Chapter 4
Characterization of the Fibre Modifications and Localization of the Functionalization Molecules

As pointed out by George et al. (2001), a clear understanding of the complex nature of surfaces in lignocellulosic substrates is needed to optimize modification procedures and thus to increase the usefulness of lignocellulosic biomass as a constituent of composite materials in technical applications. Surface chemistry and topographical features of the fibres are key parameters that influence chemical bonding and mechanical interlocking with polymer matrices, and hence govern the wetting and adhesion/adherence processes in natural fibre reinforced composites. As discussed in Chap. 1, natural fibres have heterogeneous core and surface structures. The pre-treatments and functionalizing treatments detailed in Chap. 3 also result in heterogeneous properties in terms of roughness and surface chemistry depending of their reactivity, efficiency and processes used for application. For these reasons, there is an important need for reliable and accurate experimental techniques to conduct a detailed analysis of fibre surface properties, account for the effect of fibres treatment and localize functionalizing molecules within the fibre structure. This chapter proposes a comprehensive description of the different approaches used to characterize natural fibres modifications.

4.1 Surface Energy Analysis

4.1.1 Contact Angle Measurements and Work of Adhesion

The contact angle measurement techniques are among the most established methods for investigating the surface physico-chemical properties of polymers. It consists in measuring the contact angle θ formed at the intersection of the liquid, gas and solid phases thus providing a direct evaluation of the surface wettability of a solid substrate with a defined liquid. The principle of this measurement is based on the fact that when a liquid having a surface tension γ_{LV} is placed on a solid surface displaying a surface free energy γ_{SV}, the liquid will spontaneously form a droplet

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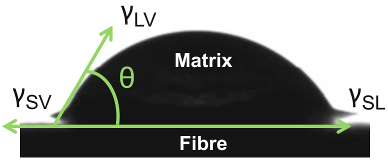

Fig. 4.1 Schematic representation of the contact angle θ, the surface free energy γ_{SV} of the solid, the surface tension γ_{LV} of the reference liquid and the interfacial tension γ_{SL} between solid and liquid on a sessile drop

(Fig. 4.1) or spread on the surface (case of complete wetting). When a droplet is formed, a relationship between the solid surface free energy and the liquid surface tension can be established at equilibrium considering that the surface tensions of each phase are vectors acting at the edge of the drop. The interfacial tension between liquid and solid is named γ_{SL}. The thermodynamic equilibrium can be described by Young's equation (4.1):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{4.1}$$

where θ is the angle formed by the liquid drop on the solid surface. It should be noted that this relation is valid for ideal, i.e. smooth and chemically homogeneous, solid surfaces and pure liquids. It is the basis of all models developed for determining the surface free energy of solids by means of contact angle measurements.

Depending on the θ value measured, the liquid is termed as wetting ($\theta < 90°$) or non-wetting ($\theta > 90°$). Using different standard liquids of suitable polarity, the dispersive (London interactions) and non-dispersive (polar, hydrogen, induction and acid-base interactions) components of the surface free energy of a solid can be determined by the Fowkes (1964), Owens, Wendt, Rabel and Kaelble (OWRK) (1969), Wu (1971) and Good and van Oss (1992) approaches. Finally, the work of adhesion adhesion W_A which is a measure of the strength of the physico-chemical interactions between two phases (e.g. fibres and polymer matrix in the liquid state during composite processing) can be deduced from the values of the dispersive $\gamma^d_{SV/LV}$, polar $\gamma^p_{SV/LV}$, Lifshitz-van der Walls $\gamma^{LW}_{SV/LV}$ and acid-base $\gamma^{AB}_{SV/LV}$, $\gamma^+_{SV/LV}$, $\gamma^-_{SV/LV}$ (with $\gamma^{AB}_{SV} = 2\sqrt{\gamma^+_{SV}\gamma^-_{SV}}$ and $\gamma^{AB}_{LV} = 2\sqrt{\gamma^+_{LV}\gamma^-_{LV}}$) components of their surface free energy (solid) or surface tension (liquid). The highest the W_A value, the better would be the quality of adhesion between the fibres and the polymer matrix. W_A can be calculated from Eq. 4.2 derived from the OWRK approach based on the geometric mean of dispersive and polar components of the liquid surface tension and solid surface free energy:

$$W_A = 2\left[\sqrt{\gamma^d_{SV}\gamma^d_{LV}} + \sqrt{\gamma^p_{SV}\gamma^p_{LV}}\right] \tag{4.2}$$

or from Eq. 4.3 derived from the Wu approach based on the harmonic mean of disperse and polar components of the liquid surface tension and solid surface free energy:

$$W_A = 4\left[\frac{\gamma_{SV}^d \gamma_{LV}^d}{\gamma_{SV}^d + \gamma_{LV}^d} + \frac{\gamma_{SV}^p \gamma_{LV}^p}{\gamma_{SV}^p + \gamma_{LV}^p}\right] \tag{4.3}$$

or from Eq. 4.4 derived from the Good and van Oss approach based on the geometric mean of the Lifshitz-van der Walls and the acid-base components of the liquid surface tension and solid surface free energy:

$$W_A = 2\left[\sqrt{\gamma_{SV}^{LW} \gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{+} \gamma_{LV}^{-}} + \sqrt{\gamma_{SV}^{-} \gamma_{LV}^{+}}\right] \tag{4.4}$$

Following the same theoretical approaches, the interfacial tension γ_{SL} between two phases, e.g. fibres and a polymer matrix, can be deduced from Dupré's equation (4.5):

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{4.5}$$

The lowest the interfacial tension value, the better would be the quality of adhesion between the fibres and the polymer matrix. Finally, combining Young's (4.1) and Dupré's (4.5) equations, the work of adhesion can be expressed as follows:

$$W_A = \gamma_{LV}(1 + \cos\theta) \tag{4.6}$$

Based on the Young-Dupré equation (4.6), the direct measurement of the contact angle angle θ of a liquid or molten polymer matrix, having a surface tension γ_{LV}, on a fibre substrate allows determining the work of adhesion between the matrix and the fibres. Obviously, too viscous polymer matrices may lead to experimental difficulties and non-reliable contact angles.

One of the major limits of the contact angle measurement methods is the conditioning of the solid substrate. In the case of the sessile drop technique (deposition of a liquid drop on a flattened solid surface as shown in Fig. 4.1), fibre fabrics or either compacted tablets of fibres are used, leading to difficulties in interpreting the data due to possible competitive phenomena. As discussed in Chap. 1, considering that natural fibres are far from being ideal material surfaces, the measured contact angles and resulting surface free energy can be greatly influenced by the chemical heterogeneity of the natural fibre substrate and its texturation (roughness, porosity, density of yarns) when conditioned in tablets or fabrics. This also involves capillarity phenomena that should influence the measurement of contact angle. A high surface roughness and a high porosity are both known to result in underestimated values of equilibrium contact angles (Blancher et al. 2005). On the other hand, 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. Texturation is also critical when comparing natural fibre fabrics having significant variations in linear and insertion density of yarns (Acera Fernández et al. 2016). The choice of the model approach used to determine the surface free energy of the fibres can also influence the results and leads to unrealistic values, particularly those obtained by the Good and van

Oss approach (Della Volpe and Siboni 1997; Shen et al. 1999). Acidic component γ_{SV}^{+} can indeed be very small while base component γ_{SV}^{-} can be too high, due to the arbitrary choice of Van Oss et al. (1979) of equal values for the acid-base components for water, $\gamma_{SV}^{+} = \gamma_{SV}^{-} = 25.5\,\mathrm{mJ/m^2}$ (Baley et al. 2006; Della Volpe and Siboni 1997; de Meijer et al. 2000). It should also be emphasized that the capacity of natural fibres to absorb and swell with solvents make the surface measurements delicate independent of the technique used. The solvents used for contact angle measurements may partially dissolve some of the non-cellulosic components present at the fibre surface. The contact angle measurements must thus be taken in the first few seconds of contact between the solvent and the fibre substrates to limit absorption, swelling and dissolving effects.

Having taken these precautions, contact angle measurement techniques can be considered as very useful to compare surface energies of samples prepared in same conditions. As an example, Le Digabel et al. (2004) have compared the compatibility of wheat straw fibres with two polymer matrices (a copolymer of PE and PP, and PBAT) with fibres. They showed that PBAT matrix have better physico-chemical interactions with wheat straw fibres than the polyolefin blend as attested by its higher work of adhesion with fibres due to its higher polar character. Such an approach was also used to explain the effect of decreasing wheat straw fibres size on their affinity with either a wheat gluten-based matrix (Montaño-Leyva et al. 2013) or a PHBV matrix (Berthet et al. 2015). The authors found that successive grinding induces an increased hydrophobicity of wheat straw fibres, possibly due to a preferential location of lignin at the surface of the grinded wheat straw fibres. This results in higher work of adhesion and lower interfacial tension for grinded wheat straw fibres/wheat gluten composites (Montaño-Leyva et al. 2013).

Besides, other techniques which imply different substrate conditioning were also used to characterize the surface free energy of natural fibres. The Washburn method which is based on the monitoring of capillary rise in a bed of fibres or powder has been used by Le Moigne et al. (2014) to characterize the effect of organosilane treatments on the wettability and hydrophobicity of flax fibres. This method allows testing a large number of fibres in a single experiment thus giving a good statistical determination of the fibre wettability.

The use of techniques implying contact angle measurements on single fibre or fibre bundle is also reported in literature. Zhou et al. (2012) used the drop-on-fibre technique on single ramie fibres to characterize the effect of plasma treatment on their surface hydrophobization and interfacial strength with PP matrix. Results showed that the increase in hydrophobicity consecutive to plasma treatments were related to an increase in interfacial adhesion (IFSS) measured by single fibre pull-out tests. Baley et al. (2006) also used the drop-on-fibre technique to determine the work of adhesion between flax fibres and epoxy and polyester matrices. In this work, no clear correlation was found between the work of adhesion and IFSS measured by debonding tests. The authors suggested that the complex structure of natural fibres must be taken into account when studying interfacial adhesion mechanisms in natural fibre reinforced composites. Mechanical interlocking and chemical interactions between the matrix and the fibres should indeed greatly influence the interfacial adhesion.

The Wilhelmy method is based on the measurement of the force acting on a solid substrate (i.e. a single fibre or fibre bundle) when vertically immersed in a solvent. Cantero et al. (2003) determined the surface energy of maleic anhydride (MA), maleic anhydride grafted polypropylene (MAPP) and silane treated flax fibres by this technique and found a significant decrease of the polar component for silane and MAPP treatments reaching the same value as PP for both polar and dispersive components. This was accompanied by a moderate improvement of flexural and tensile strength for MAPP treated flax/PP composites. Tran et al. (2013) also used the Wilhelmy method to determine the work of adhesion between coir fibres and various thermoplastic matrices (PP, MAPP, Polyvinylidene fluoride PVDF). The results were correlated with local interfacial adhesion (IFSS) measured by single fibre pull-out tests and interfacial strength of composite measured by transverse three-point bending tests (see also mechanical tests in Chap. 5.2). The authors found good agreement between the wetting analysis and the characterization of the interfacial adhesion obtained by (micro-) mechanical tests. It is worth noting that this approach could allow to better discriminate physico-chemical interaction effects characterized by the work of adhesion, and chemical interaction effects (brought by a functionalizing molecule) that can result in higher interfacial adhesion without necessarily changing the work of adhesion. Indeed, Tran et al. (2013) showed that PP and MAPP have similar work of adhesion with coir fibres but interfacial adhesion and IFSS was greatly enhanced in the case of MAPP (Fig. 4.2) due to chemical bonding between maleic anhydride functional groups of PP and hydroxyl functional groups present at the fibres surface.

