres under air plasma was found as being a key factor in the case of unsaturated polyester, while the greater surface roughness obtained with argon plasma was more beneficial in the case of HDPE due to enhanced mechanical interlocking. A study on ramie/polypropylene composites showed that fibre roughness can be increased with the time of exposure to atmospheric helium plasma, thus significantly improving their specific surface area and mechanical interlocking with the matrix (Li et al. 2013). Similarly, Ragoubi et al. (2010) also assumed that the increase in mechanical properties (13% on Young's modulus and 32% on maximum strength) observed for PP/20% hemp fibres treated with corona was related to an enhanced fibre roughness and improvement in mechanical interlocking. In another study, comparing PLA/miscanthus and PP/miscanthus composites, the authors showed that this increase in roughness observed by Scanning Electron Microscopy (SEM) was accompanied by a surface oxidation of the fibres. Indeed, X-ray Photoelectron Spectroscopy (XPS) analyzes showed an increase in the concentration of functional groups, i.e. carbonyl, hydroxyl, carboxyl, at the fibre surface, likely to favour the physico-chemical interactions with the PLA matrix (Ragoubi et al. 2012). The work of Li et al. (2013) suggested that the pre-treatment of ramie fibres with ethanol could act in synergy with an atmospheric helium plasma treatment by grafting CH_3 groups at fibre surface, and results in a reduced hydrophilicity of the fibres. Better compatibility with polypropylene matrix and improved tensile properties of the composites were achieved due to improved mechanical and physico-chemical interactions between the fibres and the matrix. Other works were conducted on the effect of atmospheric pressure plasma in cellulose–acetate–butyrate reinforced with lignocellulosic fibres (abaca, flax, hemp and sisal) and led to the same conclusions (Baltazar-y-Jimenez et al. 2008a, b).

Plasma treatments therefore appear as versatile and fast processes offering numerous possibilities for topographic and physico-chemical modifications and possibly surface functionalization of natural fibres. In this regard, they can contribute to improve the interfacial adhesion between the fibres and the matrix both in terms of mechanical interlocking and physico-chemical interactions. Nevertheless, the operating conditions must be very well controlled since long exposures drastically degrade the microstructure of natural fibres, and hence their intrinsic mechanical properties.

Gamma γ or e-beam irradiation can also be used to modify natural fibres for composites applications. The main advantage as compared to plasma treatments is that irradiation is more penetrating and can act in the bulk of the treated substrate. The effect of irradiation on lignocellulosic substrates has been mostly studied in order to improve their accessibility to chemical reagents and/or enzymes, and thereby enhance their dissolving capacity in textile processes (Viscose, Lyocell); and to increase yields of enzymatic hydrolysis for the production of ethanol and 2nd generation biofuels (Arthur 1971; Driscoll et al. 2009; Klemm et al. 1998; Loow et al. 2016). However, the operating conditions of these treatments must be carefully controlled because high radiation energies can rapidly and drastically degrade the biopolymers and the microstructure of natural fibres, primarily by chain scission processes but also oxidation phenomena if irradiation is carried out in air. Besides, it is mainly the effects of irradiation on the degradation of cellulose that have been studied (Arthur 1971; Belgacem and Gandini 2005; Bouchard et al. 2006; Ponomarev and Ershov 2014; Takács et al. 1999). These degradation processes strongly modify the physical properties of natural fibres and can lead to a significant decrease in their mechanical properties and an increase in their hydrophilicity. However, it is important to note that at relatively low irradiation doses (<30 kGy), degradation of natural fibres is limited, while significant changes in their surface physico-chemistry and topography are observed (Arthur 1971; Choi et al. 2009). Controlled irradiation conditions could thus make it possible to modify the surface properties of natural fibres and their interactions with the polymer matrices. In this regard, the works of Choi et al. (2009) and Han et al. (2006a, b, 2007) investigated the effect of pre-irradiation of kenaf and agave fibres on the properties of bio-composite materials based on unsaturated polyester, poly(butylene succinate) (PBS) and PP matrices. These studies showed that low irradiation doses (<30 kGy) can partially remove non-cellulosic components present at the fibre surface and within the primary wall (waxes, fatty acids, impurities, pectins, low molecular weight hemicelluloses…), which significantly modifies their surface roughness and tends to improve the mechanical interlocking with the matrix. Moreover, the modification of the fibre surface chemistry by oxidation and the creation of carbonyl and carboxyl groups (in particular by irradiation carried out in air) could favour in some cases their surface reactivity and their interactions towards polymer matrices.

