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Introduction on Natural Fibre Structure: From the Molecular to the Macrostructural Level

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Natural fibres are complex hierarchical bio-assemblies built-up of several biopolymers. In this chapter, the main features related to biopolymers organization within natural fibres are described. Then, the specific surface properties and porous structure of natural fibres that are key parameters as regard to fibre and interface modifications are detailed.

1.1 Main Biopolymers in Natural Fibres

Natural fibres used in composite materials often refer to plant fibres extracted from lignocellulosic biomass such as wood fibres and other plant fibres from stem, leaf, fruit and seed. Their biochemical composition can vary within the different tissues of the plant, from one plant to another and according to soil, climate, extraction conditions and maturity of plant cells. When considering the dry matter, the predominant chemical components are carbohydrates, i.e. sugar-based biopolymers including cellulose, hemicelluloses and pectins. These biopolymers are associated with a complex polymer of aromatic alcohols named lignin, and in lower amounts with proteins, extractives (e.g. fatty acids, fatty alcohols, free sterols, ferulic acid esters, waxes, sterol, and other aromatic compounds), and inorganic components that are comprised in the ash content and include minerals and metals (e.g. silica, calcium, potassium, zinc, iron, lead...) (Akin 2010; Bismarck et al. 2002; Brosse et al. 2012; Gutierrez et al. 2008; Misra et al. 1993; Yan et al. 2014). Biochemical compositions of some selected natural fibres from various origins are given in Table 1.1.

Table 1.1 Biochemical composition of some selected natural fibres

Natural fibre type	% wt cellulose	% wt hemicellulose	% wt lignin	% wt pectins	% wt fat/wax	% wt ash	MFA (S2 wall) °	Crystallinity index I_c %	Plant cells length mm/ width μm	References
Wood fibres	Hardwood	38–51	17–31	21–31	–	–	10–30	9–25.8	1.2/25	Agarwal et al. (2011), Klemm et al. (1998), Müssig et al. (2010), Sjöström (1981)
	Softwood	33–41	20–29	27–32	–	–	10–30	16.3–20.3	3.6/35	Agarwal et al. (2011), Klemm et al. (1998), Müssig et al. (2010), Sjöström (1993)
Stem fibres	Flax	60–81	11–21	0.9–5	0.9–3.8	1.5	5–10	44–48.2	4–140/2–76	Acera Fernández et al. (2016), Agarwal et al. (2011), Gorshkova et al. (2000), Klemm et al. (2005), Müssig et al. (2010)
	Hemp	57–92	6–22	2.8–13	0.8–2.5	0.7–0.8	2–6.2	44–49	8–55/3–51	Klemm et al. (2005), Müssig et al. (2010), Thygesen et al. (2005)
	Jute	51–84	12–24	5–14	0.2–4.5	0.5–2	7–10	–	1–6/5–30	Müssig et al. (2010)
	Ramie	68–87	3–17	0.2–1	1.7–2.1	0.3	7.5–12	44–62.8	40–260/5–126	Agarwal et al. (2011), Klemm et al. (2005), Müssig et al. (2010), Thakur et al. (1999)
	Miscanthus	37–45	18–36	20–26	–	1–2	–	–	–	Brosse et al. (2010), El Hage et al. (2010a, b), Montane et al. (1998), Sørensen et al. (2008)
	Kenaf	36–72	20–23	8–19	2–5	–	–	22.5	1.5–11/12–50	Agarwal et al. (2011), Müssig et al. (2010), Lilholt and Lawther (2000)
	Bamboo	26–43	15–30	21–31	–	0.9–2.8	8–10.5	–	1.5–4/25–40	Jain et al. (1992), Müssig et al. (2010), Wahab et al. (2013), Wang et al. (2010), Yu et al. (2007)
	Wheat Straw	29–55	15–27.2	12–28	–	3–9	–	20–25	1.6/13–23	

(continued)

Table 1.1 (continued)

Natural fibre type	% wt cellulose	% wt hemicellulose	% wt lignin	% wt pectins	% wt wax	% wt fat/ash	MFA (S2 wall)	Crystallinity index I_c %	Plant cells length mm/width μ m	References
Leaf fibres	Piassava	29	45–48	–	–	–	–	–	–	Silva et al. (2011, 2012), Le Digabel et al. (2004), Müssig et al. (2010)
	Sisal	43–88	4–14	0.5–10	0.2–2	0.1–0.5	10–25	55–70.9	0.5–8/4–47	Müssig et al. (2010), Varghese et al. (1994)
	Henequen	60–78	8–13	3–4	0.5	–	–	–	–8–33	Han et al. (2006a), Müssig et al. (2010)
	Banana	50–68	6–30	5–18	3–5	10–11	1.2	10–12	0.9–5.5/11–81	Joseph et al. (2002), Müssig et al. (2010)
Seed fibres	Cotton	82–96	2–6	0–1.6	0–7	0.6	20–45	56–65	10–64/12–38	Klemm et al. (1998, 2005), Müssig et al. (2010), Lilholt and Lawther (2000), Terinte et al. (2011)
Fruit fibres	Coir	32–53	0.2–0.3	40–45	3–4	–	30–49	–	0.3–1.2/12–24	Müssig et al. (2010)