4.1.2 Inverse Gas Chromatography (IGC)

Inverse gas chromatography (IGC) is a commonly used technique to characterize the physico-chemical surface properties of either nano- or micro-particles (powders or fibres) (Belgacem and Gandini 1999) and to predict the acid-base interactions with polymer matrices, as shown for example for cellulose and lignocellulosic fibres (Heng et al. 2007; Pogue et al. 1998; Tze et al. 2006; Gamelas 2013). IGC enables to predict the fibre-matrix compatibility through the determination of the surface free energy of both phases. This approach is preferred to other methods such as contact angle measurement when materials are of micro- or nanoscopic dimensions. The technique is based on the change in the time required for a probe gas (infinitely diluted in an inert carrier gas) to go through a packed column in which the material of interest has been introduced. The use of thermodynamic laws enables characterizing the solid phase in terms of surface property (Gibbs specific free energy, acid-base surface character and heat of adsorption) from the retention volume of the probe gas by the stationary phase. The use of polar (such as tetrahydrofurane THF, ethyl acetate, ethanol, acetonitrile) and

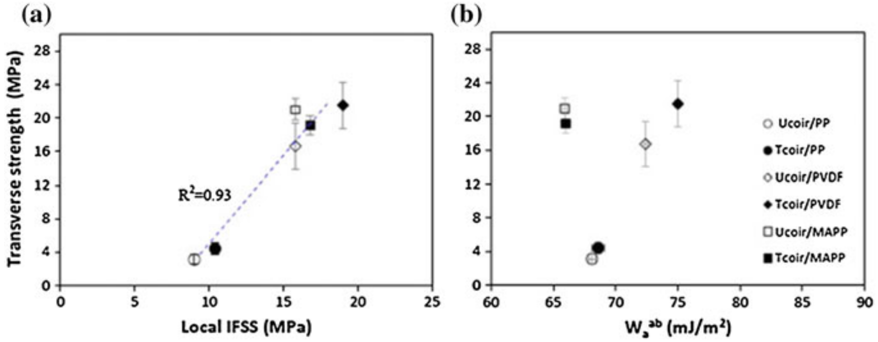

Fig. 4.2 **a** The correlation between local IFSS from the single fibre pull-out test and transverse strength from the three point bending test of unidirectional composite for different fibre–matrix composites, and **b** the transverse strength of unidirectional composites as function of the work of adhesion (W_a) calculated following the Good and van Oss approach. (U) untreated (T) alkali-treated. Reprinted from Tran et al. (2013), Fig. 5 with permission from Elsevier

non-polar (n-alkanes) probes enable the determination of both disperse and acid-base components, respectively.

IGC can be used to infer fibre-matrix interactions and predict practical adhesion between components, and potentially select either an appropriate coupling agent (Belgacem and Gandini 1999) or a modification strategy for natural fibres as done for silane treatments (Pogue et al. 1998) or MAPP grafting (Coupas et al. 1998). The surface properties of cellulose have been thoroughly studied by IGC. Regarding the dispersive component of the surface energy γ_{SV}^{d} the majority of the reported values are in the range 40–50 mJ.m^{-2} (Gamelas 2013). As regards lignocellulosic particles, Cordeiro et al. (2011a, b, 2012) characterized several lignocellulosic fibres from different botanic origins (eucalyptus, spruce, bagasse, piassava, jute, sorghum, ramie, pita Mexicana, curaua, sisal, flax, hemp, kenaf, agave, pineapple, wheat straw). They have evidenced differences in disperse energy values γ_{SV}^{d} ranging from 37 to 51 mJ.m^{-2} at 25 °C. These differences could be attributed to changes in the fibre chemical composition (Mills et al. 2008; Cordeiro et al. 2011a, b). More precisely, the increase in γ_{SV}^{d} could be related to an increase in lignin and a decrease in cellulose contents. Other authors (Belgacem et al. 1995; Papirer et al. 2000) have reported that these differences could be due to variations in other parameters such as cellulose crystallinity, arrangement and orientation of chemical groups at the fibre surface. The use of IGC at finite concentration conditions of probe gas gives also access to information on the surface heterogeneity of fibres (Cordeiro et al. 2012).

Nonetheless, IGC data should be interpreted with caution. It has been reported that care must be taken when interpreting the data, in particular the acid-base constants, which strongly depend on the employed type of physical probes and calculation approach (Gamelas 2013). It has also been stressed that only the highest-energy sites of the surface are measured. Thus, IGC results should be corroborated by the concomitant use of surface sensitive methods such as X-ray photoelectron spectroscopy (XPS), Time-of-flight secondary ion mass spectrometry (ToF-SIMS).

4.1.3 Concluding Remarks: Adhesion and Adherence Phenomena

Several studies demonstrated evidence of correlation between wettability analysis and resulting (micro-)mechanical interfacial properties. However, when studying 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. Here, it should be pointed out that most of the studies do not take into account the variation in surface free energy components of polymer matrices when being in the molten or liquid state. The calculation of the work of adhesion is usually conducted with surface free energy of the matrix that was measured in the solid state. This is likely to bias in some extent the calculated work of adhesion, if wide variations of matrix surface energy occur upon liquid/solid transitions.

On the other hand, the adherence characterizes interfacial strength between the fibres and the matrix within the consolidated composite when submitted to mechanical stresses. Hence, 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 intercellular cohesion within elementary and fibre bundles (Acera Fernández et al. 2016, 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.

4.2 Microscopic Analysis

Scanning electron microscopy (SEM) and **Atomic force microscopy (AFM)** are often used to characterize the effect of pre-treatments or fonctionalization treatments of natural fibres on their surface topography. While SEM can only provide a qualitative analysis, AFM provides detailed information on the topographical characteristics of the fibres, in particular their roughness which can be greatly influenced by treatments. These data are of primary importance when considering the interfacial adhesion with polymer matrices and the contribution of the mechanical interlocking.

Microscopic analysis nevertheless requires several precautions in the preparation of the samples. Indeed, most of lignocellulosic substrates are highly sensitive to electron beam which usually involves the use of gold or carbon sputter coating to enhance surface conductivity. This allows better imaging while protecting fibres surfaces from local degradation and related misleading interpretations on the surface topography. Environmental scanning electron microscopy (ESEM) can be used to limit desiccation of natural fibres that can also lead to local variations in their surface topography. Another well known critical issue when performing SEM or AFM experiments is the choice of areas of interest and their representativeness as regard to the overall morphological characterictics of fibre substrates. For this reason, interpretations on the effect of a specific treatment on fibre surfaces should always be taken with caution unless a systematic and statistical analysis has been conducted. Carefull observations combining both SEM and AFM imaging at different length scales appear as a recommended practice. However, it is worth mentioning that there is yet no standart methodology proposed in literature to conduct a reliable and accurate image analysing on topographical variations of natural fibres surface.

As reviewed by John and Anandjiwala (2008), many studies reported the effect of chemical pre-treatments (e.g. NaOH or acidic aqueous solutions) on the surface topography of natural fibres as observed by SEM for coir fibres (Calado et al. 2000), hemp fibres (Aziz and Ansell 2004), kenaf fibres (Edeerozey et al. 2007), jute fibres (Doan et al. 2012), flax fibres (Le Moigne et al. 2014), jute yarns (Ray et al. 2006). Most of the time, a removal of the non-cellulosic components from the cuticle and middle lamellae, i.e. waxes, fats, pectins and lignin, is reported. This can be accompagnied by the exposure of the secondary cell walls and a flakey or grooved surface with an apparent increase of the surface roughness. In contrast, Le Moigne et al. (2014) and Doan et al. (2012) reported that the functionalization of natural fibres with organo-silanes (GPS: γ-glycidylpropyl trimethoxy silane and APS: γ-aminopropyl triethoxy silane, respectively) has a tendency to smoothen the fibres surface due to the formation of a polysiloxane film that partially fill in the pores, interstices and grooves. As observed by Doan et al. (2012), the presence of surfactants in the functionalizing solution can homogeneize the thickness of the sizing film over the fibre surface.

In combination with SEM observations, AFM is a usefull technique to quantify the evolution of the fibre surface roughness consecutive to treatments. Besides, it is a non-destructive method that provides high resolution 3D images at small length scale, i.e. sub-micron level (George et al. 2001). Lee et al. (2010) studied the topography of bacterial retted kenaf fibres by AFM at two scan scales (2.5 and 1 μm^2 scan). The authors found variations in the surface roughness of the studied fibre bundles according to their location within the stem, possibly related to variations in biochemical composition along the stem and resulting decohesion and fracture mechanisms during fibre extraction. Kafi et al. (2011) analysed the fibre roughness of untreated and plasma treated jute fibres in different atmospheres. Even if variations were observed according to treatment conditions, the authors assumed that the large statistical deviation related to inhomogeneous nature of jute fibres does not allow to conclude on topographical modifications related to plasma treatment. In contrast, irradiation treatments at increasing doses on henequen fibres showed much more pronounced variations in surface topography (Han and Choi 2010). Low irradiation doses (>30 kGy) led to the removal of surface impurities from the middle lamella and the primary wall and revealed the S2 wall fibrillar structure resulting in higher surface roughness (from 58.6 to 268 nm). At high irradiation doses (200–500 kGy), striations and cracks as well as the appearance of large pores resulted in a decreased roughness. Doan et al. (2012) observed large topographical variations after chemical treatment of jute fibres by NaOH. Long overlapping super-structures (Fig. 4.3, top) were broken into 100 nm globular sub-structures with small pores (Fig. 4.3, middle). NaOH/silane (APS) treated surfaces were smoother (Fig. 4.3, bottom) due to the filling of pores and interstices by the sizing.

Studying the effect of chemical and enzymatic treatments on hemp fibres, Pietak et al. (2007) showed that under atmospheric conditions the adhesion force between the AFM tip and the fibre surface can be correlated with the water contact angle and the surface wettability of the fibre. As an exemple, the adhesion force on steam/alkaline and enzyme-treated fibres was dramatically increased. This was explained by the more hydrophilic character of these fibres (i.e. more polar with higher surface free energy and lower water contact angle) due to the increased cellulose content at their surface. In contrast, acetylation of hemp fibres resulted in decreased adhesion force due to their increased hydrophobicity (i.e. less polar, lower surface free energy and higher water contact angle). This approach is interesting since it can relate surface wettability measurements to local surface microstructures of natural fibres which are oftently morphologically and chemically heterogeneous.

Continuous progress on AFM apparatus offer the possibility to perform fast surface scanning at high resolution. Chemical modifications of the tip could also allow to cartography the distribution of functionalization treatments over the fibre surface through specific physico-chemical interactions between the modified tip and the functionalizing molecules. Finally, quantitative mechanical measurements can also be carried out, and could possibly highlight variations in surface viscoelastic behaviour consecutive to treatments, especially in the case of thick sizing layer.