As reviewed by Le Moigne et al. (2017), several studies have shown the possibility to graft and polymerize molecules carrying C=C bonds or heterocycle onto lignocellulosic substrates by free radical reactions activated by irradiation. In this regard, several monomers such as methacrylate (Khan 2005; Sharif et al. 2013; Kodama et al. 2014; Takács et al. 2005) and phosphorous (Sonnier et al. 2015) compounds were grafted onto cellulose and lignocellulosic substrates. The lifetime of free radicals formed on the surface and in the bulk of the substrates by irradiation being limited (Arthur 1971; Iller et al. 2002), the preferred route of functionalization is a pre-impregnation of the fibres by the functionalizing molecule followed by irradiation at low doses not exceeding 20 kGy. Effective grafting was observed with yields reaching up to 10–50%.

Irradiation treatments can thus be an effective strategy to modify or even functionalize natural fibres in view of their incorporation in composite materials, provided that the irradiation conditions (doses, atmosphere) are properly controlled to avoid degrading the physical properties of natural fibres (Le Moigne et al. 2017).

3.2.3   Incorporation of Amphoteric Compatibilizers

Amphoteric surfactants, which have one or more polar groups and a long aliphatic tail, could be used to improve the interactions between the fibres and the polymer matrix. One of the crucial questions of non-reactive treatment is the amount of surfactant to use. It depends on the type of interactions, the surface area occupied by the coating molecule, its alignment onto the surface and on some other factors (Moczo and Pukanszky 2008). Insufficient amount of surfactant does not achieve the desired effect, while excessive quantities lead to processing problems as well as to deterioration of the mechanical properties and appearance of the product.

As an example, Graupner (2008) proposed to use lignin as natural adhesion promoter in cotton fibre-reinforced PLA composites. The results of composites characterization showed that the interfacial adhesion between fibre and matrix could be improved by the addition of lignin. Tensile characteristics like tensile strength and Young's modulus could be improved clearly (increase of 9% and 19%, respectively), while the impact properties were decreased, probably because of the embrittlement of the composites induced by the presence of lignin.

One main drawback of such a strategy as regards the food packaging application would be the possible migration of compatibilizers towards the food. Attention should thus be paid to avoid the use of substances with low molecular weights more prone to migrate, with a preference to the use of molecules displaying a molecular weight higher than 1000 g.mol^{-1}, as mentioned in the European regulation 10/2011 (article 6).

3.3   Treatment Processes

One of the major challenges in the treatment of natural fibres for composite applications is the development of efficient and reliable treatment processes taking into account industrial feasibility. Several issues must thus be considered as the scale-up of the process, the development of discontinuous or continuous processes, compatibility with REACH policy, the use of bio-based resources, investments, running costs…. The search for clean, solvent-free processes that use minimal energy and water is also a critical issue. These treatment processes must allow the fast and homogeneous functionalization of natural fibres so as to control their surface morphological and physico-chemical properties, and thus to decrease the variability in physical properties often blamed to biocomposites while improving

their performances. Widely explored and optimized for technical glass fibres, various wet and dry processes have been developed on an industrial scale. In the remainder of this chapter, attention will be devoted to the various wet (liquid and vapour phase, supercritical fluids) and dry (reactive extrusion, dry-blending and powder impregnation) treatment processes that have been studied at lab-scale or even at pilot-scale in the case of natural fibres. It is worth noted that these treatment processes use for applying functionalizing molecules on natural fibres could be combined with physical treatments such as plasma or irradiation in order to promote an efficient and fast grafting of molecules.

3.3.1 Wet Treatment Processes

Wet treatments in the liquid phase are currently the most studied processes and those primarily used in literature dealing with natural fibre treatments. It consists mostly in treating natural fibres by immersion in a bath containing a solvent or a mixture of aqueous or organic solvents (water, ethanol, toluene, etc.), and the molecules considered for the modification (acids, bases, etc.) or the functionalization of the fibres. This method requires little equipment and can be easily implemented for lab-scale experiments on short natural fibres. Most of the literature dealing with natural fibres treatment is based on this protocol. Nevertheless, it should be pointed out that the immersion of large volumes of fibres is highly solvent consuming. Moreover, depending on the type of treatment developed, the reactivity of the functionalizing molecules could be favoured by increasing the temperature. This requires therefore the heating of the fibres on the one hand, but also the heating of large volumes of solvents, a very energy-intensive process.