1.1.1 Cellulose Microfibrils as Reinforcing Elements

Cellulose is the most abundant biopolymer on the planet, representing more than half of the Earth's biomass. It is indeed estimated that nature produces 10^{10} to 10^{11} tons of cellulose annually, which constitutes at least 50% of the total plant biomass (Hon 1994). Cellulose is a linear homopolymer of glucan with chemical formula $C_6H_{10}O_5$. It is synthesized by Cellulose Synthase Complexes (CSCs) present within the plasma membrane of plant cells (Saxena and Brown 2005). Cellulose chains are composed of anhydroglucose units (AGU) each bearing three hydroxyl reactive groups at C-2, C-3 and C-6 positions, and linked together by β -(1,4)-glycosidic bonds. Degree of polymerization (DP) of native cellulose from various origins varies from 1,000 to 30,000 with a large polydispersity, and from 200 to 3,000 after cellulose extraction (Heinze et al. 2012; Klemm et al. 1998; Krässig 1993). When synthesized and extruded by CSCs, cellulose chains have a high tendency to align and aggregate in larger entities through intra and inter-molecular hydrogen bonds (thanks to hydroxyl groups), hence giving crystalline cellulose microfibrils consisting of 18 to 90 glucan chains in higher plants and some green algae. These microfibrils have a diameter of 3 to 18 nm in the case of plant fibres (Klemm et al. 2005; Saxena and Brown 2005) and aggregates into cellulose macrofibrils of several hundred nm in diameter. Lignocellulosic substrates may contain more than 70% of highly ordered crystalline regions (Atchison 1983; Klemm et al. 2005; O'Sullivan 1997), whose main lattice forms are either type I for native cellulose (case of plant fibres, bacterial and algal cellulose) or type II for regenerated cellulose (case of viscose, Lyocell fibres). However, several imperfections occur in this structure as the less ordered regions within the microfibrils, the interstice between the microfibrils and the larger voids between the microfibrils and the macrofibrils (Krässig 1993). Thanks to this regular, well-aligned and crystallized structure, cellulose is the biopolymer that provides stiffness, strength and structural stability to natural fibres. Wide variations in cellulose content and crystallinity index I_c are reported in literature according to lignocellulosic substrates, extraction methods and analytical techniques used (see values for various natural fibres in Table 1.1).

1.1.2 Non-cellulosic Components as Matrix and Encrusting Elements

Hemicelluloses and pectins are synthesized in the Golgi, and delivered in the inner surface of cell walls to then coat cellulose microfibrils (Lerouxel et al. 2006). The hemicellulose fraction in natural fibres consists in branched heteropolysaccharides, mainly xylan, glucomannan and xyloglucan, composed of 5 ($C_5H_{10}O_5$) and 6 ($C_6H_{12}O_6$) carbon sugars: D-glucose, D-Xylose, D-Galactose, L-Fucose, D-Glucuronic acid, L-Arabinose and D-mannose (Beaugrand et al. 2017). Hemicelluloses, in their native state, are low molecular weight branched polymers that are non-crystallisable but still contribute to the structural organization of the cell walls as a matrix component. Pectins are complex high-molecular-weight acidic polysaccharides whose chain backbone is rich in galacturonic acid with different degree of methyl esterification. The most common pectic polysaccharides present in natural fibres are linear homogalacturonans (HG) and branched

rhamnogalacturonans (RG type I, RG type II). As hemicelluloses, they are present in the cell walls as matrix components but they also act as adhesives in the middle lamellae between plant cells (Beaugrand et al. 2017; Jarvis 1984; Morvan et al. 2003). Non-wood fibres (e.g. bast fibres) have significant amount of pectins in their structure (see Table 1.1).

Lignin is a three-dimensional phenylpropanoid heterogeneous, amorphous and highly cross-linked macromolecule that represents the second most abundant natural polymeric material in plants. Despite extensive investigations, the complex and heterogeneous structure of lignin is not completely understood (Argyropoulos and Menachem 1998; El Hage et al. 2010a; b; Fengel and Wegener 1989). Lignin structure varies within different plant species and is usually composed of three basic building blocks of guaiacyl, syringyl, and p-hydroxyphenyl units, although other aromatic compounds such as coumaric and ferulic acids also occur in higher plants (Akin 2010; Sjöström 1981). Lignin synthesis occurs in the presence of the already synthesized cellulose microfibrils and hemicellulose/pectin matrix. It is located in both middle lamella and cell walls, and acts as an encrusting component around cellulose microfibrils and the matrix constituents, i.e. hemicelluloses, pectins and proteins. These biopolymers are intimately associated within the cell walls through covalent and non-covalent interactions (Akin 2010; Beaugrand et al. 2017; Morvan et al. 2003).

Proteins (hydroxylamine-rich HRP, proline-rich PRP, glycine-rich GRP) are present in smaller amounts in plant cells but play a key role in the building of the cell walls (Beaugrand et al. 2017; Boudet 2002; Prat et al. 2004). In particular, they are able to interact and modify the other cell walls components during cell growth. At the end of the elongation stage of plant cells, structural proteins could form a secondary network by covalent bonding (extensin) and hydrogen interactions that blocks the plasticity of the primary wall. In addition, proteins are supposed to form covalent bonds with pectins, and also phenolic acids by forming protein-phenolic-protein cross-links (Morvan et al. 2003; Ozdal et al. 2013; Qi et al. 1995).

Concluding, although major and minor components of plant cell walls are now well identified and their chemical structure described, it should be pointed out that the nature of the interactions between the different cell walls components and the possible evolution of these interactions during cell walls building are still a subject of intense debate within the scientific community (CELL division 2017).