4.3 Elementary Analysis

4.3.1 Elemental Analysis (EA)

Elemental analysis can be used to determine the percentage of the most prevalent elements of a functionalizing treament, like carbon, hydrogen, sulfur, oxygen, nitrogen, phosphorus, silicon or fluorine. To characterize the rate of these elements, procedures based on combustion analyses (CHNS elemental analyses) or Inductively Coupled Plasma Atoms Emission Spectroscopy (ICP AES) can be used. CHNS method consists in combusting a sample in an excess of oxygen at high temperature and to separate and to analyze the combustion products. Their mass percentages can be used to calculate the composition of the sample. The same

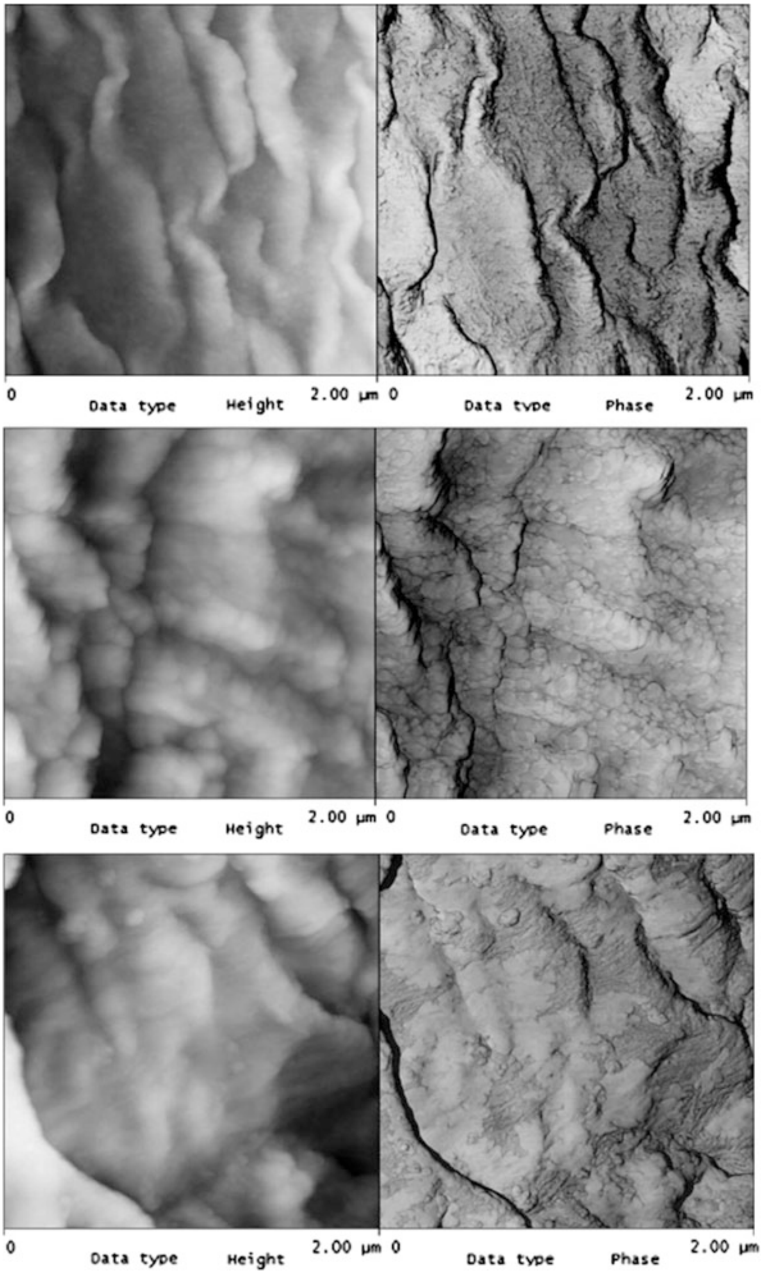

Fig. 4.3 AFM topography (left) and phase images (right) of (top) untreated jute, (middle) NaOH and (bottom) NaOH/(APS + epoxy dispersion) treated jute surfaces. Reproduced from Doan et al. 2012, Fig. 2 with permission from Elsevier

method in pyrolysis conditions can be used for oxygen rate determination. For phosphorus, silicon and fluorine, ICP AES is used which require a mineralization step before the analysis. It is worth mentioning that these technics are destructive since the samples should be milled prior to experiments.

The evolution of the concentration of the different elements present in the untreated fibres or the appearance of new elements can be related to a chemical modification due to a pretreatment or a grafting procedure. Indeed, George et al. (2015) used CHNS elemental analyses to characterize the treatment of hemp fibres by different sulfonic acid derivatives. They showed an evolution of the concentration of these elements after treatment which was related to the nature of the acid used. Dong et al. (2016) used the CHNS elemental analysis to evaluate the laccase-mediated grafting of octadecylamine on lignin moieties of jute. They showed an increase of the nitrogen concentration after grafting of the octadecylamine. Goel et al. (2011) used the same method to quantify the grafting of quaternary ammonium salt containing polymers on cotton fibres.

Dorez et al. (2014a) and Sonnier et al. (2015) analysed the phosphorus concentration investigated by ICP AES to validate their grafting procedures and calculate the grafting rate of phosphorus compounds onto flax fibres.

4.3.2 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS can be a very informative method to characterize the surface modification of natural fibres. This technique allows the chemical analysis of the uppermost 2 nm of the sample surface. The analysis is based in a first step on the sputtering of the sample using a focused primary ion beam. In a second step the ejected secondary ions are collected and analyzed with a mass spectrometer to determine the surface chemistry of the sample. This technique is generally considered to be a qualitative technique but the use of standard samples can allow also a quantitative analysis. The characterization by ToF-SIMS of natural fibres surface modification basically consists in detecting changes in the raw and treated fibres spectra. This technique is very sensitive to alterations and heterogeneity in chemical structure.

Baiardo et al. (2002) described the use of ToF-SIMS to characterize the esterification and etherification of flax fibres. Indeed, they observed for modified fibres the presence on the negative and positive spectra of typical ions obtained by fragmentation of the grafted groups. Grafting flax fibres by acetate, butyrate and valerate groups involve the appearance of $C_2H_3O_2^-$ (m/z 59), $C_4H_7O_2^-$ (m/z 87) and $C_5H_9O_2^-$ (m/z 101) peaks, respectively, on the ToF-SIMS spectra. Zafeiropoulos et al. (2003) also proved the acetylation and stearic treatment of flax fibres by ToF-SIMS analyses. Furthermore, they showed for acetylation that the fibre surface is heterogeneously grafted with rich and poor-acetyl groups areas.

Yang et al. (2009) characterized the efficiency of functionalization of cotton fabrics by polystyrene-co-butylacrylate-co-*N*-hydroxymethyl acrylamide-co-hydroxyethyl methacrylate-co-vinylbenzyltrimethylammonium chloride copolymer nanoparticles with Tof-SIMS analyses. The authors showed the presence on the spectra of peaks corresponding to each different monomer units of the copolymer. $C_2H_5O^+$ (m/z 45), $C_4H_9^+$ (m/z 57) and $C_7H_7^+$ (m/z 91) were attributed respectively to hydroxylethyl methacrylate, butyl acrylate and styrene domains. $C{=}ON^+$ (m/z 42) peak was related to the presence of *N*-hydroxymethyl acrylamide and vinylbenzyltrimethylammonium chloride units.

Moreover, Mou et al. (2016) recently reviewed the application of ToF-SIMS analyzes for the characterization of surface chemistry of lignocellulosic biomass. In this review, studies concerning various chemical modifications of natural fibres are described.

4.3.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a non-destructive method which allows the study of the chemical structure of solids surface. In the course of an XPS experiment, the sample is placed in an ultrahigh-vacuum chamber and irradiated with X-rays. The absorption of the X-rays by atoms constituting the sample leads to the ejection of core and valence electrons. These electrons named photoelectrons have energies that are characteristic of each element and sensitive to their chemical state. The amount of electrons released from the sample surface without energy loss is measured. The intensities of these electrons are proportional to the concentration of the atoms from which they are ejected. The data are represented as intensity versus electron energy graphics. However, it should be noted that X-rays penetrate the sample surface up to several micrometers, but only a small part of the electrons have sufficient energy to escape into the vacuum system. These electrons which can be analyzed are generally ejected from elements located close to the surface (0–10 nm).

XPS was used to characterize the chemical modification of various natural fibres: flax (Acero et al. 2014; Kodal et al. 2015; Rasch et al. 2014; Zafeiropoulos et al. 2003), jute (Dong et al. 2016; Plackett et al. 2005), Spanish broom (Totolin et al. 2008), miscanthus (Ragoubi et al. 2012), coconut (Acero et al. 2014), ramie (Zhou et al. 2014) and hemp (George et al. 2015; Truss et al. 2016). Generally, spectra of treated fibres were compared to those of untreated fibres to evaluate the difference of chemical composition. Indeed, the chemical modification (pretreatment or functionalization) can change the configurations or concentration of basic elements (C, O, H) found in natural fibres or introduce new elements at fibres surface.

Different pretreatments were characterized by XPS analyses based on the identification of changes in C/O/N ratios: water washing (Truss et al. 2016), alkaline (Rasch et al. 2014; Kodal et al. 2015; Truss et al. 2016), retting (Zafeiropoulos et al. 2003), corona discharge (Ragoubi et al. 2012), irradiation (Han et al. 2006).

Functionalization procedures were also characterized by XPS: chemical esterification (Zafeiropoulos et al. 2003; Rasch et al. 2014; George et al. 2015), silanization (Kodal et al. 2015), polymer grafting-from (Plackett et al. 2005), cold plasma (Totolin et al. 2008; Ragoubi et al. 2012) and enzymatic procedures (Acero et al. 2014; Dong et al. 2016).

4.3.4 Energy-Dispersive X-Ray Spectroscopy (EDX)

Chemical composition of natural fibres surface can be determined by energy dispersive analysis of X-rays (EDX). Usually, the EDX analyzer is coupled with SEM. A beam of accelerated electrons is focused on the surface to analyze, producing characteristic X-rays within a small volume (typically 1 to 9 μm^3) of the specimen. So the thickness of the surface layer investigated by EDX is significantly higher than XPS (5–10 nm thin surface layer). The emitted X-rays are characteristics of the elements present in the material and their energies and intensities allow determining the nature and relative concentration of these elements.

EDX was used to characterize the pretreatment or the functionalization of several natural fibres: cotton (Chen and Chiang 2008; Csiszár and Fekete 2011; El-Nahhal et al. 2012; Monier et al. 2014; Mucalo et al. 1995; Selvam and Sundrarajan 2012), flax (Csiszár and Fekete 2011; Dorez et al. 2014b; Paladini et al. 2015; Sonnier et al. 2015), hemp (Truss et al. 2016), miscanthus (Gea Rodi et al. 2016), kenaf (Xu et al. 2009), wheat (Jiang et al. 2009) or rice straw (Yu et al. 2009). Generally, this method is used to determine the evolution in chemical composition of natural fibres before and after a defined treatment. A variation in concentration of original elements can be observed or new elements can be detected after the treatments. So, this method allows evaluating the efficiency of pretreatment or functionalization procedures by determining the evolution in chemical composition of natural fibres.

EDX was also used to validate a multistep functionalization procedure. Indeed, El-Nahhal et al. (2012) used EDX analyses to prove the coating of cotton fibres by CuO and then its modification to obtain CuS. Selvam and Sundrarajan (2012) used this analysis to characterize the functionalization of cotton fibres by poly-*N*-vinyl-2-pyrrolidone in a first step and the introduction of ZnO nanoparticles in a second step. Using EDX, Monier et al. (2014) proved the modification of cotton fibres by polyacrylonitrile and then the insertion of phenyl thiosemicarbazide moieties to finally produce chelating fibres.

EDX analyses can also be used to evidence regioselective distribution of chemical treatments, based on differences of elementals concentration between surface and bulk of fibres. Indeed, Jiang et al. (2009) show a difference of efficiency for lipase treatment of wheat straw between inner and outer surface. They showed that contrary to the inner surface, silica of the wheat straw outer surface was considerably removed during the lipase treatment.

Some authors used EDX to carry out elemental imaging on fibres and characterize the localization of the functionalizing molecules within the fibre. Indeed, Dorez et al.

(2014b) and Sonnier et al. (2015) cartographied the phosphorus element to prove the efficiency of grafting of phosphonated agents within flax fibres. Moreover, the authors used this method to determine the specific localization of the functionalizing agent over the fibre cross-section. As shown in Fig. 4.4, dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) was able to penetrate in the bulk of the fibres, whereas dimethylvinyl phosphonate (MVP) stayed located at the fibres surface.