The treatment of long fibres conditioned in the form of yarns, rovings or fabrics can be carried out continuously in a single bath containing the functionalizing molecules in sufficient concentration, hence requiring smaller volumes of solvents. This type of technology widely used in the textile industry (fabrics padding) and sizing of glass fibre rovings has also been developed for natural fibres, in particular for flax fibres which offer a wide variety of conditioning ranging from yarn to fabric. Van de Weyenberg et al. (2006) used a continuous process to treat flax rovings in alkaline solutions of sodium hydroxide (NaOH). Their process also integrated in-line rinsing and drying modules and an impregnation section of flax rovings by an epoxy resin (Fig. 3.4). Despite the efficiency of the process, the authors report the importance of rinsing which must be optimized to allow the complete elimination of caustic soda. In fact, the presence of residual caustic soda in flax rovings at the end of the treatment process led to a significant decrease in the performances of the epoxy based biocomposites. Moreover, continuous processes often involve shorter treatment cycles, and therefore require very good reactivity and diffusion of the molecules used for pre-treatment or functionalization due to the short contact time with the fibres. Indeed, too long treatment cycles can result in

significant mechanical degradation of the fibres due to friction, which can cause their early breakage during the treatment process.

Other technologies of wet treatments in the liquid phase derived from the paper, textile or agri-food industries can be adapted for the treatment of natural fibres. Spraying has been used by Rachini et al. (2012) at lab-scale to functionalize short hemp fibres with 3-(triethoxysilyl)propylsuccinic anhydride silane (SiAn) for their further reaction with vinyl trimethoxy silane (VTMO) by a reactive compounding approach. In addition to the small volumes of solvents required, spraying has the advantage to allow a direct application of the functionalizing molecules onto the fibres. Therefore, the kinetics of diffusion of the molecules from the treatment bath to the fibres is not a limiting factor. A spraying device adapted on a conveyor as used in the papermaking or the manufacturing of medium-density fibreboard (MDF) would make it possible to implement a continuous treatment process, the greatest difficulty being then the homogenization of the treatment on the bed of short fibres or the fabrics. In this regard, a carding method has been developed at pilot-scale by (Lee et al. 2009) for the preparation of a mat of poly(lactic acid) PLA fibres and kenaf fibres (Fig. 3.5) which was then treated with a γ-glycidoxypropyl trimethoxy silane (GPS). It should be noted that the treatment step was not carried out continuously but by dipping the kenaf/PLA fibres mat into the GPS silane solution. The resulting treated fibre mats were then stacked and processed by thermo-compression for the consolidation and manufacture of the composite material. The study showed that the silane treatment was highly beneficial to composite performances in terms of flexural strength and modulus, heat deflection temperature and dimensional stability, even at low concentration of functionalizing molecules (1 pph). Moreover, the low scattering of the mechanical properties indicated a good homogeneity of the composite laminates obtained. Such a carding process for the production of thermoplastic fibre/natural fibre mats coupled with a continuous treatment device open up very interesting prospects for the serial production by thermo-compression of natural fibres based composite panels. This technology could also be easily transposed to already existing commingled thermoplastic/natural fibres products developed and commercialized on an industrial scale by several companies worlwide.
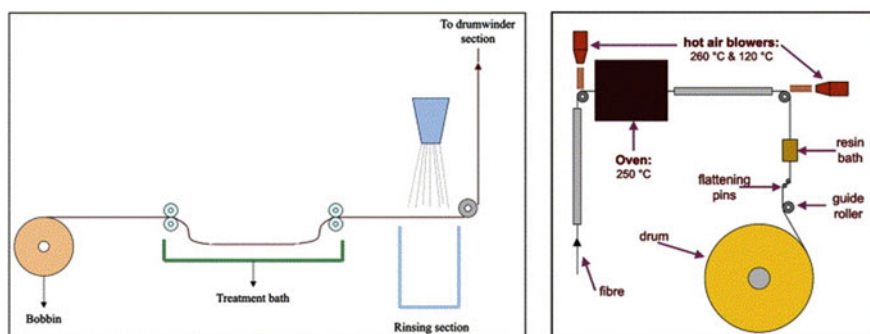

Fig. 3.4 Sketch of the treatment section and the successive drying section in the fully continuous production set-up. Reprinted from Van de Weyenberg et al. (2006), Fig. 5 with permission from Elsevier

Wet treatments in the vapour phase, mostly developed for pulp and paper-making, are alternative methods that limit the volumes of solvent used. They consist in heating and vaporizing the functionalizing molecule, and then condensing it on the substrate to be treated. Nevertheless, the molecules used must be thermally stable in order to avoid any degradation during the vaporization phase.