1.2 Cell Walls Microstructure and Plant Cells Organization

1.2.1 Building of Cell Walls

The building of plant cell walls is engineered by numerous Cellulose Synthase Complexes (CSCs) present in the plasma membrane which produce and deposit cellulose microfibrils on the cell outer surface (Lerouxel et al. 2006). To achieve this, the CSCs are thought to be intimately linked and guided by microtubules (Gu 2017), and to move along the plasma membrane while they deposit the cellulose microfibrils (Fig. 1.1). A meaningful evidence of this movement was demonstrated by Paredes et al. (2006). In fact, the authors were able to obtain an *in vivo*

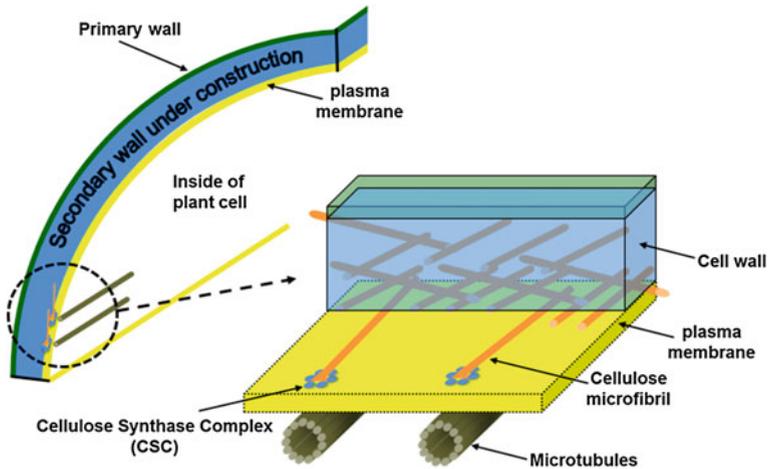


Fig. 1.1 Building of the cell walls. The CSCs localized in the plasma membrane synthesize and deposit the cellulose microfibrils along the cell wall. Several distinct cell wall layers in terms of composition and orientation are produced by this mechanism

visualization of the kinetics of cellulose deposition and movement of CSCs by fluorescently labelling the CESA proteins, subunits constituting the CSCs.

Cellulose microfibrils and macrofibrils are the basic fibrillar elements of the cell wall building. During growth and elongation, plant cells possess only a very thin cell wall, named primary (P) wall, which surrounds the plasma membrane and the cytoplasm. After completion of their growth, the thickness of cell walls increases significantly by the successive deposition of concentric inner layers of cellulose microfibrils, constituting the secondary (S) wall (Fig. 1.1). At the end of the biosynthesis, the plant cell dies and the resulting central channel, named lumen, is more or less narrowed depending of the maturity of the cell. The resulting fibre cells, so-called elementary fibres, undergo wide variations in length and diameter according to fibre type (see Table 1.1).

1.2.2 Cell Walls Morphology and Composition

As shown schematically in Fig. 1.2, the cell walls morphology of elementary fibres consists in several layers of cellulose microfibrils having different thickness and microfibrillar angle (MFA). Microfibrils are embedded in a matrix of hemicelluloses, pectins, proteins which are associated with a lignin network, thereby forming a complex, tri-dimensional bio-assembly (Beaugrand et al. 2017; Klemm et al. 1998, 2005; Krässig 1993). In this structure, the outer layer, the primary (P) wall is 0.1–0.5 μm thick with a random microfibrillar orientation, and it is rich in non-cellulosic components, i.e. hemicelluloses, pectins and proteins, that contribute in particular to its plasticity during cell growth. At the end of cell growth, lignin can be also found in the primary wall and

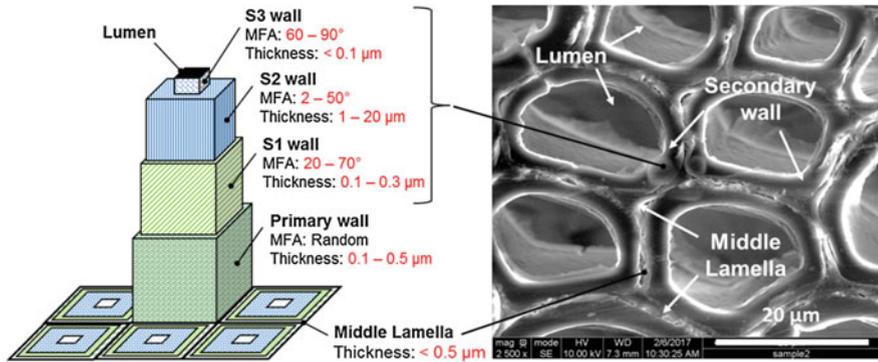


Fig. 1.2 a General cell wall structure of natural fibres, with: middle lamella (ML), primary P wall, secondary S1 wall, secondary S2 wall (main body), secondary S3 wall, lumen. For each wall, indications about their thickness and overall microfibrillar angle (MFA) are given according to (Klemm et al. 1998; Krässig 1993; Warwicker et al. 1966; Müssig et al. 2010); b wood fibre cells showing detail of middle lamellae, cell walls and lumen

contributes to the stiffness and hydrophobicity of cell walls. The concentric inner layers constituting the secondary (S1) and (S2) walls are 0.1–0.3 μm and 1–20 μm thick, respectively. In S1 wall, microfibrils are parallel and densely packed in a flat S-helix with variable angles function of natural fibre type (50 to 70° for wood fibres and 20 to 30° for cotton fibres). The S2 wall constitutes the main body of natural fibres and its overall microfibrillar angle varies significantly according to fibre type and their role in plants. The microfibrils in cotton are well aligned with periodical reversal in a so-called S-Z fashion and oriented around 35–45° to the fibre axis. For other natural fibre sources such as wood, flax, hemp... the microfibrils are positioned in an extended helix with a low MFA (see values in Table 1.1). Basically, low MFA will result in higher strength and stiffness in the fibre direction. The amount of non-cellulosic components decreases gradually within the S walls which are mainly composed of cellulose and hemicelluloses. In the case of cotton fibres, the S walls contain almost only cellulose, around 99%. The last layer deposited closest to the fibre lumen, i.e. the S3 wall, is not always present and very thin (<math>< 0.1 \mu\text{m}</math>). Its microfibrils are aligned in a flat helix with a high MFA, e.g. 60 to 90° for wood fibres (Klemm et al. 1998; Krässig 1993; Warwicker et al. 1966).