4.3.5 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a common technique used for the study of crystalline structures and atomic spacing. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. The characteristic diffractogram obtained in a classic analysis provides a fingerprint for the crystal structure presents in the sample. The comparison of this fingerprint with standard reference patterns and measurements allows identification of the crystalline form. So the technique allows the identification of crystalline material, the distinction between amorphous and crystalline material and the quantification of the percent of crystallinity for a partially crystalline sample.

XRD is frequently used to evaluate the crystalline index of natural fibres because of its availability and ease of use. This technique allows the characterization of chemical modifications of the natural fibres by proving the evolution of crystallinity. Indeed usually in the literature authors show with XRD the modification of natural fibres by the characterization of an evolution of the crystallinity degree. This parameter is evaluated as the ratio between the area under the crystalline peaks and that under the amorphous halo, appearing as a broad hump in the XRD pattern. Indeed, chemical treatment procedures applied to natural fibres can involve an evolution in the degree of crystallinity of cellulose.

Several fibres were characterized after chemical modification by XRD: flax (Kodal et al. 2015; Le Moigne et al. 2014; Marques et al. 2015; Moawia et al. 2016; Ouajai et al. 2004), hemp (Aruan Efendy and Pickering 2014; Ouajai et al. 2004), sisal (Bharti et al. 2013), jute (Moawia et al. 2016), coconut (Thakur et al. 2015; Thakur et al. 2016), spanish broom (Totolin et al. 2008), cannabis indica (Singha 2011), harakeke (Aruan Efendy and Pickering 2014), curauá (Marques et al. 2015) or abaca (Cai et al. 2015).

XRD was often used to characterize the effect of alkali treatments on natural fibres. For low NaOH concentrations, an increase of the crystallinity degree has been reported (Aruan Efendy and Pickering 2014; Bharti et al. 2013; Cai et al. 2015; Marques et al. 2015; Ouajai et al. 2004). This was attributed to the removal of amorphous materials (e.g. lignin, hemicellulose and wax) from the fibre. Increase of fibre crystallinity with alkali treatment has also been suggested to occur due to better packing and stress relaxation of cellulose chains. However, a decrease of the crystallinity can be also observed for high alkali concentration (Kodal et al. 2015; Ouajai et al. 2004).

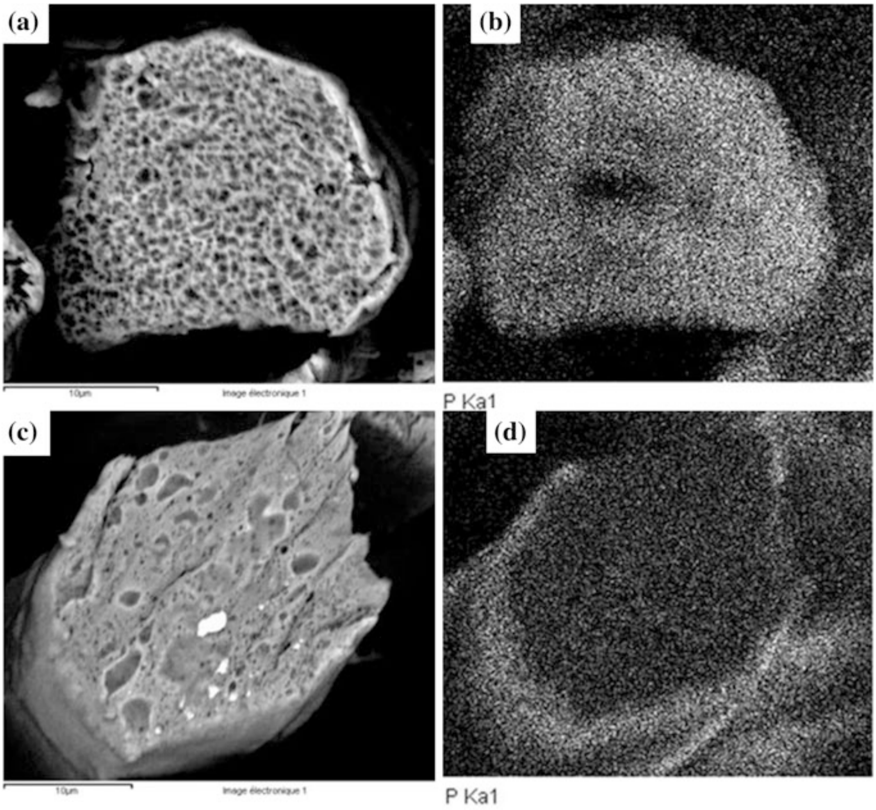

Fig. 4.4 SEM observations of flax fibres grafted by **a** dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) and **c** dimethylvinyl phosphonate (MVP). Phosphorus imaging using EDX analysis of flax fibres grafted by **b** MAPC1 and **d** MVP. Reproduced from Sonnier et al. (2015) with permission from Elsevier

Furthermore, alkali treatments at high concentrations can lead to allomorphic changes in the crystalline structure of natural fibres, i.e. conversion of cellulose I in cellulose II (Cai et al. 2015; Kodal et al. 2015).

XRD was also used to characterize the grafting of organic molecules (Kodal et al. 2015; Thakur et al. 2015, 2016; Totolin et al. 2008) and macromolecules (Bharti et al. 2013; Moawia et al. 2016; Ouajai et al. 2004; Singha 2011) onto natural fibres. The grafting is generally associated to a decrease of the crystallinity index which could be explained on the basis that grafting causes disturbance in the crystalline regions of the fibre leading to the creation of amorphous regions. Thus, as the degree of grafting increases, the amorphous regions become more and more predominant.

4.3.6 Solid State Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance in the solid state (solid state NMR) is a powerful technique to characterize the modification of natural fibres. Indeed, this method which allows obtaining information about the detailed chemical structure of molecules and macromolecules and their quantification, can be used to prove the chemical modification of natural fibres. The modifications of several natural fibres were studied by this method: flax (Dorez et al. 2014b), cotton (Mucalo et al. 1995; Yang et al. 2012), ramie (Yamanaka et al. 2005, 2006), hemp (Branda et al. 2016), jute (Manna et al. 2013; Roy et al. 2013), sisal (Martins et al. 2006), palm tree (Rout et al. 2016), pineapple (Shih et al. 2014), bamboo (Kim et al. 2016) and alfa stem (Borchani et al. 2015).

The modification of the fibres chemical composition due to chemical treatment can be easily studied by ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR study. Indeed, several authors proved the partial or total removal of lignin or hemicellulose due to alkali treatments by the evolution of signals characteristic of aromatic carbons of lignin or carboxyl groups of hemicellulose (Borchani et al. 2015; Manna et al. 2013; Martins et al. 2006; Rout et al. 2016; Roy et al. 2013). Kim et al. (2016) also studied the evolution of these signals by ^{13}C NMR for bamboo fibres after exposition to natural ageing during one year.

^{13}C NMR can also shows the appearance of new signals attributed to the introduction of new chemical groups after modification of natural fibres. Indeed Roy et al. (2013) proved the modification of jute fibres by polyphenolic tannin with the appearance of signals of aromatic carbons characteristic of the functionalizing agent. Manna et al. (2013) proved by ^{13}C NMR the grafting of fatty acids onto jute fibres using a bio-catalyzed esterification. After treatment, they were able to show the appearance of signals of the carbons associated to fatty acid chains and ester functions.

The evolution of the crystallinity and microfibillar angle of natural fibres with the chemical modification can also be studied using ^{13}C CP-MAS NMR and XRD. Yamanaka et al. studied these structural evolutions after modification of ramie fibres by formaldehyde (Yamanaka et al. 2005) and gamma γ-irradiation (Yamanaka et al. 2006).

Solid-state NMR analyses are most often based on ^{13}C nuclei but other nuclei can be used like: ^{1}H (Yang et al. 2012), ^{29}Si (Branda et al. 2016; Shih et al. 2014) or ^{31}P (Dorez et al. 2014b; Mucalo et al. 1995).

4.4 Infrared and Raman Spectroscopy Analysis

Infrared (IR) spectroscopy and Raman spectroscopy are among the most widely used techniques for the determination of molecular structure. These methods exploit changes in vibrational energy state of molecules when subjected to excitation radiation in selected regions. IR and Raman spectroscopies differ in the means by which photon energy is transferred to molecules but they are complementary more than competing techniques. The molecular vibrational frequencies are nearly the same, only the vibrational band intensities differ.

In *IR spectroscopy*, the vibrational excitation is achieved by radiating the sample with a broad-band source radiation in the infrared region. The molecule is excited at a higher vibrational state by directly absorbing the infrared radiation.

The origin of *Raman spectroscopy* is an elastic and inelastic scattering effect. The excitation radiation source is monochromatic and is much more energetic than infrared radiation. In elastic scattering (Rayleigh scattering), the molecule is excited in a virtual state, and then relaxes to the original vibrational state by re-emitting a photon at the same frequency as the incident radiation light. In this case, the molecule absorbs no energy from the incident radiation. In inelastic scattering (Raman scattering), the excited molecule relaxes at a different vibrational level. When the final vibrational state is lower in energy than the original one, Raman bands are called anti-Stockes lines. When it is higher, they are called Stockes lines.

For both spectroscopies, a plot of absorbance versus wavenumber is obtained. The wavenumber, ν in cm^{-1}, is the number of waves per cm. It is equal to the reciprocal of the wavelength λ in µm, and to the frequency ν divided by the light velocity.

Numerous papers considered IR and Raman spectroscopy as relevant techniques to determine (i) the primary plant cell wall composition (as hemicelluloses, cellulose, galacturonic acid) (Abidi et al. 2014; Himmelsbach and Akin 1998; Szymanska-Chargot et al. 2015) and interactions between components (Stevanic and Salmén 2008), (ii) but also the water sorption in natural fibres (Celino et al. 2014), (iii) or the grafting efficiency of molecules onto the natural fibre surface (Mosiewicki et al. 2011). This section is focused on the last aspect, i.e. the influence of natural fibres surface modifications (pre-treatments and functionalization treatments) on IR and Raman absorption spectrum.

Effect of natural fibres pre-treatments. As *retting pre-treatments* act by degrading non-cellulosic components of natural fibres, the main change in IR spectra described in literature (Li and Pickering 2008; Zhang et al. 2008) is an intensity reduction versus the retting time for peaks located at 1736 and 1268 cm^{-1}, assigned to C=O stretching of carboxylic ester in pectin and waxes and to COO stretching in lignin respectively, whatever the retting techniques used.

Dehydration, dihydroxylation and decarboxylation reactions are the most common reactions occurring during a *thermal pre-treatment* such as torrefaction that involves a heating of biomass in an inert environment at temperatures between 180 and 280 °C. For Mei et al. (2016) dihydroxylation reaction of hemicellulose from corn stalk induced a decrease of the peak intensity of O-H groups (3400–3200 cm^{-1}) with the increase in torrefaction temperature. On the opposite the C-H breakages yielding CH_4, C_2H_4 and C_2H_6 in gaseous products did not induce noticeable changes on IR spectra. The main modification concerns C-O-C (1160 cm^{-1}) and C=O (1735 cm^{-1}) peaks representing the generation of CO and CO_2 and of ketones and aldehydes respectively.