Zhang et al. (2007) studied the possibility to hydrophobize cellulose fibres by vapour deposition of alkenyl succinic acid anhydrides (ASA) and alkyl ketene dimers (AKD), chemicals commonly used in the papermaking industry (Cunha and Gandini 2010). Generally added in the form of emulsions into the pulp slurry or sprayed on the paper surface, these molecules are used to limit ink absorption, and thus avoid the blotting effect. Nevertheless, they have a low reactivity towards cellulose substrates and their distribution over the fibre surface is not perfectly homogeneous. Vaporization of these molecules in view of their condensation on cellulose substrate was studied. Indeed, vapour transport of sizing chemicals is likely to promote a fast and good distribution, since vapour diffusion would occur in three dimensional within the substrate. By analysing the chemical composition of the ASA and AKD vapours using FTIR spectroscopy, the authors showed that compositions of ASA in the vapour or the liquid state were similar, whereas AKD vapours were rich in fatty acids due to their thermal hydrolysis. Zhang et al. (2007) concluded that vapour deposition could be a relevant process for paper sizing with ASA. Studying AKD vapour deposition on cellulose substrate, Hutton and Shen (2005) also concluded that AKD vapour deposition contributes only minimally to the overall AKD sizing mechanism.

Cunha et al. (2010) developed a vapour deposition process assisted by a carrier gas for the hydrophobization and lipophobization of cellulose fibres. This method consists in the diffusion of the functionalizing molecule under pressure through the substrate allowing a homogeneous treatment at the surface but also in the bulk of the material. Nitrogen gas was propelled through a solution of trichloromethylsilane (TCMS) and the N_2/TCMS mixture was streamed through the cellulose paper filter to allow TCMS condensation. The reaction of TCMS and cellulose fibres produced hydrochloric acid
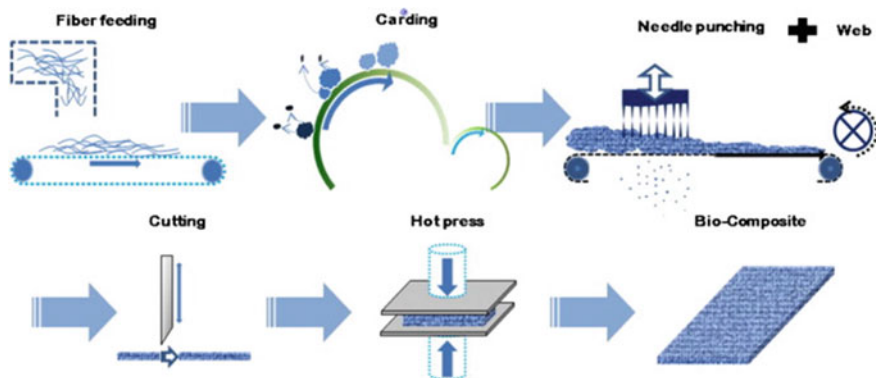

Fig. 3.5 Carding process for the manufacturing of PLA/Kenaf bio-composite panels. Reprinted from Lee et al. (2009), Fig. 1 with permission from Elsevier

that was removed by bubbling the gaseous waste in a NaOH aqueous solution (Fig. 3.6). The results demonstrated that this process was a fast and efficient approach to functionalize cellulose fibres. Strong hydrophobization and lipophobization was achieved as proved by the drastic increase of the contact angles with both polar and apolar liquids, e.g. from 36° to more than 130° with water.

Another process of cellulose functionalization conducted in the vapour phase, called chromatogenic chemistry, was investigated and described by Stinga (2008), Berlioz et al. (2008) and Schmid et al. (2012). Chromatogenic chemistry can be used for the grafting of long-chain fatty acid chloride reagents on the surface of cellulosic substrates. This treatment process does not require the use of solvents, and also allows the continuous removal of by-products coming from the esterification reaction of fatty acids with cellulose hydroxyl groups through the hot gas stream used for the transport of the functionalizing molecules. The molecules, i.e. fatty acid chlorides, are first finely dispersed on the surface of cellulosic substrates. A hot, inert gas stream is then applied in order to reach the vapour pressure of the molecule. The resulting liquid/vapour equilibrium allows the diffusion of the molecules. Indeed, the gas stream carries the gaseous molecules within the substrate, hence gradually displacing the liquid/vapour equilibrium front. This mechanism allows the progressive diffusion of the functionalizing molecules in the bulk of the substrate, which is of great interest to achieve a homogeneous treatment in a bed of fibres. Upon diffusion, grafting of the molecules on cellulose by esterification occurs and by-products of the reaction are evacuated from the substrate by the gas flow, thus avoiding any degradation of cellulose fibres. The diffusion and the grafting of the functionalizing molecules is determined by the nature and composition of the cellulosic substrate, the concentration and chain length of fatty acid chlorides, and the temperature of the gas stream. In their study, the authors obtained interesting hydrophobic properties with cellulosic substrates treated by this process, but no grease or gas barrier properties.

