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Interfaces in Natural Fibre Reinforced Composites: Definitions and Roles

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Natural fibres are a real opportunity to replace conventional synthetic fibres in composite applications. However, even if they have several advantages in comparison to synthetic fibres (lightness, carbon balance, price...), their moisture sensitivity, their poor compatibility with polymer matrices and their low thermal stability and flammability makes their modification by chemical or physical treatments essential. The final performances of any (nano)composite system strongly depend on the filler content and intrinsic properties (stiffness, strength, aspect ratio, morphology...) but also on the filler/matrix interface region. Studying and controlling the interfacial properties and their impact on macroscopic properties thus constitutes a key issue to understand and model the structure/functional properties relationships in biocomposites and improve their performances. In this chapter, the multiple and multi-scale interfaces in natural fibre based composites is described. The importance and role of the fibre/matrix interface on mechanical performances and durability, and main strategies to enhance the interfacial adhesion is discussed. Finally, an opening towards new functionalities that could be achieved by fibre and interface modifications is addressed.

2.1 Multiple and Multi-scale Interfaces Systems

As described in Chap. 1, natural fibres are complex and hierarchical composite systems with different inter- and intra-cellular interfaces. Indeed, elementary fibres are gathered in fibre bundles and glued by the middle lamella rich in non-cellulosic components, especially pectins and lignin. Also, plant cell walls are made of several concentric layers varying in biochemical composition and structure, in particular microfibrillar orientation. At the supramolecular level, the network of cellulose microfibrils is embedded in a biopolymer matrix made of hemicelluloses, pectins, proteins and lignin. These inter- and intra-cellular interfaces are considered as weak zones, and are partly responsible for the complex breakage and dispersion mechanisms of natural fibres when incorporated in polymer composites. As will be

discussed, this results in specific composites microstructure with multiple and multi-scale interfaces.

Le Moigne et al. (2011) studied the fibre size and shape distributions of flax, sisal and wheat straw fibres after compounding in a polypropylene (PP) matrix. As observed in Fig. 2.1, a large variation in the size and shape of the fibres was observed and three main entities can be defined: the elementary fibres consisting of individualized and slender plant cells, the fibre bundles consisting of parallel elementary fibres still glued together by the middle lamella and the particles having low aspect ratio comprised between 1 and 2. Based on rheo-optical experiments, Castellani et al. 2016 were able to distinguish several mechanisms of fibre breakage when exposed to shearing in a polymer matrix: (i) fragile (case of flax and sisal), (ii) fatigue, i.e. cumulated strain (case of hemp), or (iii) peeling (case of miscanthus). These mechanisms are thought to be intimately related to the biochemical composition and structure of natural fibres. In particular, the strength of cohesion between the elementary fibres ensured by the middle lamella should play a key role in the dispersion processes. It has been found that flax fibres easily separate in elementary fibres when incorporated by melt compounding in a polypropylene matrix, possibly due to their low lignin content (Le Moigne et al. 2011; Oksman et al. 2009). Even if a direct correlation between biochemical composition and structural properties of natural fibres and their dispersion mechanisms under processing is still hard to define, Castellani et al. (2016) assumed that higher lignin content is related to higher inter-cellular cohesion, and hence lower amount of individualized elementary fibres in the melt.

On the other hand, Acera Fernández et al. (2016) studied the dispersion state of flax yarns in flax tow fabrics reinforced epoxy composites prepared by thermo-compression. The authors showed that the extraction of non-cellulosic components contributing to inter-cellular cohesion within the fibre bundles results in a considerably enhanced dispersion of flax yarns within the matrix, related to an individualization of fibre bundles into elementary fibres (Fig. 2.2). These results show that even for composites processes involving low shearing as thermo-compression, the dispersion of fibre bundles can occur if the inter-cellular cohesion is altered.