The major changes in IR spectra of natural fibres owing to an *alkaline pre-treatment (mercerization)* of natural fibres were addressed by several authors, among them Elenga et al. (2013), Gwon et al. (2010), Kabir et al. (2013) and Krishnaiah et al. (2017). Cellulose related functional groups with characteristic peaks at 900 and 1430 cm^{-1} (designated as C-H bending of amorphous and crystalline cellulose) and at 1373 cm^{-1} (assigned to C-OH stretching of crystalline cellulose) remain unchanged for alkalized fibres. The main effect is the reduction of the peak located at 1730–1740 cm^{-1} attributed to C=O stretching as a consequence of the extraction of hemicellulose and lignin and/or the formation of ionic carboxylates in the incompletely extracted samples, in which the corresponding peak appears at lower frequencies (1590 cm^{-1}). Hemicellulose degradation can be also revealed by the shift of C-H bending and C-O stretching peaks of hemicellulose to higher wavelengths (1348–1354 cm^{-1}). The increase by 12 cm^{-1} of aromatic C-H in plane deformation and C-O stretching in primary alcohol (guaiacyl) of lignin (located at 1024 cm^{-1}) indicates also that lignin is removed because of the alkaline treatment. Raman spectroscopy can be also very attractive as water does not interfere with the sample signal contrary to IR spectroscopy. Polymorphic transformation of cellulose I into cellulose II as a function of alkali concentration can be detected by analysing the Raman spectra below 1500 cm^{-1} (Dinan et al. 2002; Jahn et al. 2002).

A complete study was carried out by De Rosa et al. (2011) on *bleaching pre-treatments* of okra (*Abelmoschus esculentus*) fibres in presence of sodium chloride. Limited differences with the raw fibres were shown. The main spectra changes are an increase in the 898 cm^{-1} band attributed to the symmetric in-phase ring-stretching mode, a decrease of the 1430 cm^{-1} band attributed to CH_2 bending and a disappearance of the carbonyl peak due to the removal of a substantial portion of uric acid. Bleached then acetylated fibres are similar to the barely bleached fibres except the presence of an additional vibration peak near 1235 cm^{-1} due to C-O stretching of acetyl groups. The analysis of bleached then alkalinized fibres gave clear evidence of the removal of hemicellulose and lignin with the disappearance of both C=O and C-O stretching bands of acetyl groups (1730 cm^{-1} and 1240 cm^{-1}, respectively). The effect of potassium permanganate solutions is considered as similar to bleaching. Nevertheless, IR studies (De Rosa et al. 2011) showed that it led to a more extensive delignification. As a result, the band located at 1050 cm^{-1} assigned to O-H bending vibration of cellulose increases whereas the absorption in the range of 1450–1600 cm^{-1} related to skeleton vibrations of the aromatic ring decreases. The decrease in the splitting of CH bonds of methyl and methylene groups (stretching vibrations in the range 2850–2920 cm^{-1}) also suggests removal of lignin-like structures.

Changes in IR spectra due to *physical pre-treatments* such as plasma treatment are also noticeable, especially in the range 800–1100 cm^{-1} as shown by Bonazi et al. (2013), Scalici et al. (2016) and Sinha (2009). A change from shoulder to peak is particularly observed near 1100 cm^{-1} (C-O-C symmetric glycosidic stretching or ring-stretching mode) as well as a new peak at 1060–1050 cm^{-1} (C-OH secondary alcohol stretching vibration of the cellulose backbone) and is assigned to a modification in the polysaccharide structure, primarily cellulose. An increase in the intensity of the peak located at 896 cm^{-1} attributed to β-glycosidic linkages between monosaccharides (sugar units of hemicelluloses) was also observed and may be due to cleaning effect of plasma treatment on the fibre surface. Finally, Morshed et al. (2010) reported that C-O-C asymmetric stretching vibration of cellulose and hemicelluloses observed at 1235 cm^{-1} is more prominent after air plasma compared to argon plasma due to cellulose oxidation.

No impact on IR spectra was obtained for other physical treatments such as *ultrasound treatment*. Nevertheless the combination of alkali and ultrasound treatments successfully confirm the removal of hemicellulose, lignin and pectin (disappearance of the peak corresponding to the C-O stretching of acetyl groups of lignin at 1261 cm^{-1}, shift to higher wavelengths of the peak assigned to C-O stretching of lignin at 1053 cm^{-1}) (Krishnaiah et al. 2017).

Effect of functionalization treatments. The efficiency of *acetylation* that is considered as a rather attractive method regarding its effect on natural fibre hydrophobic character was also revealed by IR experiments (Adebajo et al. 2006; Bertoti et al. 2009; Datta and Kopczynska 2015; De Rosa et al. 2011; Khalil et al. 2001; Zafeiropoulos et al. 2003). Acetic anhydride is commonly used for acetylation reaction with cellulose to form cellulose acetate. The reaction between hydroxyl groups at the fibre surface and acidic groups results in ester bond formation (C=O stretching at 1725 cm^{-1} and C-O stretching in the range 1225–1235 cm^{-1}). If acetyl groups are in free form (beared by acetic acid) then the C=O stretching should be at a position below 1725 cm^{-1}. Furthermore, if acetyl groups are beared by acetic anhydride two peaks should appear for C=O stretching, one at around 1780–1830 cm^{-1} and another at around 1780–1800 cm^{-1} attesting for the presence of two ketonic carbons. Moreover it is interesting to note that Zafeiropoulos et al. (2003) compared different spectroscopy methods for analysing the acetylation efficiency performed on flax fibres and concluded to a lower sensitivity of the IR method compared to XPS and ToF-SIMS methods in this case.

Several authors (Abdelmouleh et al. 2002, 2004, 2007; Asumani et al. 2012; Belgacem and Gandini 2005; Bledzki and Gassan 1999; Kushwaha and Kumar 2010; Le Moigne et al. 2014; Rong et al. 2001; Valadez-Gonzalez et al. 1999; Xie et al. 2010; Yu et al. 2010) used IR spectroscopy to show that hydrolysed *organosilanes*, i.e. silanols Si-OH, can be adsorbed on fibre surface while self-condensing in polysiloxanes, and then can be grafted on it depending on the experimental conditions. The condensation and grafting reaction produces Si-O-C and Si-O-Si bonds (asymmetric stretching in the range 1200–1140 cm^{-1}, symmetric stretching at 1370 and 965 cm^{-1} and 700 and 1040 cm^{-1} respectively). The presence of non-grafted Si-OH groups (large band around 1015 cm^{-1}) and of residual unhydrolyzed Si-OCH_3 groups (peaks in the range 1100–1080 cm^{-1}) means that full hydrolysis, self-condensation and grafting were not achieved. The previously cited authors studied, through IR analysis, the influence of the silane concentration (from 0.45 to 10 wt%), of the soaking time (from 5 min to 24 h), of the bath temperature BT (from 20 to 70 °C), of the curing temperature CT (from 45 to 120 °C) and of an alkaline pre-treatment on the efficient grafting of silanes.

Figure 4.5 is an example of a complete IR study carried on by Le Moigne et al. (2014) in the case of the grafting of a commercially used organosilane (γ-glycidyloxypropyl trimethoxy silane GPS) onto flax fibres. Based on this study, it was shown that optimized soaking and curing conditions can be found to graft organosilanes onto natural fibres.

Many studies were focused on the reaction of cellulose with *isocyanates*. Modifications can be distinctively observed in the IR spectra with the presence of an additional peak at 1705 cm^{-1} corresponding to alkylic urethane stretching vibration, and more precisely to new carbamate linkage. In some studies residual unreacted isocyanate were detected (2270 cm^{-1}) (Girones et al. 2007; Ly et al. 2008).

Concluding, IR and Raman spectroscopies are largely considered as quick and relevant tools for detecting changes in chemical structure at the natural fibre due to surface modifications such as pre-treatments or functionalization treatments. Nevertheless they are less sensitive compared to other spectroscopy methods such as XPS or ToF-SIMS techniques. Besides, IR spectroscopy is more widely used than Raman spectroscopy despite the fact that water does often interfere with the IR signals contrary to Raman signals.

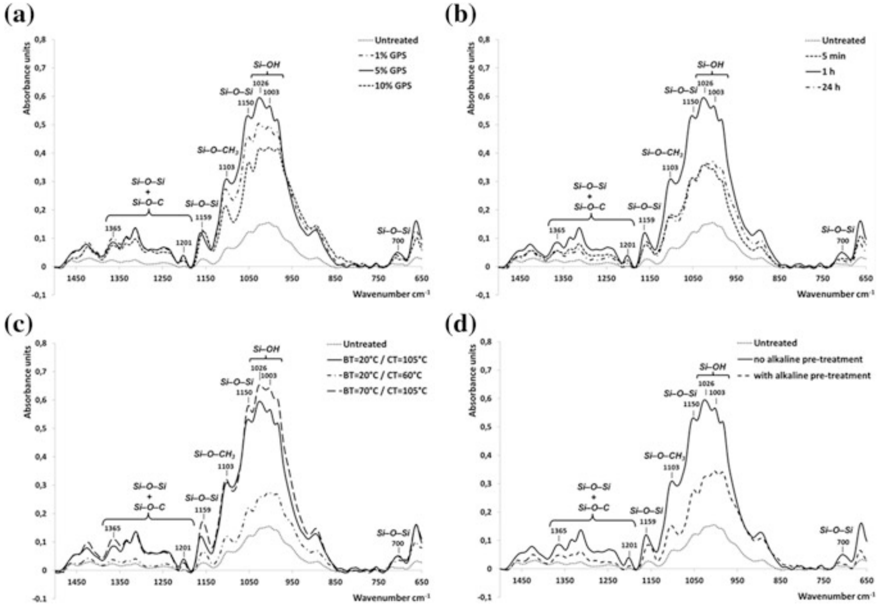

Fig. 4.5 IR spectra of untreated and treated flax fibre bundles. Influence of **a** GPS concentration (soaking time = 1 h; BT = 20 °C; CT = 105 °C; no alkaline pre-treatment), **b** soaking time (5% GPS; BT = 20 °C; CT = 105 °C; no alkaline pre-treatment), **c** bath and curing temperatures (5% GPS; soaking time = 1 h; no alkaline pre-treatment), **d** an alkaline pre-treatment (5% GPS; soaking time = 1 h; BT = 20 °C; CT = 105 °C). Adapted from Le Moigne et al. (2014)

4.5 Thermal Analysis

Thermal analyses were often used to characterize the natural fibres before and after chemical modifications. Because of its accessibility thermogravimetric analysis (TGA) is the most popular method of analysis but some authors also used Pyrolysis coupled with Gas Chromatography and Mass Spectrometry (Py-GC/MS) and Pyrolysis Combustion Flow Calorimetry (PCFC) apparatus to characterize the modification of natural fibres.

4.5.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is commonly used to determine the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an inert or air atmosphere. These mass losses or gains are due to phenomena of decomposition, oxidation, or volatiles molecules desorption. TGA allows quantitative analysis and measurements are used primarily to determine the composition of materials and to study their thermal stability.

The chemical modification of natural fibres involves generally modification of their thermal degradation profile. In the literature TGA was used by authors to characterize a wide range of chemical treatments for various natural fibres (Table 4.1).

The first change which can be observed by authors on TGA thermograms is the evolution of the moisture content which can increase or decrease in function of the modification. The grafting of hydrophilic groups or the removal of hydrophobic products increases the temperature and the weight loss rate due to water release (Goel et al. 2011; Jiang et al. 2009). In contrast, the grafting of hydrophobic groups onto the natural fibre decrease the moisture content and hence the weight loss rate (Totolin et al. 2008). Borchani et al. (2015) suggested that the alkali treatment of alfa stem fibres decreases their moisture content due to an increase of their crystallinity degree.

When the difference in thermal stability of natural fibres and functionalizing agent is large enough, the presence of the grafted molecules can be easily proved by the presence on the TGA thermogram of its characteristic weight loss at defined temperature (Goel et al. 2011; Luna-Straffon et al. 2014; Plackett et al. 2005). Besides, authors describe after the modification of natural fibres an evolution of the thermal stability with an increase or decrease of the degradation temperatures and a change in the residue rate. For functionalization procedures, these evolutions are directly related to the thermal stability of the grafting agent. Indeed, Goel et al. (2011) show for cotton an increase thermal stability when fibres were modified with poly(2-hydroxyethyl methacrylate) chains and a decrease thermal stability with poly([2-(acryloyloxyethyl)]trimethylammonium chloride).