These vapour phase processes are therefore of great interest because they require little or no solvents and could allow a fast, effective and possibly homogeneous treatment of natural fibres. Nevertheless, they require the use of easily vaporizable and thermally stable molecules and therefore do not apply to all the functionalizing molecules used for natural fibres treatment. Moreover, their implementation in the context of natural fibre based composite materials still need to be investigated.

Supercritical fluid assisted processes are commonly used in the food and pharmaceutical industry for the extraction and production of flavourings, colourings, essential oils and purification of compounds. In particular, supercritical carbon dioxide (Sc-CO_2) is often used because it is nontoxic, non-flammable, chemically inert, and its supercritical conditions are easily reached (P $\approx$ 7.29 MPa and T $\approx$ 31 °C). Under these supercritical conditions, sc-CO_2 exhibits intermediate physico-chemical properties between those of a gas and a liquid. Its high diffusivity coefficient, low viscosity, non-polar character and low surface tension give it good transfer and diffusion properties even in poorly porous materials, as well as high solvating capacity (Hijazi 2014; Fages 2003).

Hutton and Parker (2009) investigated the possibility to use of sc-CO_2 to treat cellulose fibres with AKD. The treatment of cellulose substrates was conducted with a

Fig. 3.6 Schematic representation of the vapour deposition process assisted by nitrogen gas used to treat cellulose substrate with TCMS. Reprinted from Cunha et al. (2010), Fig. 2 with permission from Elsevier
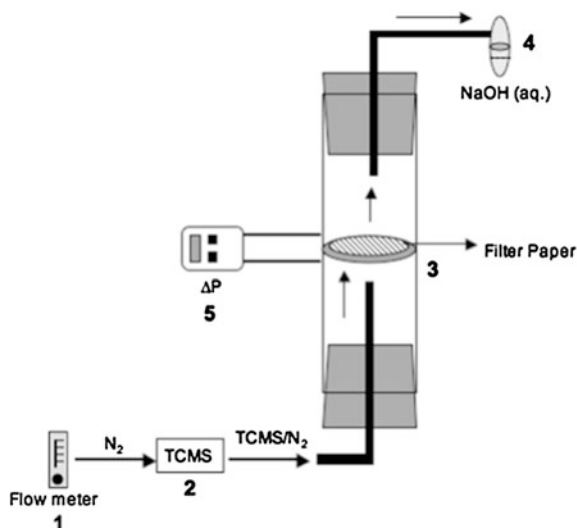
modified supercritical fluid extractor. Sc-CO_2 was send through a circu-lating loop containing a AKD/heptane solution. After mixing, the high pressure mixture was sent through the vessel containing the cellulose substrate, where im-pregnation occurred. After depressurization, carbon dioxide reverted back to gase-ous state and is readily eliminated, leaving the cellulose substrate suitably impregnated with the AKD/heptane solution. The results showed that the AKD was uniformly distributed at the surface and in the bulk of the substrate at five times greater than the concentration obtained using conventional impregnation techniques. Furthermore, the water con-tact angles obtained after treatment (>90 °) were comparable to those obtained with other techniques. The authors therefore assumed that this process could be beneficial to decrease the overall quantity of AKD while reaching the same level of sizing.

It should be noted that the use of sc-CO_2 has also developed in the last few years in the field of textile colouring, in particular for natural fibres (cotton, wool, silk…) (Arputharaj et al. 2016).

Sc-CO_2 assisted processes are thus efficient and solvent-free methods that are very promising for the treatment of natural fibres. Besides, they are already widely used in the agri-food industry and could therefore be implemented on an industrial scale. Nevertheless, functionalizing molecules and/or their solvents must have a good affinity with sc-CO_2 in order to ensure their efficient transfer and diffusion through the substrate.

3.3.2 Dry Treatment Processes

Dry treatment processes consist in functionalizing and compatibilizing natural fibres with the matrix during the composites preparation, either by means of reactive processes, in particular reactive extrusion used for the compounding of

short natural fibres based composites, or by the pre-impregnation of natural fibres with the polymer matrix and the coupling agent using dry-blending or powder impregnation processes.

Reactive extrusion involves the direct incorporation of coupling agents during composites compounding, and therefore does not require the use of solvents. Many works use this process to functionalize natural fibres and modify the fibre/matrix interface, in particular in the case of polyolefin matrices for which maleated or silanized polymers, i.e. MAPP, MAPE, VTS grafted PP or PE, are most often used as coupling agents (Kazayawoko et al. 1999; Nachtigall et al. 2007; Xie et al. 2010). Organosilane and isocyanate molecules can also be incorporated by reactive extrusion (Lee and Wang 2006; Petinakis et al. 2009; Rachini et al. 2012; Sahoo et al. 2011). Coupling agents that do not cause the release of by-products during the grafting reaction with the fibres or the polymer matrix are generally preferred.