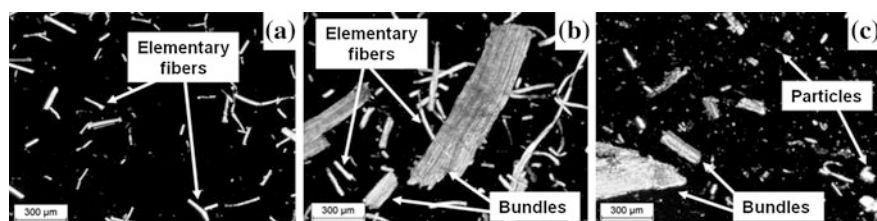


Fig. 2.1 Optical microscopy images obtained in light transmission mode between crossed polarizers of composites diluted with Decalin®: **a** PP/4% MAPP/40% flax; **b** PP/4% MAPP/40% sisal and **c** PP/4% MAPP/40% wheat straw. Three entities are found: elementary fibres, bundles and particles. Reprinted from Le Moigne et al. (2011), Fig. 2 with permission from Elsevier

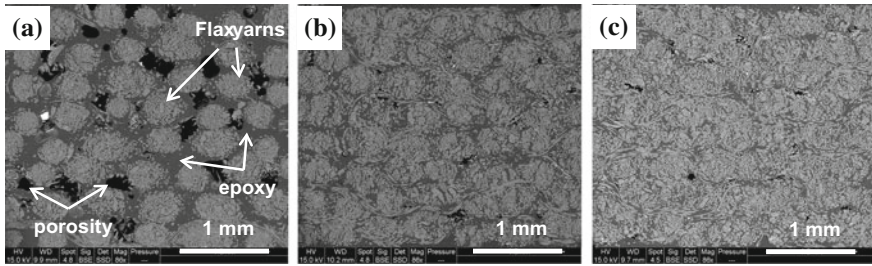


Fig. 2.2 SEM micrographs of transverse cross section of flax tow fabrics reinforced epoxy composites for different extraction treatments: **a** untreated, **b** ethanol, **c**NaOH 1%

The dispersion state of natural fibres is thus greatly influenced by the composition and structural organization of natural fibres, their extraction/conditioning, and subsequent processing steps used to manufacture composites. This results in wide variations in terms of fibres/matrix and fibre/fibre interactions, and hence the type and quantity of interfaces developed.

When considering the functionalization of natural fibres for improving the interfacial adhesion in composites, the dispersion state of the fibres is critical. Indeed natural fibres are usually treated with functionalizing molecules as received, i.e. in the form of fibre bundles, and are then dispersed in the polymer matrix during composites processing. Good dispersion will result in an enhanced specific surface area of natural fibres, and a considerably enhanced interfacial coupling with the matrix. However, as pointed out by Le Moigne et al. (2014), only a limited surface of the fibres exposed to the matrix will be effectively functionalized. As illustrated in Fig. 2.3, due to dispersion, the amount of treated fibres surface exposed to the matrix after processing would be greatly decreased (initial perimeter of the treated fibre bundle to the final perimeter of the dispersed elementary fibres), thereby reduces the efficiency of the functionalization treatment. Typically, for a treated fibre bundle of $240 \pm 150 \mu\text{m}$ in diameter, its dispersion during processing will lead to a final amount of exposed treated surfaces of roughly $11 \pm 7\%$ (considering a bundle with a simple square section and an average elementary fibre diameter of $20 \mu\text{m}$). Therefore, the larger are the fibre bundles before treatment and