Table 4.1 Natural fibres characterized by TGA after chemical modifications

Fibre	Functionalization treatment
Flax	• Esterification (acetyl, butyryl, or valeryl) and etherification (ethyl or isopropyl) (Baiardo et al. 2002) • Acetylation (Bledzki et al. 2008) • Alkali (Marques et al. 2015) • Grafting of phosphonated polymers and copolymers (Dorez et al. 2014c) • Grafting of octadecylphosphonic acid (Dorez et al. 2014b)
Cotton	• Grafting of epichlorohydrin (Xue et al. 2009) • Grafting of polyacrylamide (Hong et al. 2009) • Grafting of acrylate polymers bearing quaternary salt groups (Goel et al. 2011) • Grafting of cyclodextrin derivatives (Cabrales et al. 2012; Hiriart-Ramírez et al. 2012; Salah et al. 2015) • Grafting of polyacrylate bearing amino groups (Luna-Straffon et al. 2014)
Jute	• Grafting of polystyrene (Plackett et al. 2005) • Alkali (Marques et al. 2015) • Grafting of octadecylamine (Dong et al. 2016)
Hemp	• Sulfonic acid derivatives (George et al. 2015) • Silica coating (Branda et al. 2016)
Coconut	• Grafting of syringaldehyde (Thakur et al. 2015) • Grafting of ferulic acid (Thakur et al. 2016)
Miscanthus	• Grafting of poly(mercaptopropyl)methylsiloxane (Gea Rodi et al. 2016)
Sisal	• Alkali, peroxide and polyacrylates grafting (Bharti et al. 2013)
Spanish broom	• Fatty acids grafting (Totolin et al. 2008)
Cannabis indica	• Grafting of polyacrylic acid (Singha 2011)
Weat straw	• Lipase treatment (Jiang et al. 2009)
Curaua	• Alkali (Marques et al. 2015)
Alfa stem	• Alkali (Borchani et al. 2015)

4.5.2 *Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC/MS)*

Pyrolysis on-line coupled to gas chromatography with mass spectrometric detection (Py-GC/MS) is based on the instantly pyrolysis of the sample until its decomposition and then on the introduction of the formed pyrolyzates into a capillary column for separation and detection using mass spectrometry. The pyrolysis method does not necessary require special preparation of the sample and analysis can be directly conducted on natural fibres.

Generally, this method is used to characterize the modification of the pyrolyzates nature or concentration after fibre treatment. The acid treatment of wheat or rice straw (Reeves and Galletti 1993; Yu et al. 2009) and the alkali treatment of corn fibres (Mészáros et al. 2009) showed modification of the composition of these fibres with removal of some compounds like hemicellulose or lignin and an increase in the cellulose fraction. The same evolution was found by Chang et al. (2012) for bagasse using a torrefaction treatment. The Py-GC/MS analysis clearly shows the evolution of fibres composition after the thermal treatment.

Some authors used also this technic to prove the presence of functionalizing molecules by the appearance of new products after pyrolysis when natural fibres were modified. Indeed, Plackett et al. (2005) grafted polystyrene chains onto jute fibres using Atom Transfer Radical Polymerization (ATRP) and showed by Py-GC-MS analyses the presence of styrene in large quantity for modified fibres. Dorez et al. (2014b) proved the grafting of octadecylphosphonic acid (ODPA) on flax fibres by the presence of a series of peaks that are assigned to the decomposition products of the alkyl chain of the ODPA molecule (Fig. 4.6).

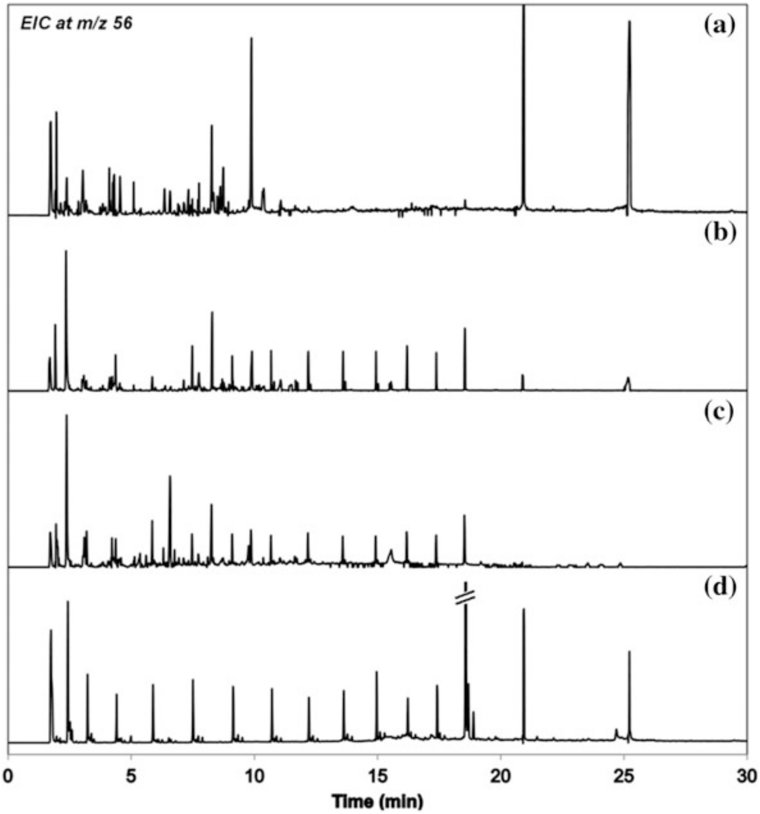

Fig. 4.6 EIC at m/z 56 of pyrograms of **a** flax treated with ethanol, **b** flax grafted by ODPA, **c** flax grafted by ODPA and treated by soxhlet extraction (Tfl/ODPAsox) and **d** ODPA. Reprinted from Dorez et al. (2014b) with permission from Elsevier

4.5.3 Pyrolysis Combustion Flow Calorimetry (PCFC)

Pyrolysis Combustion Flow Calorimetry (PCFC) was developed to allow the investigation of fire behaviour of samples at microscopic scale. PCFC measures the energy released by the combustion of volatile products obtained by the pyrolysis of a sample heated from ambient to high temperature. Sample weights of around 2–5 mg are pyrolyzed at 1 °C.s^{-1} and the degradation products are routed in a combustor at 900 °C where they are completely oxidized. The oxygen consumption is used to measure the value of heat released by combustion of these pyrolysis products. The curve representing the value of heat release rate (HRR) as a function of temperature gives information about flammability of the studied material.

Dorez et al. (2014b) characterized the modification of flax fibres by octadecylphosphonic acid (ODPA) using PCFC. The difference of stability between flax and ODPA allowed proving the grafting of ODPA by the presence of the degradation peak attributed to ODPA. The grafting rate was also calculated using PCFC analysis. The authors found that PCFC was more sensitive to the presence of the surface modifier than TGA. In another study, the same authors proved the grafting of phosphonated copolymers by PCFC (Dorez et al. 2014c). In this work, no new peak was observed due to the grafting molecule but a change of fibre flammability with a decrease of the degradation temperature and total of heat released rate (HRR). Sonnier et al. (2015) showed the same modifications of flammability for flax fabrics after the grafting of phosphonated polymers using an electron beam irradiation procedure.

References

Abdelmouleh M, Boufi S, Belgacem MN, Dufresne A (2007) Short natural fibre reinforced polyethylene and natural rubber composites: effect of silane coupling agents and fibres loading. Comp Sci Techn 64:1627–1639

Abdelmouleh M, Boufi S, MN, Duarte AP, Salah AB, Gandini A (2004) Modification of cellulosic fibres with functionalised silanes: development of surface properties. Int J Adhes Adhes 24:43–54

Abdelmouleh M, Boufi S, Salah AB, Belgacem MN, Gandini A (2002) Interaction of silane coupling agents with cellulose. Langmuir 18:3203–3208

Abidi N, Cabrales L, Haigler CH (2014) Changes in the cell wall and cellulose content of developing cotton fibers investigated by FTIR spectroscopy. Carb Polym 100:9–16

Acera Fernández J, Le Moigne N, Caro-Bretelle AS, El Hage R, Le Duc A, Lozachmeur M, Bono P, Bergeret A (2016) Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites. Ind Crops Prod 85:93–108

Acero E, Kudanga T, Ortner A, Kaluzna I, de Wildeman S, Nyanhongo GS, Guebitz GM (2014) Laccase functionalization of flax and coconut fibers. Polymers 6:1676–1684

Adebajo MO, Frost RL, Kloprogge JT, Kokot S (2006) Raman spectroscopic investigation of acethylation of raw cotton. Spectrochem Acata Part A 64:448–453

Aruan Efendy MG, Pickering KL (2014) Comparison of harakeke with hemp fibre as a potential reinforcement in composites. Compos Part A Appl Sci Manuf 67:259–267

Asumani OML, Reid RG, Paskaramoorthy R (2012) The effects of alkali–silane treatem, t on the tensile and flexural properties of short fibre non–woven kenaf reinforced polypropylene composites. Comp Part A Appl Sci Manufact 43:1431–1440

Aziz SH, Ansell MP (2004) The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites: part 2–cashew nut shell liquid matrix. Compos Sci Technol 64(9):1231–1238

Baiardo M, Frisoni G, Scandola M, Licciardello A (2002) Surface chemical modification of natural cellulose fibers. J Appl Polym Sci 83:38–45

Baley C, Busnel F, Grohens Y, Sire O (2006) Influence of chemical treatments on surface properties and adhesion of flax fibre–polyester resin. Compos Part A Appl Sci Manuf 37:1626–1637

Belgacem MN, Czeremuszkin G, Sapieha S, Gandini A (1995) Surface characterization of cellulose fibres by XPS and inverse gas chromatography. Cellulose 2(3):145–157

Belgacem MN, Gandini A (1999) IGC as a tool to characterize dispersive and acid–base properties of the surface of fibers and powders. In: Pefferkorn E (ed) Interfacial phenomena in chromatography. Marcel Dekker, New York, pp 41–124

Belgacem MN, Gandini A (2005) The surface modification of cellulose fibres for use as reinforcing elements in composite materials. Comp Interfaces 12:41–75

Berthet MA, Angellier-Coussy H, Chea V, Guillard V, Gastaldi E, Gontard N (2015) Sustainable food packaging: valorising wheat straw fibres for tuning PHBV–based composites properties. Compos Part A Appl S 72:139–147

Bertoti AR, Luporini S, Esperidiao MCA (2009) Effects of acethylation in vapor phase and mercerization on the properties of sugarcane fibers. Carb Polym 77:20–24

Bharti B, Kalia S, Kumar S, Kumar A, Mittal H (2013) Surface functionalization of sisal fibers using peroxide treatment followed by grafting of poly(ethyl acrylate) and copolymers. Int J Polym Anal Charact 18:596–607

Blancher G, Morel MH, Gastaldi E, Cuq B (2005) Determination of surface tension properties of wheat endosperms, wheat flours and wheat glutens. Cereal Chem 82(2):158–165

Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci 24:221–274

Bledzki AK, Mamun AA, Lucka-Gabor M, Gutowski VS (2008) The effects of acetylation on properties of flax fibre and its polypropylene composites. Express Polym Lett 2:413–422

Bonazi E, Sever K, Sarikanat M, Seki Y, Demir A, Ozdogan E, Tavman I (2013) Effects of the atmospheric plasma treatments on surface and mechanical properties of flax fiber and adghesion between fiber–matrix for composite materials. Comp Part B 45(1):565–572

Borchani KE, Carrot C, Jaziri M (2015) Untreated and alkali treated fibers from Alfa stem: effect of alkali treatment on structural, morphological and thermal features. Cellulose 22:1577–1589