Although being essential to understand and confirm the efficiency of this approach, only few studies compared the effects of a prior functionalization of the fibres before compounding and a compatiblization carried out by reactive extrusion. Arbelaiz et al. (2005) compared the properties of PP/flax composites prepared from flax fibres treated with 5% w/w of MAPP dissolved in xylene (Mn = 3900 g/mol and Mw = 9100 g/mol), maleic anhydride (MA), and vinyl trimethoxy silane (VTMO) prior to compounding; with the properties of PP/flax composites compatibilized with these same molecules during compounding (5% w/w for MAPP and 4.5% w/w for MA and VTMO with the addition of a dicumyl peroxide peroxide DCP initiator). The authors showed that the direct incorporation of MAPP into the PP matrix during compounding did not lead to significant differences as compared to the treatment of flax fibres with MAPP prior compounding. The flexural and tensile moduli and strength of the composites were indeed similar for the two compatibilization methods. These results demonstrate that with the materials and processing conditions used, MAPP polymer chains were able to efficiently migrate to the fibre/matrix interface during compounding, thus having the same effect on the interfacial adhesion and composites reinforcement than a direct grafting of MAPP onto the fibres surface. It should be noted that the molar mass of MAPP (relatively low in Arbelaiz et al. 2005) should play an important role on the diffusion capacity of the chains during compounding, and hence on their effective migration at the interface. In the case of the MA and VTMO molecules, the authors observed a much greater efficiency of the treatments when carried out by reactive compounding. However, it should be noted that DCP was used for reactive compounding, whereas in the case of prior treatment of flax fibres with MA and VTMO molecules, the authors did not mention the use of DCP during composite preparation. This could have limited the reaction between the PP matrix and the MA and VTMO molecules grafted onto the fibres. Indeed, DCP allow to initiate the free radical grafting between the coupling agents bearing C=C double bonds and polyolefine matrices. Besides, the use of DCP during compounding may result in a partial crosslinking of the PP matrix which could be responsible for the better tensile and flexural mechanical performances of the composites produced by reactive compounding.

Mohanty et al. (2006) studied the rheological behaviour in the molten state of PP/jute fibres composites compatibilized through the direct functionalization of the fibres with MAPP (Mw = 47,000 g/mol) dissolved in xylene. For composites PP/jute fibres 30% w/w, the authors clearly observed an increase in viscosity with the treated fibres, that was related to the enhanced fibre/matrix interactions brougth by the presence of MAPP at the interface. The studies of Twite-Kabamba et al. (2009) and Le Moigne et al. (2013) on the melt rheological behaviour of PP/hemp fibres and PP/flax fibres composites compatibilized with MAPP (Mn = 12,000 g/mol and Mn = 24,800 g/mol, respectively) by reactive compounding clearly showed that part of the MAPP chains may not migrate to the fibre/matrix interface. Indeed, for composites with low fibre contents (up to 20% w/w), the presence of 2% MAPP in the composite was able to counterbalance the increase in viscosity due to incorporation of natural fibres. The viscosity of the composite was thus greatly reduced and comparable to that of neat PP matrix. These results show that a significant amount of free unbounded MAPP molecules can remain in the matrix without migrating at the fibre/matrix interface, and thus not participate to reinforcement of the composite. In this regard, Snijder and Bos (2000) studied the compatibilization effect of MAPP in PP/flax fibres composites according to quantity, grafting rate, molar mass distribution and macromolecular structure (homo- or copolymers) of the MAPP molecules, and showed that optimum conditions could be determined as a function of fibre content to enhance the mechanical properties of the composites.

The compatibilization of natural fibre reinforced polymer composites by means of reactive processes appears as an easy and eco-friendly approach, and is already implemented at an industrial scale. However, it should be considered that the addition of coupling agents during compounding gives rise to two antagonistic effects: (i) a reinforcing effect due to the improvement of fibre/matrix interactions if the migration of the coupling agent at the interface is effective (Fig. 3.7 a), (ii) a plasticization of the matrix if the coupling agent does not migrate correctly and stay as free unbounded molecules within the matrix (Figs. 3.7b and c). The processing conditions (temperature, mixing time, shearing…) as well as the chemical structure and physico-chemical characteristics of the coupling agent play a key role in the diffusion of the latter, and hence on the improvement of the interfacial adhesion through reactive extrusion.