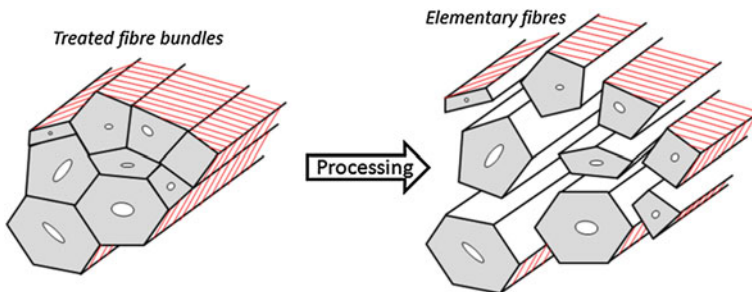


Fig. 2.3 Illustration of treated fibre surfaces (dashed zones) before processing and the ones exposed to the matrix after processing. Reprinted from Le Moigne et al. (2014), Fig. 6 with permission from Elsevier

processing, the least efficient would be the treatment as concerned the resulting quantity of functionalized fibre surfaces exposed to the matrix. This underlines the necessity to individualize fibre bundles into elementary fibres as much as possible during the extraction phases prior any subsequent functionalization and processing to manufacture composite materials.

Another interesting phenomenon that highlights the role of the intra-cellular cohesion is the occurrence of decohesion between the cell wall layers that are often observed on failure surface of broken composites (Fig. 2.4a). This phenomenon was also observed by Le Duigou et al. (2012) when performing microdroplet debonding test on elementary fibres (Fig. 2.4b). This phenomenon indicates that the physico-chemical interactions occurring at the fibre/matrix interface can be in some cases stronger than the strength of the interactions between the cell wall layers. This can originate from functionalization treatments that were able to create covalent bonds between the matrix and the fibre surface. Besides, the pre-treatments and the solvents used for functionalization treatments may also be responsible for the weakening of the fibre structure, and the decohesion of the cell wall layers due to the removal of matrix components, i.e. pectins, hemicelluloses and lignin.

Concluding, when natural fibres are incorporated in a polymer matrix, several types of interfaces should thus be considered (Acera Fernández et al. 2016; Bismarck et al. 2002): (i) the interface between the polymer matrix and the individualized elementary fibres and/or the fibres bundles, (ii) the interface in between the elementary fibres within the fibre bundles, and (iii) the interface between the layers within the cell walls. Each of these interfacial zones has its own characteristics in terms of physico-chemical interactions and strength of cohesion. Besides, interfaces should not be considered as defined geometrical limits. It is known that interfacial zones are transition phases, called interphases, which develop over a certain thickness between bulk matrix and bulk fibre. These three-dimensional zones include the two-dimensional zone of contact between the reinforcement and the matrix (interface), but also a zone of finite thickness extending on both sides of the interface within the reinforcement and especially within the matrix (Herrera-Franco and Drzal 1992).

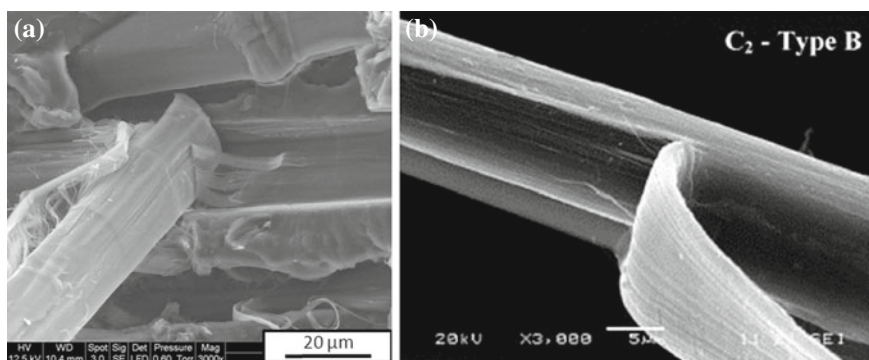


Fig. 2.4 Evidence of cell wall decohesion after **a** tensile and **b** debonding tests. Reprinted from **a** Le Moigne et al. (2014), Fig. 13 and **b** Le Duigou et al. (2012), Fig. 6 with permission from Elsevier