1.2.3 Plant Cells Organization

Elementary fibres are separated by the middle lamella, rich in pectins and lignin, which act as adhesives and gathered them into fibre bundles in wood and within the stem, fruit or leaf of annual plants (Fig. 1.3). In the case of bast fibres (flax, hemp, jute, kenaf...), fibre bundles used in biocomposite materials are mostly extracted from the external ring of the stem localized between the epidermis (Ep) and the xylem (X) (i.e. core tissues) (Fig. 1.3a and b). Elementary fibres can also be already

individualized as for cotton fibres (Fig. 1.3d). A combined method using optical microscopy associated with a 3-D mid-infrared transmission was used by Morvan et al. (2003) to analyse the distribution of the different cellulosic and non-cellulosic components across flax stem sections. The authors showed that stem surface (epidermal region) is composed mainly of pectins and waxes. Underneath the epidermis, the internal zone rich in bast fibres, where cellulose is predominant, showed substantial amounts of pectins and acetylated non-cellulosic polysaccharides accumulated in the primary wall and middle lamella that act as adhesives in the cohesion of flax fibre bundles. Aromatic components (e.g. lignins) and non-cellulosic polysaccharides appeared to be more concentrated in the core tissues of flax stems. Other methods based on selective staining are also classically used in plant biology to study the distribution of cellulosic and non-cellulosic components across the stem section of plants. For example, Kaack et al. (2003) showed that in miscanthus, the concentration of lignin and cellulose are high in the outer ring underneath the epidermis, and then their concentration decreases exponentially towards the internal part of the stem. The cells around the vascular bundles were also shown to be rich in lignin and cellulose. These observations thus show that natural fibres extracted from plants can undergo wide variations in biochemical

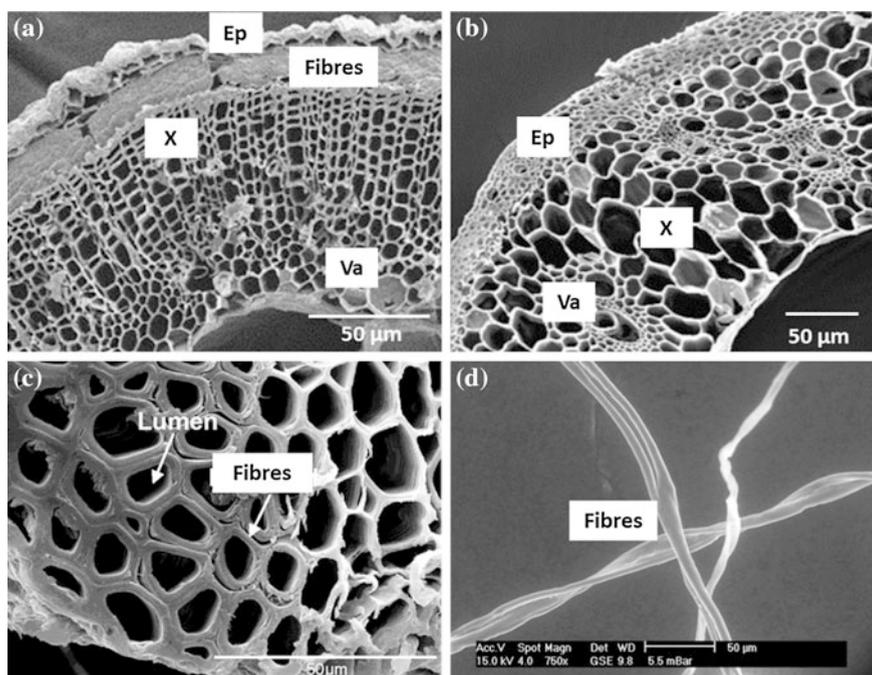


Fig. 1.3 SEM pictures of plant cells from various origins. **a** flax (stem); **b** wheat straw (stem); **c** sisal (leaf); **d** cotton (seed). Ep : epidermis; Fibres; X : xylem; Va : vascular bundles. SEM pictures reprinted from Akin et al. (2007), Fig. 1a; Yu et al. (2008), Fig. 1 Fidelis et al. (2013), Fig. 1 with permission from Elsevier

composition according to plant tissues considered and their location within the different parts of higher plants.

1.3 Surface Properties and Porous Structure of Natural Fibres

As described in the preceding paragraphs, natural fibres are complex hierarchical bio-assemblies built-up of several biopolymers with their own intrinsic physico-chemical characteristics. When incorporating natural fibres in a polymer matrix, their surface physico-chemistry and topography play a key role in the mechanisms of adhesion and wetting, especially at the first contact between the matrix and the fibres during composites processing. Surface chemistry of natural fibres is also of great importance since reactive functional groups present at their surface are likely to interact with the matrix to form hydrogen or covalent bonds that could significantly enhance the fibre/matrix adherence within the consolidated composite. Other interfacial phenomena such as mechanical interlocking related to roughness, transcrystallization of thermoplastics, variation in degree of cross-linking in thermosets could also be influenced by the surface properties of natural fibres. Besides, additives, matrix reagents and oligomers or functionalizing molecules can also migrate within the bulk of natural fibres through their accessible porous structure. In this regard, advanced knowledge on the surface characteristics and porous structure of natural fibres is therefore required to better understand and control interfacial properties in natural fibre reinforced composite materials.