Dry-blending consists in the preparation of pre-mixes of natural fibres, polymer matrix and additives in powder form. One simple method is to use a high-speed mixer at controlled temperature to prepare a pre-compound of polymer-coated fibres in view of its subsequent processing. This technique is often used for the production of PVC/wood fibres mixtures (Sombatsompop et al. 2003; Matuana et al. 2001), before they are melt-blended in an extruder. Besides the incorporation of several additives during dry-blending (stabilizers, lubricants, $CaCO_3$, TiO_2), Matuana et al. (2001) reported the possibility to add an aminosilane coupling agent (APS) in the formulation so as to improve interfacial adhesion between PVC matrix and wood fibres. Ayrilmis et al. (2011b) have also used this process to prepare pre-compounds of PP/coconut fibres compatibilized with different amounts of MAPP powders, and manufacture mats that were thermocompressed to obtain

composite panels for automotive interior applications. The authors emphasized the industrial benefit to combine dry-blending and thermocompression in terms of costs and productivity compared to conventional extrusion and injection processes. Ayrilmis et al. (2011b) and Mohanty et al. (2002) also argued that dry-blending is less degrading for natural fibres structure, since they do not undergo high shearing during processing as in extrusion and injection moulding.

Dry powder impregnation is used for the preparation of thermoplastic prepregs of natural fibres. A thermoplastic polymer powder is spread on the fabrics, then heated to be melted and stuck on the fibres (Reux and Verpoest 2012). This method has been used by Dehondt group to prepare the TwinFlax P-Preg products which are flax fabrics impregnated with polyamide 11 (PA11) or polypropylene (PP) (Flax Technic® 2017). These products were developed to manufacture composite laminates by thermo-compression. It should be noted that the producer does not mention if a coupling agent was incorporated during the impregnation process.

Another innovative technique of dry powder impregnation was developed and patented in 2003 by the French company Fibroline (Marduel 2003). This technique relies on the use of an alternating electric field for the dry impregnation of powders within fibrous, filamentary and/or porous networks. The fibrous substrate is continuously conveyed and covered with powder, then to be treated between two electrodes under high tension electric field (from 10 to 50 kV). The gas located between the electrodes is ionized, and the charged powder particles repel each other, which allow impregnating homogeneously the fibrous substrate (Bouzouita 2011). Bouzouita et al. (2010) used the Fibroline process to prepare polypropylene (PP)/hemp fibres composites manufactured by thermocompression. The authors showed that this process altered the hemp fibre surface, causing surface oxidation and possible removal of lipophilic components as revealed by XPS, and an increase in roughness as observed by SEM. A drop in the Young's modulus and elongation at break of the Fibroline-treated fibres was observed. Nevertheless, the fibre surface modifications were able to
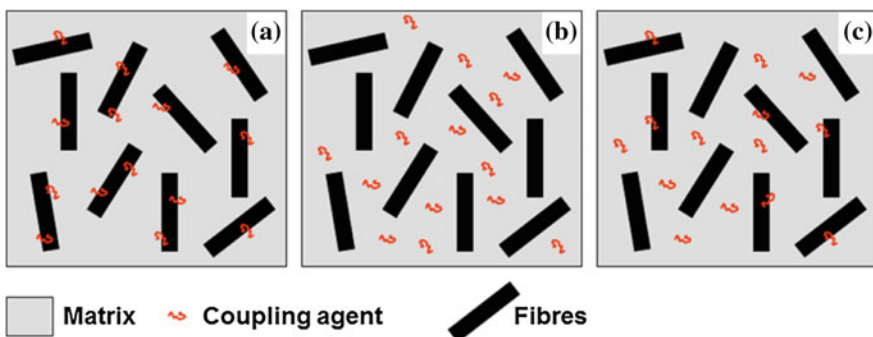

Fig. 3.7 Possible localization of the coupling agent molecules within the composite microstructure after reactive compounding. **a** All the molecules diffuse at the interface and are grafted on the fibres; **b** all the molecules stay free in the matrix; **c** only a part of the molecules diffuse at the interface and are grafted on the fibres

improve mechanical interlocking between the fibres and the PP matrix, and hence the stress transfer at the interface as revealed by IFSS measurements and improvement in mechanical properties of the composites. This was explained by an enhanced roughness and residual stresses induced by the formation of a transcrystalline zone at the interface for the Fibroline-treated fibres (Bouzouita 2011).

3.4 Concluding Remarks

Improving mechanical properties of natural fibres based composites, especially their strength, implies the developement of functionalization and compatibilization strategies. The creation of an interphase with better interfacial adhesion between natural fibres and polymer matrices should be achieved to ensure an optimum stress transfer and provide protection against ageing.