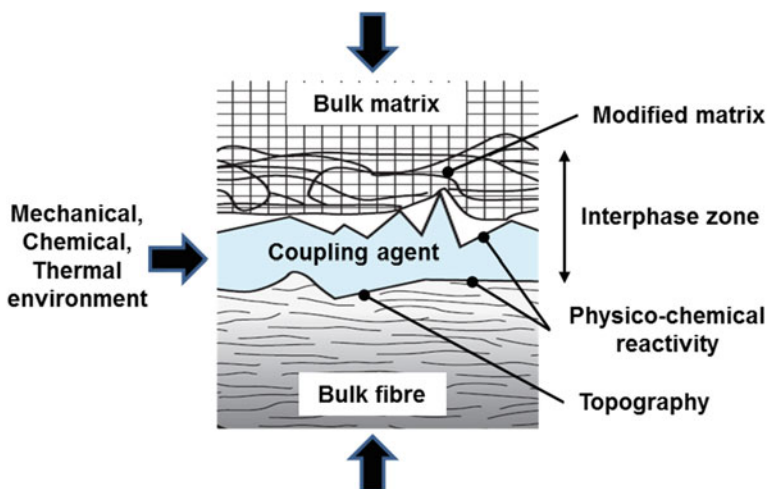


Fig. 2.5 Fibre/matrix interphase in a composite material. Adapted from Bergeret and Krawczak (2006)

According to literature, the interphase thickness in composite materials varies from several hundred nanometers to a few microns (Cech et al. 2013; Heman 2008; Kim et al. 2001; Le Moigne et al. 2014), but the matrix can be affected to much greater thicknesses (on the order of a hundred micrometers) for some thermosets composites (Heman 2008; Ikuta et al. 1993; Bergeret and Krawczak 2006). The complexity of the interphase is illustrated schematically in Fig. 2.5. The interphase incorporates chemisorption and physisorption effects, chemical interactions, cross-linking density gradients or crystal texture modifications (transcrystallization), as well as defects (interfacial porosities and other local anomalies). (Bergeret and Krawczak 2006; Herrera-Franco and Drzal 1992)

2.2 Importance and Role of the Fibre/Matrix Interface

The growing interest in the understanding of the fibre/matrix interface (or interphase) of composites is fully justified because of the crucial role played by this zone in the material properties. Particular mention should be made of its essential contribution to the transmission of mechanical forces, as well as its protective role with regard to the ageing of composites, especially in a moist environment (Fig. 2.6).

A fundamental requirement for obtaining high-performance composites is the efficiency of the stress transfer which takes place at the fibre/matrix interface. Fibres support the applied mechanical load while the matrix transfers and redistributes it from one fibre to the other through the interface, provided that the fibre/matrix adherence is good enough. Indeed, one of the most common modes of damage in composites is the rupture at the interface. Adhesive interfacial failure occurs for weak fibre/matrix

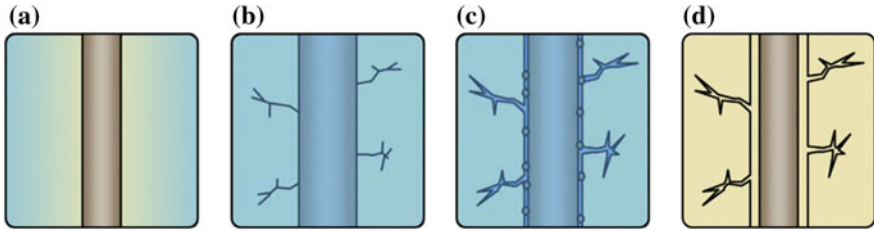


Fig. 2.6 Damage mechanisms likely to occur in lignocellulosic fibres reinforced composites during hydrothermal ageing: **a** Water diffusion into the composite, **b** Swelling of fibres leading to microcracks within the matrix, **c** diffusion of water and possible leaching of water-soluble substances from fibres and matrix, **d** Decohesion of fibre/matrix interface during drying. Reprinted from (Regazzi et al. 2016) with permission from Elsevier