1.3.1 Surface Physico-Chemistry

Many studies investigated the surface physico-chemistry of natural fibres through contact angle (CA) or Inverse Gas Chromatography (IGC) measurements with various polar and non-polar liquid and gas. Based on these techniques, it is possible to determine the surface free energy γ_{SV} of natural fibres and its dispersive γ_{SV}^d , polar γ_{SV}^p , Lifshitz-van der Waals γ_{SV}^{LW} , and acid-base γ_{SV}^{AB} , γ_{SV}^+ , γ_{SV}^- components. These values can be further used to determine the interfacial tension γ_{SL} and the theoretical strength of the physico-chemical interactions between fibres and matrix defined as the work of adhesion W_A (see Sects. 4.1 and 4.2 in Chap. 4 for details about experimental techniques and theoretical approaches). Table 1.2 reports values of surface free energy measured on various lignocellulosic substrates and pure cell wall components.

Considering the additive character of the surface free energy, it could be possible to calculate the theoretical surface free energy of natural fibres based on the sum of the surface energy components of each of the cell walls biopolymers (i.e. cellulose, hemicelluloses, lignin, pectins...) and their respective amounts within the fibre. However, the

complex and heterogeneous surface and structure of natural fibre substrates do not allow such simple approach (Baley et al. 2006; de Meijer et al. 2000).

First of all, natural fibres can be highly porous, especially in the case of fibre bundles with large lumen. This causes a significant absorption of the solvents used for CA measurements due to capillary penetration into natural fibres structure, and hence a continuous decrease in contact angle (de Meijer et al. 2000). Capillary effects can also occur between the fibres. Moreover, surface roughness could also greatly influence the contact angle. In particular, a regular and micro- or nano-scaled texturation of the substrate can considerably increase the contact angle with a liquid, and hence decrease the calculated surface free energy if not corrected. This phenomenon is at the basis of the superhydrophobicity of surfaces, and was earlier described and modelled by Wenzel (1936) and Cassie—Baxter (1944). For all these reasons, the determination of the surface free energy of natural fibres is thus influenced by the conditioning of the samples, and characteristics of surfaces exposed to the solvents. Indeed, the sessile drop method implies the conditioning of natural fibres in the form of compacted tablets. Washburn method is based on the monitoring of the capillary rise in a bed or yarn of fibres, whereas Wilhelmy and Drop-on-fibre techniques used single elementary fibres or fibres bundles. Obviously, capillary and roughness effects will be more or less pronounced depending of the conditioning and technique used.

Another critical factor of variation in surface free energy of lignocellulosic substrates is the heterogeneous distribution of the cell walls components within the fibre structure (Baley et al. 2006; de Meijer et al. 2000). As previously described, cellulose is mostly present in the bulk of the fibres, while non-cellulosic components can be present in large amount at the fibre surface. As can be seen in Table 1.2, natural fibres can be hydrophobic with low polarity and low surface free energy. In particular, the presence of lipophilic components at the fibre surface can greatly reduce the hydrophilicity of natural fibres. The content and nature of these lipophilic surface components vary according to natural fibre type. Marques et al. (2010) analysed by gas chromatography—mass spectrometry the lipophilic extractives of four different natural fibres, i.e. flax, hemp, sisal and abaca. Several lipophilic components were identified: fatty alcohols, fatty acids, alkanes, aldehydes, steroids, free and conjugated sterols, triterpenoids and ester waxes. Molecular weights of these components can be relatively high: for example, ester waxes containing up to 50 carbon atoms were identified for flax fibres. Great differences were also observed between the different fibre types. Hence, the concentration of fatty acids content was 552 mg per 100 g for flax versus 9 mg per 100 g for sisal or abaca. Total content of extractives was also significantly higher for flax. Van Hazendonka et al. (1993) showed that surface free energy and polar component of flax fibres were significantly increased after extraction of fatty acids present at their surface, i.e. from 28.5–34.2 mJ/m² to 40.3–43.1 mJ/m² and from 0.7–2.9 mJ/m² to 2.7–5.5 mJ/m², respectively. Subsequent removal of pectins, hemicelluloses and lignin resulted in a gradual increase of the surface tension to reach the one of pure cellulose. Baltazar-y-Jimenez and Bismarck (2007) also showed that surface and bulk properties of natural fibres vary according to the cell walls components and functional groups present at their surface. By means of zeta (ζ)-potential and wetting measurements on various lignocellulosic substrates, the authors found that their critical surface tension was nearly a linear function of

Table 1.2 Surface free energy γ_{SV} and its dispersive γ_{SV}^d , polar γ_{SV}^p , Lifshitz-van der Waals γ_{SV}^{LW} , acid-base γ_{SV}^{AB} , γ_{SV}^+ , γ_{SV}^- (with $\gamma_{SV}^{AB} = 2\sqrt{\gamma_{SV}^+ \gamma_{SV}^-}$) components for some selected natural fibres and their constituting cell wall components