Fibre pre-treatments such as retting, chemical or thermal treatments can be beneficial to the quality and performances of biocomposites by promoting the individualisation of fibre bundles into elementary fibres with higher aspect ratio and specific surface area. Besides, they can be used to remove weakly bonded inter-cellular components and enhance fibre surface roughness. This substantially improves the mechanical performances of biocomposites by increasing interfacial adhesion due to better mechanical interlocking with the matrix. Pre-treatments are also used to increase the surface reactivity of the fibres prior to their functionalization. Nevertheless, all these treatments are likely to decrease the intrinsic properties of the fibres due to the degradation of the biopolymers constituting the cell walls, and must therefore be carried out with caution.

Functionalization treatments of natural fibres can improve significantly the interfacial adhesion within the composites by the formation of an interphase between fibres and matrix. Whether physical or chemical, functionalization treatments allow topographical and physico-chemical surface modifications that promote the wetting of the fibres by the polymer matrix during processing, and hence mechanical interlocking. The most significant improvements in mechanical properties of biocomposites are obtained when physical, i.e. entanglements or hydrogen bonds, or chemical, i.e. covalent bonds, can be established between the fibres and the matrix, in particular through the use of multi-functional coupling agents (such as organosilanes and isocyanates), radical chemistry or grafted polymers (Fig. 2.8 in Chap. 2). The effectiveness of these treatments is generally enhanced by the prior use of a fibre pre-treatment. As seen in Fig. 3.8, the increase in mechanical performances that can be expected from interface modifications with pre-treatments or functionalization is in the range of 40% for both modulus and strength, although increases up to 70% were achieved. The main limitations are related to the intrinsic intra- and inter-cellular cohesion in natural fibres and the potential modification of the intrinsic properties of fibres cause by the use of solvents upon functionalization procedures that can degrade biopolymers from the cell walls. Properties of polymer matrices can also be altered by the diffusion of functionalizing agents or reaction
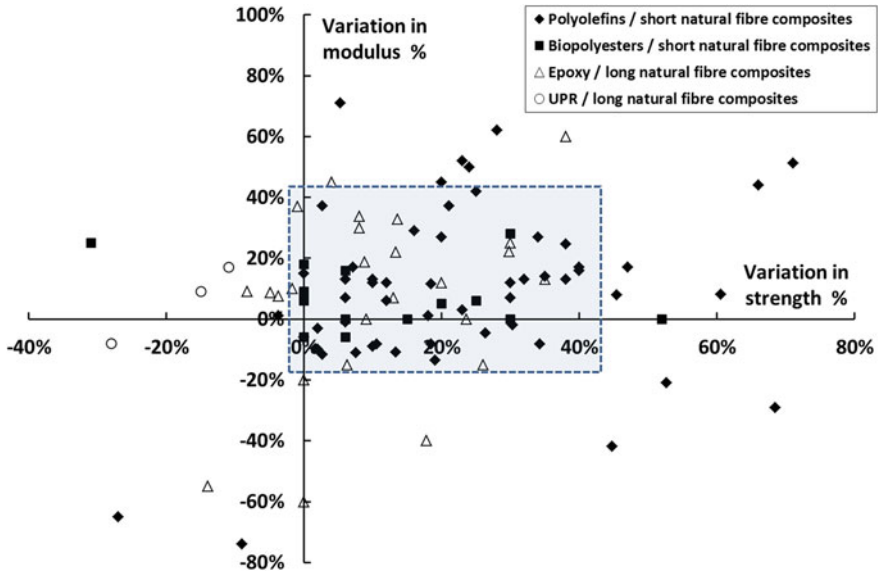
Fig. 3.8 Ashby plot—variation in modulus versus variation in strength of natural fibre reinforced composites consecutive to pre-treatments and/or functionalization of natural fibres. Non-exhaustive set of data taken from literature for polyolefins and biopolyesters/short fibre composites (tensile properties) and epoxy and unsaturated polyester (UPR) resins/long fibre composites (flexural or tensile properties)

by-products. There is thus a need for the development of specific treatments and processes that would promote fibre dispersion while offering an optimum exposure of reactive and/or functionalized fibre surfaces to the matrix without weakening the fibre structure or altering the polymer matrix.

Finally, a critical issue lies in the possibility to implement functionalization treatments into economically competitive production processes. In this regard, the elaboration of short fibres biocomposites by reactive extrusion with in situ formation of the interphase is to date the strategy that was the most studied and developed on an industrial scale. Nevertheless, current research is increasingly oriented towards the development of upstream functionalization processes of natural fibres, particularly adapted for the production of structural biocomposites reinforced with long fibres (woven fabrics), whether by using liquid, vapor, supercritical CO_2 or dry processes. The resulting functionalized reinforcements can be then processed with polymer matrices by conventional composite manufacturing methods (e.g. infusion, thermo-compression...) during which the adsorbed or grafted coupling agent will react with the matrix to form a high performance interphase.

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