adherence and is characterized by crack propagation between the fibres and the matrix. On the contrary, cohesive interfacial failure occurs for strong fibre/matrix adherence and results in a rupture within the matrix, a part of the matrix remaining bonded onto the fibres. Thus, the bonding strength at the interface largely influences the final properties of the composite and the role of the interfacial adhesion on their structural integrity is now commonly accepted. However, it is worth noting that improving interfacial adhesion is not a *sine qua non* to optimize the mechanical performances of composites. Indeed, strong interfacial interactions do produce composites with high stiffness and high strength, but also contribute to their brittleness, low toughness, and sensitivity to impact. Conversely, a weak fibre/matrix adherence or a flexible interphase can greatly enhance the energy absorption upon impact. The choice of an appropriate fibre/matrix coupling strategy can thus lead to a relevant compromise between these two antagonistic aspects. The interface is therefore one of the key elements of weighting of composites properties. In this regard, the characterization of the interface/interphase zone and the interfacial adhesion is critical to properly understand the behaviour of the composites and to tailor certain of their properties.

Moreover, the interface quality also greatly influences the ageing behaviour of composites. This zone of contact between fibres and matrix has long been considered to be the most sensitive region to the aggression of moisture and fluids in general. As a proof, glass/polymer composites made from non-sized fibres exhibit a drastic decrease of their mechanical properties when they are exposed to water, especially at high temperatures. Considering the moisture sensitivity of most natural fibres, controlling interfacial properties in order to improve the durability of biocomposites has become a critical issue for their development in composites applications. Indeed, moisture absorption of natural fibre polymer composites is a major concern in their outdoor applications. Regazzi et al. (2016) studied the changes in physical and mechanical properties of biocomposites during hydrothermal ageing. The authors demonstrated that the strong sensitivity of PLA/flax composites to temperature and water was responsible for the drastic loss of their mechanical properties. They assumed that in case of a weak fibre/matrix interface, the substantial swelling of lignocellulosic fibres in the transverse direction induces hoop stresses in the matrix leading to plastic strain and micro-cracks

(Fig. 2.6b). The diffusion kinetics of water molecules is then accelerated through the bulk matrix as well as along the fibre/matrix interface (Fig. 2.6c). After drying, the shrinkage of fibres results in larger interstices and voids between fibres and matrix (Fig. 2.6d). Besides, an extensive swelling of the matrix can lead to shear stresses within the fibres and at the interfaces, due to the almost nonexistent swelling of fibres in their longitudinal direction. Finally, the resulting interfacial shearing is likely to contribute to fibre/matrix decohesion, and hence to the weakening of the interface and of the mechanical properties of the composite.

One of the solutions to overcome these harmful effects is to prevent the fluid from reaching the interface or the fibre by selecting suitable coupling agents or coating treatments in order to enhance the interfacial adhesion and create an effective barrier to moisture and fluids. The achievement of a stronger and suitable interface between matrix and fibres could reduce the hygroscopicity of lignocellulosic based materials and allow their widespread use in outdoor applications.

2.3 Strategies to Control Interfacial Adhesion in Natural Fibre Reinforced Composites

Interfacial adhesion in natural fibres based composites is mainly governed by the quantity of fibre/matrix interface developed and the nature and strength of the interactions between the polymer matrix and the fibres. When studying the quality of the interfacial adhesion in natural fibres based composites, it appears important to differentiate the adhesion and adherence phenomena. On the one hand, the adhesion is a purely physico-chemical phenomenon that is governed by the surface free energy and roughness of fibres and surface tension of polymer matrix. It characterizes the wettability of natural fibres towards a molten or liquid polymer matrix during their first contact upon composites processing. On the other hand, the adherence characterizes the interfacial strength between the fibres and the matrix within the consolidated composite when submitted to mechanical stresses. Thereby, other parameters such as fibre/matrix chemical interactions and mechanical interlocking, transcrystallinity (Ning et al. 2012, Wang et al. 2011) of thermoplastic matrices or variations in degree of cross-linking of thermosets at the fibre/matrix interface, or the strength of intra and inter-cellular cohesion within elementary and fibre bundles (Fuentes et al. 2015, Le Duigou et al. 2012, Le Moigne et al. 2014) should also greatly influence the adherence and the resulting interfacial adhesion.