Substrates	Techniques/Calculation	γ_c mJ/m ²	γ_{SV} mJ/m ²	γ_{SV}^d ; γ_{SV}^{LW} mJ/m ²	γ_{SV}^p ; γ_{SV}^{AB} mJ/m ²	γ_{SV}^+ mJ/m ²	γ_{SV}^- mJ/m ²	References
Wood (various species)	Wilhelmy - Sessile drop (CA)/OWRK	10.8–57	40.0–87.8	0.4–45	11.5–86.14	0.0–2.86	3.29–67.35	de Meijer et al. (2000)
Flax	Drop-on-fibre (CA)/OWRK		62.5(±1.7)	26.6(±0.6)	35.9(±1.1)			Baley et al. (2006)
Flax	Drop-on-fibre (CA)/Good and van Oss		61.43	36.68	23.23	3.01	43	Baley et al. (2006)
Flax	Wilhelmy (CA)/OWRK		25.5–36	2.67–10.82	14.7–33.3			Velde and Kiekens (1999)
Flax	Wilhelmy (CA)/OWRK		43.5	23.5	20			Cantero et al. (2003)
Flax	Washburn (CA)/Zisman plot approach	33.6 (±0.3)						Baltazar-y-Jimenez and Bismarck (2007), Aranberri-Askargorta et al. (2003)
Flax	Floating test/OWRK - Wu		28.6–34.2	27.8–31.3	0.8–2.9			Van Hazendonka et al. (1993)
Hemp	Wilhelmy (CA)/OWRK		32.8(±4.4)	12.25 (±6.6)	20.6(±4.8)			Shahzad (2013)
Hemp	Wilhelmy (CA)/OWRK		35.2	20	15.2			Park et al. (2006a)
Hemp	Wilhelmy (CA)/Good and van Oss		35.2	31.6	3.6	0.48	6.76	Park et al. (2006a)
Hemp	Washburn (CA)/Zisman plot approach	31.0 (±0.2)						Baltazar-y-Jimenez and Bismarck (2007), Aranberri-Askargorta et al. (2003)
Sisal	Sessile drop (CA)/OWRK		34.7	26.9	7.7			Orue et al. (2015)

(continued)

Table 1.2 (continued)

Substrates	Techniques/Calculation	γ_c mJ/m ²	γ_{SV} mJ/m ²	$\gamma_{SV}^d, \gamma_{SV}^{LW}$ mJ/m ²	$\gamma_{SV}^p, \gamma_{SV}^{AB}$ mJ/m ²	γ_{SV}^+ mJ/m ²	γ_{SV}^- mJ/m ²	References
Sisal	Washburn (CA)/Zisman plot approach	33.1 (±0.2)						Baltazar-y-Jimenez and Bismarck (2007), Aranberri-Askargorta et al. (2003)
Jute	Wilhelmy (CA)/OWRK		29.5	20.7	8.8			Park et al. (2006a)
Jute	Wilhelmy (CA)/Good and van Oss		29.5	26.4	3.52	0.64	4.84	Park et al. (2006a)
Jute	Wilhelmy (CA)/OWRK		37	23	14			Doan et al. (2012)
Wheat straw	Sessile drop (CA)/OWRK		44.5 ± 0.5	21.1 ± 4.5	23.4 ± 0.6			Berthet et al. (2016)
Bamboo	Wilhelmy (CA)/Good and van Oss		45.3(±1.2)	43.2(±1.0)	2.4	0.1 (±0.0)	14.5 (±1.2)	Fuentes et al. (2015)
Bamboo	Washburn (CA)/Good and van Oss		45.5	42.29	3.22	0.16	16.23	Shen et al. (2004)
Cellulose	Wilhelmy (CA)/OWRK		68.5	27.5(±1.5)	41(±2.9)			Westerlind and Berg (1988)
Cellulose	Wilhelmy (CA)/Wu		69.5	26.5(±1.1)	43.0(±2.4)			Westerlind and Berg (1988)
Cellulose	Sessile Drop (CA)/OWRK		50	30	20			Abdelmouleh et al. (2004)
Cellulose	Sessile Drop (CA)/Fowkes			40–42				Eriksson et al. (2007)
Cellulose (40 °C)	IGC			31.9				Belgacem et al. (1995)
Hemicelluloses (wood)	Sessile Drop (CA)/Zisman plot	33–36.5						Luner and Sandell (1969)
Hemicelluloses (wood)	Sessile Drop (CA)/OWRK		35.3–39.5					Luner and Sandell (1969), Van Hazendonka et al. (1993)

(continued)

Table 1.2 (continued)

Substrates	Techniques/Calculation	γ_c mJ/m ²	γ_{SV} mJ/m ²	$\gamma_{SV}^d, \gamma_{SV}^{IW}$ mJ/m ²	$\gamma_{SV}^p, \gamma_{SV}^{AB}$ mJ/m ²	γ_{SV}^+ mJ/m ²	γ_{SV}^- mJ/m ²	References
Hemicelluloses (wood)	Sessile Drop (CA)/Good and van Oss		50.2	37.6	12.6	0.75	53.1	Van Oss (2006)
Pectins	-	-	-	-	-	-	-	No data available in literature for bulk pectins
Lignin (wood)	Sessile Drop (CA)/OWRK		57-58.8	33.7-44.5	31.1-23.4			Notley and Norgren (2010)
Lignin (wood)	Sessile Drop (CA)/Good and van Oss		53.2-56.4	33.7-46.8	9.6-19.5	1.5-4.1	14.1-23.3	Notley and Norgren (2010)
Waxes	Sessile Drop (CA)/OWRK		26.5	26.5	0			Van Hazendonka et al. (1993), Bartell and Zuidema (1936)

the cellulose content. Variations in zeta (ξ)-potential over time were also greatly correlated with moisture adsorption measurements, flax being an exception due to the potential presence of proteins at their surface.

Beyond experimental and morphological aspects, physico-chemical surface properties of natural fibres are thus greatly influenced by the distribution of cellulosic and non-cellulosic components across their section and at their surface. Separation and treatment processes (as decortication, retting or chemicals, see details in Chap. 3) used to improve fibre quality can affect significantly their biochemical composition, and hence their resulting surface free energy and polarity.

1.3.2 Surface Chemistry

While the surface chemistry of glass fibres or pure cellulosic substrates is primarily determined by their reactive hydroxyls groups, the above described structural organization of biopolymers within natural fibres results in the potential presence of a wide variety of functional groups at their surface.