Branda F, Malucelli G, Durante M, Piccolo A, Mazzei P, Costantini A, Brigida S, Pennetta M, Bifulco A (2016) Silica treatments: a fire retardant strategy for hemp fabric/epoxy composites. Polymers 8(8):313

Cabrales L, Abidi N, Hammond A, Hamood A (2012) Cotton fabric functionalization with cyclodextrins. J Mater Environ Sci 3:561–574

Cai M, Takagi H, Nakagaito AN, Katoh M, Ueki T, Waterhouse GI, Li Y (2015) Influence of alkali treatment on internal microstructure and tensile properties of abaca fibers. Ind Crops Prod 65:27–35

Calado V, Barreto DW, d'Almeida JRM (2000) The effect of a chemical treatment on the structure and morphology of coir fibers. J Mater Sci Mater 19(23):2151–2153

Cantero G, Arbelaiz A, Llano-Ponte R, Mondragon I (2003) Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. Compos Sci Technol 63:1247–1254

Celino A, Gonçalves O, Jacquemein F, Fréour S (2014) Qualitative and quantitative assessment water sorption in natural fibres using ATR–FTIR spectroscopy. Carb Polym 101:163–170

Chang S, Zhao Z, Zheng A, He F, Huang Z, Li H (2012) Characterization of products from torrefaction of sprucewood and bagasse in an auger reactor. Energy Fuels 26:7009–7017

Chen CY, Chiang CL (2008) Preparation of cotton fibers with antibacterial silver nanoparticles. Mater Lett 62:3607–3609

Cordeiro N, Gouveia C, Moraes AGO, Amico SC (2011a) Natural fibers characterization by inverse gas chromatography. Carbohydr Polym 84(1):110–117

Cordeiro N, Gouveia C, John MJ (2011b) Investigation of surface properties of physico–chemically modified natural fibres using inverse gas chromatography. Ind Crops Prod 33:108–115

Cordeiro N, Ornelas M, Ashori A, Sheshmani S, Norouzi H (2012) Investigation on the surface properties of chemically modified natural fibers using inverse gas chromatography. Carbohydr Polym 87:2367–2375

Coupas AC, Gauthier H, Gauthier R (1998) Inverse gas chromatography as a tool to characterize lignocellulosic fibers modified for composite applications. Polym Compos 19:280–286

Csiszár E, Fekete E (2011) Microstructure and surface properties of fibrous and ground cellulosic substrates. Langmuir 27:8444–8450

Datta J, Kopczynska P (2015) Effect of kenaf fibre modification on morphology and mechanical properties of thermoplastic polyurethane materials. Ind Crops Prod 74:566–576

de Meijer M, Haemers S, Cobben W, Militz H (2000) Surface energy determinations of wood: comparison of methods and wood species. Langmuir 16:9352–9359

Della Volpe C, Siboni S (1997) Some reflections on acid–base solid surface free energy theories. J Colloid Interf Sci 195(1):121–136

De Rosa IM, Kenny JM, Mohd M, Manirussaman M, Monti M, Puglia D, Santulli C, Sarasini F (2011) Effect of chemical treatments on the mechanical and thermal behaviour of okra (Abelmoschus esculentus) fibres. Comp Sci Technol 71:246–254

Dinan E, Vignon M, Chanzy H, Heux L (2002) Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose 2. Cellulose 9:7–18

Doan TTL, Brodowsky H, Mäder E (2012) Jute fibre/epoxy composites: surface properties and interfacial adhesion. Compos Sci Technol 72(10):1160–1166

Dong A, Wu H, Fan X, Wang Q, Yu Y, Cavaco-Paulo A (2016) Enzymatic hydrophobization of jute fabrics and its effect on the mechanical and interfacial properties of jute/PP composites. Express Polym Lett 10:420–429

Dorez G, Taguet A, Ferry L, Lopez-Cuesta JM (2014a) Phosphorous compounds as flame retardants for polybutylene succinate/flax biocomposite: Additive versus reactive route. Polym Degrad Stab 102:152–159

Dorez G, Otazaghine B, Taguet A, Ferry L, Lopez-Cuesta JM (2014b) Use of Py–GC/MS and PCFC to characterize the surface modification of flax fibres. J Anal Appl Pyrolysis 105:122–130

Dorez G, Otazaghine B, Taguet A, Ferry L, Lopez-Cuesta JM (2014c) Improvement of the fire behavior of poly(1,4–butanediol succinate)/flax biocomposites by fiber surface modification with phosphorus compounds: molecular versus macromolecular strategy. Polym Int 63:1665–1673

Edeerozey AM, Akil HM, Azhar AB, Ariffin MZ (2007) Chemical modification of kenaf fibers. Mater Lett 61(10):2023–2025

Elenga RG, Djemia P, Tingaud D, Chauveau T, Maniongui JG, Dirras G (2013) Effects of alkali treatment on the microstructure, composition and properties of the Raffia textilis fiber. Bioressources 8(2):2934–2949

El-Nahhal IM, Zourab SM, Kodeh FS, Selmane M, Genois I, Babonneau F (2012) Nanostructured copper oxide–cotton fibers: synthesis, characterization, and applications. Int Nano Lett 2(1):14

Fowkes FM (1964) Attractive forces at interfaces. Ind Eng Chem 56(12):40–52

Fuentes CA, Brughmans G, Tran LQN, Dupont-Gillain C, Verpoest I, Van Vuure AW (2015) Mechanical behaviour and practical adhesion at a bamboo composite interface: physical adhesion and mechanical interlocking. Compos Sci Technol 109:40–47

Gamelas JAF (2013) The surface properties of cellulose and lignocellulosic materials assessed by Inverse Gas Chromatography: a review. Cellulose 20:2675–2693

Gea Rodi E, Mangeon C, Dessauw E, Sansalone V, Lemaire T, Renard E, Langlois V (2016) Functionalization of miscanthus by photoactivated thiolene addition to improve interfacial adhesion with polycaprolactone. ACS Sustain Chem Eng 4:5475–5482

George J, Sreekala MS, Thomas S (2001) A review on interface modification and characterization of natural fiber reinforced plastic composites. Polym Eng Sci 41(9):1471–1485

George M, Mussone PG, Bressler DC (2015) Modification of the cellulosic component of hemp fibers using sulfonic acid derivatives: surface and thermal characterization. Carbohydr Polym 134:230–239

Girones J, Pimenta MTB, Vilaseca F, de Carvalho AFJ, Mutje P, Curvelo AAS (2007) Blocked isocyanates as coupling agents for cellulose base composites. Carbohyd Polym 68:537–543

Goel NK, Kumar V, Rao MS, Bhardwaj YK, Sabharwal S (2011) Functionalization of cotton fabrics by radiation induced grafting of quaternary salt to impart antibacterial property. Radiat Phys Chem 80:1233–1241

Good RJ, van Oss CJ (1992) The modern theory of contact angles and the hydrogen bond components of surface energies. In: Loeb GI, Schrader ME (eds) Modern approaches to wettability. Plenum Press, New York, pp 1–27

Gwon JG, Lee SY, Doh GH, Kim JH (2010) Characterization of chemically modified wood fibers using FTIR spectroscopy for biocomposites. J Appl Polym Sci 116:3212–3219

Han S, Cho D, Park W, Drzal L (2006) Henequen/poly(butylene succinate) biocomposites: electron beam irradiation effects on henequen fiber and the interfacial properties of biocomposites. Compos Interface 13:231–247

Han SO, Choi HY (2010) Morphology and surface properties of natural fiber treated with electron beam. In: Méndez–Vilas A, Díaz J (eds) Microscopy: science, technology, applications and education. Formatex Research Center, pp 1880–1887

Heng JYY, Pearse DF, Thielmann F, Lampke T, Bismarck A (2007) Methods to determine surface energies of natural fibres: a review. Compos Interface 14(7–9):581–604

Himmelsbach DS, Akin DE (1998) Near infrared Fourier transform Raman spectroscopy of flax (Linum usitatissimum L.) stems. J Agric Food Chem 46:991–998

Hiriart-Ramírez E, Contreras-García A, Garcia-Fernandez MJ, Concheiro A, Alvarez-Lorenzo C, Bucio E (2012) Radiation grafting of glycidyl methacrylate onto cotton gauzes for functionalization with cyclodextrins and elution of antimicrobial agents. Cellulose 19:2165–2177

Hong KH, Liu N, Sun G (2009) UV–induced graft polymerization of acrylamide on cellulose by using immobilized benzophenone as a photo–initiator. Eur Polym J 45:2443–2449

Jahn A, Schroder MW, Futing M, Schenzel K, Diepenbrock W (2002) Characterization of alkali treated flax fibres by means of FT–Raman spectroscopy and environmental scanning electron microscopy. Spectrochem Acta Part A 58(10):2271–2279

Jiang H, Zhang Y, Wang X (2009) Effect of lipases on the surface properties of wheat straw. Ind Crops Prod 30:304–310

John MJ, Anandjiwala RD (2008) Recent developments in chemical modification and characterization of natural fiber-reinforced composites. Polym Compos 29(2):187–207

Kabir MM, Wang H, Lau KT, Cardona F (2013) Effects of chemical treatments on hemp fibre structure. Appl Surf Sci 276:13–23

Kafi AA, Magniez K, Fox BL (2011) A surface–property relationship of atmospheric plasma treated jute composites. Compos Sci Technol 71(15):1692–1698

Khalil HPSA, Ismail H, Rozman HD, Ahmad MN (2001) The effect of acetylation on interfacial shear strength between plant fibres and various matrices. Eur Polym J 37:1037–1045

Kim YS, Lee KH, Kim JS (2016) Weathering characteristics of bamboo (Phyllostachys puberscence) exposed to outdoors for one year. J Wood Sci 62:332–338

Kodal M, Topuk ZD, Ozkoc G (2015) Dual effect of chemical modification and polymer precoating of flax fibers on the properties of short flax fiber/poly(lactic acid) composites. J Appl Polym Sci 132

Krishnaiah P, Ratnam CT, Manickam S (2017) Enhancements in crystallinity, thermal stability, tensile modulus and strength of sisal fibres and their PP composites induced by the synergistic effect of alkali and high intensity ultrasound (HIU) treatments. Ultrason Sonochem 34:729–742

Kushwaha PK, Kumar R (2010) Effect of silanes on mechanical properties of bamboo fiber–epoxy composites. J. Reinf Plast Comp 29:718–724

Le Digabel F, Boquillon N, Dole P, Monties B, Averous L (2004) Properties of thermoplastic composites based on wheat–straw lignocellulosic fillers. J Appl Polym Sci 93:428–436

Le Duigou A, Bourmaud A, Balnois E, Davies P, Baley C (2012) Improving the interfacial properties between flax fibres and PLLA by a water fibre treatment and drying cycle. Ind Crops Prod 39:31–39

Le Moigne N, Longerey M, Taulemesse JM, Benezet JC, Bergeret A (2014) Study of the interface in natural fibres reinforced poly (lactic acid) biocomposites modified by optimized organosilane treatments. Ind Crops Prod 52:481–494

Lee S, Shi SQ, Groom LH, Xue Y (2010) Properties of unidirectional kenaf fiber–polyolefin laminates. Polym Compos 31:1067–1074

Li Y, Pickering KL (2008) Hemp fibre reinforced composites using chelator and enzyme treatments. Comp Sci 38:3293–3298

Luna-Straffon MA, Contreras-García A, Brackman G, Coenye T, Concheiro A, Alvarez–Lorenzo C, Bucio E (2014) Wound debridement and antibiofilm properties of gamma–ray DMAEMA–grafted onto cotton gauzes. Cellulose:3767–3779

Ly B, Thielemans W, Dufresne A, Chaussy D, Belgacem MN (2008) Surface functionalization of cellulose fibres and their incorporation in renewable polymeric matrices. Comp Sci Technol 68:3193–3201