On this basis, several strategies can be developed to control interfacial adhesion in composite materials (Fig. 2.7). Modifying the surface free energy of the fibres and its polar and dispersive components can significantly improve the work of adhesion with the matrix, and hence favour their wetting and impregnation during processing. Functionalizing natural fibres is used to enhance their reactivity towards the matrix and achieve a better chemical and/or physico-chemical coupling. It should be pointed out that coupling agents can also be incorporated within the matrix to further react with the fibres during processing. Improved mechanical

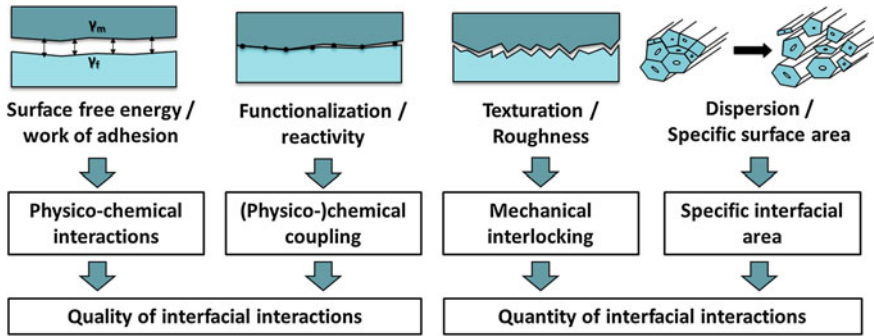


Fig. 2.7 Strategies to control interfacial adhesion in natural fibres based composites

interlocking could be achieved by controlling the surface texturation and roughness of the fibres. Finally, controlling the dispersion state of natural fibres within the matrix should greatly enhance the specific surface area of the fibres, and hence the quantity of interfacial interactions with the matrix.

As concerned the functionalization and compatibilization of the fibres with the polymer matrix (Fig. 2.8), coupling agents, i.e. functional (polymerizable) molecules are added on the fibres or incorporated into the matrix during processing so as to react with both fibre and matrix and create covalent bonds (ester, urethane...) (a). Long chain grafted polymers are also used to favour physical entanglements within the matrix (b). Considering the polar character of natural fibres, long-distance interactions such as hydrogen bonding (c) can be searched with the use of polar coupling agents or polar matrices, bearing for example hydroxyl or amine groups. Obviously, these approaches can be combined leading to the following different fibre/matrix coupling possibilities: (i) covalent/covalent, (ii) covalent/entanglement, (iii) hydrogen bond/entanglement, (iv) hydrogen bond/covalent, (v) hydrogen bond/hydrogen bond. Finally, it should be mentioned that interactions can naturally occur between natural fibres and some polymer matrices bearing polar groups, possibly through Van der Waals and hydrogen bonding (Raj et al. 2011; Le Moigne et al. 2014). The nature of the fibre/matrix interactions thus created will determine the interfacial bonding strength, and the resulting stress transfer and protective efficiency of the interface.

Concluding, natural fibre reinforced composites are multiple and multi-scale interfaces systems originating from the inter- and intra-cellular cohesion in plant cells and the dispersion state of natural fibres in the polymer matrix. Improving the quantity and the quality of fibre/matrix interface could be achieved by developing 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 fibres structure. This constitutes one of the main challenges for the industrial implementation of natural fibre reinforced composites with advanced structural properties. Chapter 3 provides a comprehensive overview of the pre-treatments and functionalization treatments that are used to control the interfacial adhesion in natural fibre reinforced composites.