When considering the overall biochemical composition of natural fibres (e.g. of flax in Fig. 1.4), one can expect the presence at their surface of hydroxyls groups –OH from cellulose but also from non-cellulosic components. These hydroxyl groups can have different reactivity if being bound to saturated carbons, i.e. primary and secondary alcohols of cellulose, hemicelluloses, pectins, and lipophilic components (fatty alcohols and free sterols), or bound to unsaturated carbons, i.e. phenols of lignin and other aromatic compounds such as coumaric and ferulic acids. Belgacem and Gandini (2005) reported that organosilanes better react with lignin substrates because of the much more pronounced acidic character of their phenolic hydroxyl groups as compared to hydroxyl groups of cellulose (Castellano et al. 2004). Dorez et al. (2014) also showed that octade-cylphosphonic acid (ODPA) was strongly reactive towards phenolic hydroxyl groups of lignin, whereas no reaction with hydroxyl groups of cellulose and hemicelluloses was evidenced.

Carboxyl groups –COOH can also be found at the surface of natural fibres and are primarily bear by pectins, hemicelluloses (galacturonic acid and glucuronic acid units) and fatty acids, but also by some proteins (e.g. acidic amino acids in glycine-rich proteins of flax) (Beaugrand et al. 2017; Marques et al. 2010; Morvan et al. 2003). Finally, natural fibres surface can also present low amounts of aldehydes –COH and esters –COOR that are bear by some lipophilic components (aldehydes, sterol esters and ester waxes) (Marques et al. 2010).

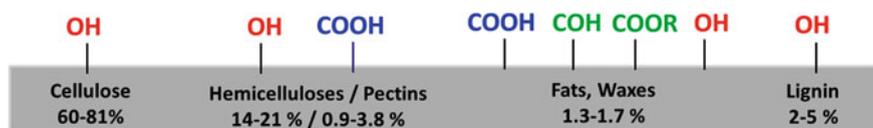


Fig. 1.4 Overall biochemical composition of flax fibres and possible reactive functional groups at their surface

Nevertheless, some of the non-cellulosic components present at the fibre surface are weakly bonded to cell walls and are likely to be easily removed by chemical or mechanical treatments. Ethanol or toluene treatments can remove efficiently and selectively lipophilic components (Acera Fernández et al. 2016; Bismarck et al. 2002). Acera Fernández et al. (2016) removed up to 77% of lipophilic components from flax tow by a hot (75°C) toluene/ethanol treatment. Acidic and (ethylene-diamine-tetra-acetic acid (EDTA) treatments are used to extract pectins from middle lamellae and cell walls, whereas alkaline treatments are known to remove substantial amounts of lignin, pectins and hemicelluloses (Acera Fernández et al. 2016; Lefeuvre et al. 2015). Even hot water can remove substantial amounts of weakly bonded non-cellulosic components, such as oligosaccharides originating from the cortical tissues and pectins from the middle lamella (Acera Fernández et al. 2016; Bourmaud et al. 2010; Le Duigou et al. 2012; Lefeuvre et al. 2015). Besides, mechanical shearing and friction occurring during natural fibre processing for their extraction, separation and conditioning in semi-products (short fibres, roving, woven fabrics) are likely to remove weakly bonded non-cellulosic components, especially those present in the middle lamella. These processes are indeed intended to alter the cell junctions and to promote the separation of fibre bundles into elementary fibres.

Concluding, the surface chemistry of natural fibres and the potential reactions occurring at their surface should be interpreted with caution. Beyond the classical reaction schemes reported in literature that only involve hydroxyl groups of cellulose, many side reactions with other reactive functional groups of non-cellulosic components, i.e. phenols, carboxylic acid, aldehydes and esters, are likely to occur (see for example reaction schemes proposed by Le Moigne et al. 2014 for organo-silane treated flax fibres in PLA matrix). As discussed above, better reactivity towards functionalizing molecules can be achieved in some cases with these functional groups (Castellano et al. 2004; Dorez et al. 2014). Baltazar-y-Jimenez and Bismarck (2007) also pointed out that fibre extraction, separation and treatment processes (as decortication, retting or chemicals, see details in Chap. 3) used to improve fibre quality can affect significantly the surface physico-chemistry and chemistry of natural fibres. In this regard, the use of well-chosen fibre separation and treatment processes is a critical issue to control the surface properties of natural fibres and their interactions with coupling agents and polymer matrices in view of their implementation in composites applications (Bismarck et al. 2002). A breakthrough could be made by a better analysis and knowledge of the functional groups present at the surface of natural fibres after a defined separation and treatment protocol.

1.3.3 Porous Structure, Specific Surface Area and Roughness

The complex structure of natural fibres is also characterized by a system of pores, capillaries, voids, and interstices. There is a wide distribution of pores in terms of

size, shape and accessibility (Klemm et al. 1998; Krässig 1993). Therefore, a total pore volume and an average pore size could not be sufficient to give a complete and precise description of the porous system in lignocellulosic substrates. Besides, pore size and volume analysis are highly dependent of the technique used. Small angle X-ray scattering (SAXS) gives information on the pore structure in the range 2–80 nm, while mercury porosimetry gives data on accessible open-pores in the range of 15 nm to 420 μm (Klemm et al. 1998; Choi et al. 2009). Nitrogen adsorption measurements determines pore size distribution in the range 1.6 to 300 nm (Han and Choi 2010; Choi et al. 2009). Other techniques such as size-exclusion chromatography or calculation from apparent density measurements are also used. Data on porous structure of various lignocellulosic and cellulosic substrates are given in Table 1.3. As can be seen, there are wide variation in terms of porosity and total pore volume for the different cellulosic and lignocellulosic substrates. This can be explained by variation in their structure density that implies significant differences in their micro- and macro-porous structure. Besides, cells lumen can be more or less pronounced according to fibre type and maturity, and the choice of the measurement technique will determine whether these large pores are included in the pore size distribution. Typically, the pore size distribution will be greatly enlarged for natural fibres having large lumen when using mercury porosimetry. Crossing different techniques thus appears as a reliable approach to obtain comprehensive and consistent results on the porous structure of a defined lignocellulosic substrate.