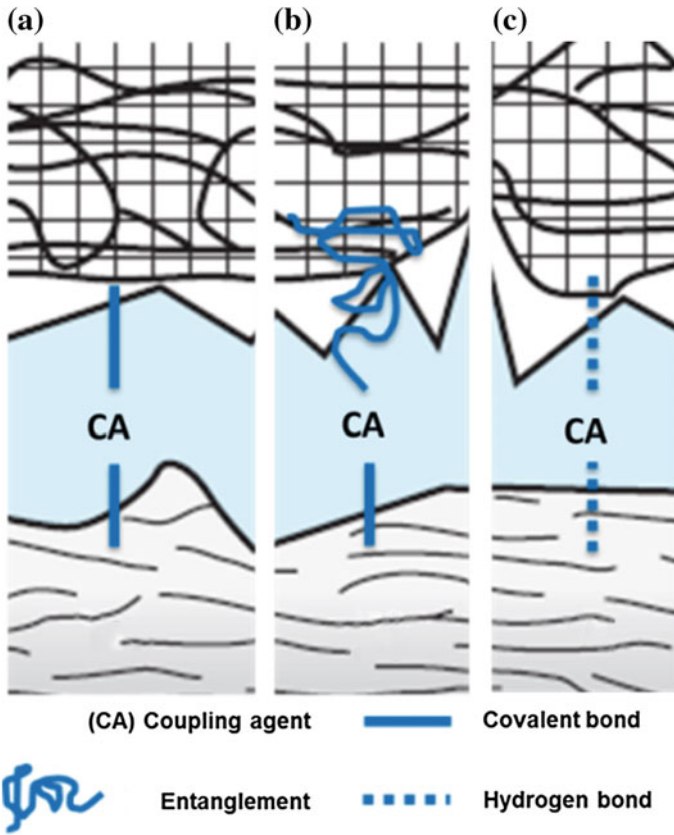


Fig. 2.8 Functionalization strategies to control the physico-chemical coupling between natural fibres and polymer matrices

2.4 Modifying Natural Fibres and Interfaces in Composites: Opportunities for New Functionalities?

The modification of the interface and the effect of interfacial adhesion on the mechanical properties of natural fibre reinforced composites are already well studied by using either experimental analytical or numerical approaches. Indeed, lignocellulosic fibres are primarily used as reinforcing agents intended to be used for automotive, building, sports and leisure or aeronautic applications, thus explaining the numerous studies on the mechanical properties of such materials. However, fibre and interface modifications are also an opportunity to introduce new functionalities in natural fibre based composites.

One original approach is the surface modification of natural fibres to enhance their electrical conductivity. Razak et al. (2012) modified kenaf fibres by conducting polyaniline via an in situ polymerization approach. The obtained coated fibres achieved new electrical properties, without sacrificing their mechanical properties

and natural fibre characteristics. Using another strategy, Trihotri et al. (2013) reported the modification of sisal fibres for the control of electrical properties in epoxy composites. The authors used a silver conducting paint to coat sisal fibres and showed that incorporation of the modified natural fibres in epoxy based composites can significantly enhance their dielectric properties.

The high intrinsic porosity of natural fibres (see Table 3, Sect. 3.3, Chap. 1) can also be exploited for bulk modifications and the incorporation of active chemicals for the control of fibres and composites properties. Indeed, natural fibres could be used for the encapsulation of functional or reactive molecules as it is already carried out with some natural mineral fillers like halloysite. This tubular clay is indeed used in different applications for the loading and the release of antioxidants, anticorrosion agents, flame-retardant agents, drugs or proteins (Lvov et al. 2016). Hu et al. (2010) obtained highly conductive cotton textiles using a simple “dipping and drying” process with single-walled carbon nanotube ink. The authors proposed the use of the resulting porous conductive textiles for wearable electronics or energy storage applications. Xia et al. (2016) loaded kenaf fibres with boron nitride for the control of their thermal conductivity. The authors showed a significant increase of the thermal conductivity of epoxy composites when these modified fibres were incorporated. Sonnier et al. (2015) modified the fire behavior of flax fibres by the grafting of phosphonated molecules using an irradiation process. The authors showed that the penetration of the grafting agent into the bulk of elementary fibres allowed achieving high levels of grafting which significantly modified the fire behavior of flax fibres but also of a polyester composite filled with these phosphonated fibres.

As concerns the mass transfer properties, it is worth noting that lignocellulosic fibres were rarely used in membrane or food packaging applications to modulate mass transfers of composites. Till now, only a few laboratories are closely interested in the understanding and modelling of the structure/mass transfer properties relationships in composite materials, with the majority of the studies devoted to layered silicate nanocomposites, polymers from fossil resources and/or separating membrane applications. It clearly emerges from this context a need for fundamental researches turned towards the analysis of mass transfers in biocomposites and the development of modelling approaches that consider an increasing complexity of microstructures involving in particular the interfaces. Existing models currently used to predict mass transfers in (nano)composites primarily aim at predicting permeability or diffusivity of the (nano)-composite material from the permeability or diffusivity of each single component (matrix and particle), the particle content and its in situ aspect ratio and orientation within the composites structure. These models usually consider two compartments, i.e. the matrix and the filler, and the three following hypotheses: (i) impermeable (tortuosity-based models) or permeable particles (models for mix of polymers for instance), (ii) perfect adhesion between the filler and the matrix, and (iii) no modification of the mass transfer properties of the matrix induced by the presence of fillers. But in most cases, the third assumption is incompatible with the second one, since the establishment of a strong filler/matrix interphase inevitably induces structural changes of the polymer matrix (cross-linking degree for thermosets, crystallinity degree for semi-crystalline thermoplastics, molecular weight, free volume, etc.). For all aforementioned models, when a deviation between experimental values and values predicted

by “two-phase” models is noted, it is generally attributed to the existence of a third phase at the filler/matrix interface, called interphase or interfacial zone, that generally displays different mass transfer properties than the ones of the fillers and the matrix (Wolf et al. 2016). The deviation between experimental and predicted values could also be attributed to changes in mass transfer properties of each individual constituent. Finally, in the case of biocomposites, tortuosity models based on the hypothesis that fillers are impermeable obstacles increasing the diffusion pathway cannot be validated anymore since lignocellulosic particles could be permeable to gases or solutes (and even more than the matrix). As an example, it was shown for PHBV/wheat straw composites that changes in interfacial adhesion induced by the torrefaction of fibres allowed to modulate the water vapour permeability (WVP) of materials. Higher WVP was observed in the case of untreated fibres as compared to torrefied fibres (Berthet et al. 2016a). This was ascribed to the more hydrophobic character of torrefied fibres concomitantly to a tortuosity effect favoured by a better dispersion of fibres and an improved interfacial adhesion with the PHBV. A good knowledge of the fibre/matrix interface is thus fundamental to choose the most appropriate strategy able to modulate the compatibility between the two constituents and the resulting mass transfer properties of the composite material depending on the targeted application. In the field of food packaging, a strong filler/matrix adhesion is not necessary targeted. For example, an increase in gas and water vapour permeability could be preferred in the case of respiring food products such as fresh fruits and vegetable while a barrier material would be required in the case of sandwiches (Berthet et al. 2016b).

Concluding, these few examples emphasize that original approaches are currently developed to modify natural fibres in the bulk and to tailor and model interfacial properties in biocomposites. This constitutes a real opportunity for the development of innovative biocomposite materials with novel functional properties, and will certainly be one of the key for implementation of natural fibre reinforced composites in industrial applications.

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