Due to this porous system, the total volume and surface area of lignocellulosic fibres available for functionalization treatments exceed by far the geometrical outer surface of the fibres. Depending of their molecular weight and reactivity, functionalizing molecules are likely to migrate in the bulk of the fibres within their porous structure (see Chap. 4, Sect. 3.4). The total pore volume and specific surface area have therefore to be considered as key parameters with regard to accessibility, reactivity and functionalization of lignocellulosic fibres. It should be pointed out that wide variations occur in the determination of the specific surface area of cellulosic and lignocellulosic substrates, values ranging from 0.3 to 1000 m^2/g (Table 1.3). Again, the origin of the substrate and the analysing technique are determinant. Indeed, the size of accessible interstices but also interactions between substrates and sorbates (e.g. swelling of substrates in the presence of water vapour) could significantly differ according to the technique used (Klemm et al. 1998). Most of the data available in literature are based on sorption measurements with nitrogen or water vapour as sorbates. SAXS, size-exclusion technique or model calculation from pore volume measurements assuming a defined shape of the pores are also used (Klemm et al. 1998). In literature, typical values of specific surface area measured by N_2 adsorption for lignocellulosic fibres range between 0.2 and 5 m^2/g , while specific surface area can reach several hundred m^2/g when using water vapour sorption.

The porous and irregular structure of natural fibres also results in a non-negligible surface roughness which plays a key role in the wettability and interfacial adhesion mechanisms in composites. As described above (Sect. 3.1), micro- or nano-scaled texturation of natural fibre surfaces can significantly decrease their wettability with respect to polymer matrix during processing. On the other hand, it can considerably enhance the interfacial mechanical interlocking in the consolidated composite (see Sects. 2.1 and 2.2 in

Table 1.3 Porosity, specific surface area and roughness of various lignocellulosic and cellulosic substrates

Substrates	Porosity %	Total pore volume mm ³ /g	Pore size nm	Specific Surface area m ² /g	Roughness (rms) nm	References
Flax	10.7	34–52		0.31–1.4	10.8–35	Bismarck et al. (2002), Le Duigou et al. (2012), Legras et al. (2015), Müssig et al. (2010)
Hemp		52		0.75	~ 50	Bismarck et al. (2002), George et al. (2014)
Jute	14–15				41	Kafi et al. (2011), Müssig et al. (2010)
Ramie	7.5					Müssig et al. (2010)
Sisal	17					Müssig et al. (2010)
Kenaf				0.5	26.1–119.5	Legras et al. (2015), Lee et al. (2010)
Henequen		1050	17165	0.230–0.245	58.6	Han and Choi (2010), Choi et al. (2009)
Abacá	17–21					Müssig et al. (2010)
Banana	35–53					Müssig et al. (2010)
Cotton/Cotton linters	1.7–6.6	45–87	11.6–13.1	0.6–135		Klemm et al. (1998)
Wood sulfite pulp	0.7–17.3	72	10.1–25.4	0.35–1000		Klemm et al. (1998)
Wood sulfate pulp	1.2		13.1	3.7		Klemm et al. (1998)
Viscose fibre	6.6	18–73		0.3–292		Klemm et al. (1998)
Cellulose powders	1.4–2.5		4.4–15.9	5.2–15.8		Klemm et al. (1998)
Microcrystalline Cellulose				135–274		Klemm et al. (1998), Driscoll et al. (2009)
Cellulose (from cotton)		50		0.45		Bismarck et al. (2002)

Chap. 5). Studies conducted by Atomic Force Microscopy (AFM) report root-mean-square (rms) roughness ranging from 10 to more than 100 nm depending of the lignocellulosic and the size of the analysis area (Table 1.3). In comparison, a glass fibre is much smoother and homogeneous. A roughness between 2.4 and 3.3 nm was measured for a de-sized E-glass fibre over an area of 1 μm^2 (Le Duigou et al. 2012). Similar values were measured by Zhuang et al. (2010).

Finally, the porous structure and resulting specific surface area and roughness of natural fibres are highly sensitive to pre-treatments. Mercerization of pure cellulose powder leads to a decrease in pore diameter and an enhancement of surface micropores, while enzyme treatments could enlarge the existing pores (Fink et al. 1992). Acid hydrolysis increases the pore system by removing amorphous cellulose from the surface and revealing the microfibrillar structure of cellulose fibres (Zhao et al. 2007). The removal of non-cellulosic components from natural fibres with solvents or alkaline or acidic aqueous solutions could result in an increase of pore volume. Physical treatments such as e-beam or gamma (γ) irradiation also induce modifications in the porous structure. At low irradiation

dose (<30 kGy), the removal of surface components from the fibres, i.e. waxes, impurities, pectins and primary wall, is accompanied by a significant increase of the specific surface area and roughness. A maximum specific surface area of 18.9 m²/g measured by mercury porosimetry was reached at 30 kGy (Choi et al. 2009). This was correlated with an increase in root-mean-square (rms) roughness up to 268 rms at 30 kGy as measured by AFM due to the presence of small pores, and the exposure at the fibre surface of well textured microfibrillar structures from the secondary S walls (Han and Choi 2010). At high irradiation doses (200 to 500 kGy), striations and cracks as well as the appearance of large pores are observed (Choi et al. 2009; Han et al. 2006b; Han and Choi 2010; Takács et al. 1999, 2000). Besides, drying-wetting cycles result in an irreversible reduction of the pore volume due to the closing of the smallest pores, a well-known mechanism for lignocellulosic substrates called hornification (Park et al. 2006b).

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