Manna S, Saha P, Roy D, Sen R, Adhikari B, Das S (2013) Enhanced biodegradation resistance of biomodified jute fibers. Carbohydr Polym 93:597–603

Marques MDFV, Melo RP, Araujo RDS, Lunz JDN, Aguiar VDO (2015) Improvement of mechanical properties of natural fiber–polypropylene composites using successive alkaline treatments. J Appl Polym Sci 132(12)

Martins MA, Forato LA, Mattoso LHC, Colnago LA (2006) A solid state 13C high resolution NMR study of raw and chemically treated sisal fibers. Carbohydr Polym 64:127–133

Mei Y, Che Q, Yang Q, Draper C, Yang H, Zhang S, Chen H (2016) Torrefaction of different parts from corn stalk and its effect on the characterization of products. Ind Crops Prod 92:26–33

Mészáros E, Jakab E, Gáspár M, Reczey K, Varhegyi G (2009) Thermal behavior of corn fibers and corn fiber gums prepared in fiber processing to ethanol. J Anal Appl Pyrolysis 85:11–18

Mills RH, Gardner DJ, Wimmer R (2008) Inverse gas chromatography for determining the dispersive surface free energy and acid–base interactions of sheet molding compound–part ii 14 lignocellulosic fiber types for possible composite reinforcement. J Appl Polym Sci 110 (6):3880–3888

Moawia RM, Nasef MM, Mohamed NH, Ripin A (2016) Modification of flax fibres by radiation induced emulsion graft copolymerization of glycidyl methacrylate. Radiat Phys Chem 122:35–42

Monier M, Akl MA, Ali WM (2014) Modification and characterization of cellulose cotton fibers for fast extraction of some precious metal ions. Int J Biol Macromol 66:125–134

Montaño-Leyva B, da Silva GGD, Gastaldi E, Torres-Chávez P, Gontard N, Angellier-Coussy H (2013) Biocomposites from wheat proteins and fibers: structure/mechanical properties relationships. Ind Crops Prod 43:545–555

Morshed MM, Alam MM, Daniels SM (2010) Plasma treatment of natural jute fibre by RIE80 plus plasma tool. Plasma Sci Technol 12(3):325–329

Mosiewicki MA, Marcovich NE, Aranguren MI (2011) Characterization of fiber surface treatments in natural fiber composites by infrared and Raman spectroscopy. Interface Eng Nat Fibre Compos Maximum Perform:117–145 Chap. 4

Mou HY, Wu S, Fardim P (2016) Applications of ToF–SIMS in surface chemistry analysis of lignocellulosic biomass: a review. BioResources 11(2):5581–5599

Mucalo MR, Yokogawa Y, Suzuki T, Kawamoto Y, Nagata F, Nishizawa K (1995) Further studies of calcium phosphate growth on phosphorylated cotton fibres. J Mater Sci Mater Med 6:658–669

Ning N, Fu S, Zhang W, Chen F, Wang K, Deng H, Zhang Q, Fu Q (2012) Realizing the enhancement of interfacial interaction in semicrystalline polymer/filler composites via interfacial crystallization. Prog Polym Sci 37:1425–1455

Ouajai S, Hodzic A, Shanks RA (2004) Morphological and grafting modification of natural cellulose fibers. J Appl Polym Sci 94:2456–2465

Owens D, Wendt R (1969) Estimation of the surface free energy of polymers. J Appl Polym Sci 13:1741–1747

Paladini F, Picca RA, Sportelli MC, Cioffi N, Sannino A, Pollini M (2015) Surface chemical and biological characterization of flax fabrics modified with silver nanoparticles for biomedical applications. Mater Sci Eng C 52:1–10

Papirer E, Brendle E, Balard H, Vergelati C (2000) Inverse gas chromatography investigation of the surface properties of cellulose. J Adhes Sci Technol 14(3):321–337

Pietak A, Korte S, Tan E, Downard A, Staiger MP (2007) Atomic force microscopy characterization of the surface wettability of natural fibres. Appl Surf Sci 253(7):3627–3635

Plackett D, Jankova K, Egsgaard H, Hvilsted S (2005) Modification of jute fibers with polystyrene via atom transfer radical polymerization. Biomacromol 6:2474–2484

Pogue RT, Ye J, Klosterman DA, Glass AS, Chartoff RP (1998) Evaluating fiber–matrix interactions in polymer–matrix composites by inverse gas chromatography. Comp Part A Appl Sci 29A:1273–1281

Ragoubi M, George B, Molina S, Bienaimé D, Merlin A, Hiver JM, Dahoun A (2012) Effect of corona discharge treatment on mechanical and thermal properties of composites based on miscanthus fibres and polylactic acid or polypropylene matrix. Compos Part A Appl Sci Manuf 43:675–685

Rasch R, Stricher A, Truss RW (2014) Energy filtered low voltage "in lens detector" SEM and XPS of natural fiber surfaces. J Appl Polym Sci 131:1–7

Ray D, Sengupta SP, Rana AK, Bose NR (2006) Static and dynamic mechanical properties of vinylester resin matrix composites reinforced with shellac–treated jute yarns. Ind Eng Chem Res 45(8):2722–2727

Reeves JB, Galletti GC (1993) Use of pyrolysis—gas chromatography/mass spectrometry in the study of lignin assays. J Anal Appl Pyrolysis 24:243–255

Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM (2001) The effect of fiber treatments on the mechanical properties of unidirectional sisal–reinforced epoxy composites. Comp Sci Technol 61:1437–1447

Rout AK, Kar J, Jesthi K, Kumar A (2016) Effect of surface treatment on the physical, chemical, and mechanical properties of palm tree leaf stalk fibers. Bioresources.com 11:4432–4445

Roy A, Adhikari B, Majumder SB (2013) Equilibrium, kinetic, and thermodynamic studies of azo dye adsorption from aqueous solution by chemically modified lignocellulosic jute fiber. Ind Eng Chem Res 52:6502–6512

Salah F, El Ghoul Y, Roudesli S (2015) Bacteriological effects of functionalized cotton dressings. J Text Inst 5000:1–11

Scalici T, Fiore V, Valenza A (2016) Effect of plasma treatment on the properties of Arundo Donax L. leaf fibres and its bio–based epoxy composites: a preliminary study. Comp Part B 94:167–175

Selvam S, Sundrarajan M (2012) Functionalization of cotton fabric with PVP/ZnO nanoparticles for improved reactive dyeability and antibacterial activity. Carbohydr Polym 87:1419–1424

Shen W, Sheng YJ, Parker IH (1999) Comparison of the surface energetics data of eucalypt fibers and some polymers obtained by contact angle and inverse gas chromatography methods. J Adhes Sci Technol 13:887–890

Shih YF, Huang RH, Yu YH (2014) Preparation and characterization of sol–gel–modified pineapple leaf fiber/polylactic acid composites. J Sol-Gel Sci Technol 70:491–499

Singha AS (2011) Kinetics of graft copolymerization of acrylic acid onto cannabis indica fibre. Iran Polym J 20:913–929

Sinha E (2009) Effect of clod plasma treatment on macromolecular structure, thermal and mechanical behaviour of jute fiber. J Ind Text 38(4):317–339

Sonnier R, Otazaghine B, Viretto A, Apolinario G, Ienny P (2015) Improving the flame retardancy of flax fabrics by radiation grafting of phosphorus compounds. Eur Polym J 68:313–325

Stevanic JS, Salmén L (2008) Characterizing wood polymers in the primary cell wall of Norway spruce (Picea abies (L.) Karst.) using dynamic FT–IR spectroscopy. Cellulose 15:285–295

Szymanska-Chargot M, Chylinska M, Kruk B, Zdunek A (2015) Combining FT–IR spectroscopy and pmultivariate analysis for qualitative and quantitative analysis of the cell wall composition changes during apples development. Carb Polym 115:93–103

Thakur K, Kalia S, Kaith BS, Pathania D, Kumar A (2015) Surface functionalization of coconut fibers by enzymatic biografting of syringaldehyde for the development of biocomposites. RSC Adv 5:76844–76851

Thakur K, Kalia S, Pathania D, Kumar A, Sharma N, Schauer CL (2016) Surface functionalization of lignin constituent of coconut fibers via laccase–catalyzed biografting for development of antibacterial and hydrophobic properties. J Clean Prod 113:176–182

Totolin MI, Vasile C, Tibirna CM, Popescu MC (2008) Grafting of spanish broom (Spartium junceum) fibers with fatty acids under cold plasma conditions. Cellul Chem Technol 42:317–333

Tran LQN, Fuentes CA, Dupont-Gillain C, Van Vuure AW, Verpoest I (2013) Understanding the interfacial compatibility and adhesion of natural coir fibre thermoplastic composites. Compos Sci Technol 80:23–30

Truss RW, Wood B, Rasch R (2016) Quantitative surface analysis of hemp fibers using XPS, conventional and low voltage in–lens SEM. J Appl Polym Sci 133:1–9

Tze WTY, Gardner DJ, Tripp CP (2006) Cellulose fiber/polymer adhesion: effects of fiber/matrix interfacial chemistry on the micromechanics of the interphase. J Adhes Sci Technol 20 (15):1649–1668

Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ (1999) Effect of fiber surface treatment on the fiber–matrix bond strength of natural diber reinforced composites. Comp Part B 30:309–320

Van Oss CJ, Omenyi SN, Neumann AW (1979) Negative Hamaker coefficients: II. Phase separation of polymer solutions. Colloid Polym Sci 257(7):737–44

Wang Y, Tong B, Hou S, Li M, Shen C (2011) Transcrystallization behavior at the poly(lactic acid)/sisal fibre biocomposite interface. Compos Part A Appl Sci 42:66–74

Wu S (1971) Calculation of interfacial tension in polymer systems. J Polym Sci Part C Polym Symp 34:19–30

Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Silane coupling agents used for natural fiber/polymer composites: a review. Comp Part A Appl Sci Manufact 41:806–819

Xu Y, Kawata S, Hosoi K, Kawai T, Kuroda S (2009) Thermomechanical properties of the silanized–kenaf/polystyrene composites. Express Polym Lett 3:657–664

Xue CH, Jia ST, Zhang J, Tian LQ (2009) Superhydrophobic surfaces on cotton textiles by complex coating of silica nanoparticles and hydrophobization. Thin Solid Films 517:4593–4598

Yamanaka A, Yoshikawa M, Abe S, Tsutsumi M, Oohazama T, Kitagawa T, Fujishiro H, Ema K, Izumi Y, Nishijima S (2005) Effects of vapor–phase–formaldehyde treatments on thermal conductivity and diffusivity of ramie fibers in the range of low temperature. J Polym Sci Part B Polym Phys 43:2754–2766

Yamanaka A, Izumi Y, Terada T, Ema K, Tsutsumi M, Nakamura M, Oohazama T, Kitagawa T, Fujishiro H, Abe S, Nishijima S (2006) Radiation effect on the thermal conductivity and diffusivity of ramie fibers in a range of low temperatures by γ rays. J Appl Polym Sci 100:5007–5018

Yang C, Gao P, Xu B (2009) Investigations of a controllable nanoscale coating on natural fiber system: effects of charge and bonding on the mechanical properties of textiles. J Mater Sci 44:469–476

Yang H, Esteves ACC, Zhu H, Wang D, Xin JH (2012) In–situ study of the structure and dynamics of thermo–responsive PNIPAAm grafted on a cotton fabric. Polymer 53:3577–3586

Yu CT, Chen WH, Men LC, Hwang WS (2009) Microscopic structure features changes of rice straw treated by boiled acid solution. Ind Crops Prod 29:308–315

Yu T, Ren J, Li S, Yuan H, Li Y (2010) Effect of fiber surface–treatments on the properties of poly (lactic acid)/ramie composites. Comp Part A 41:499–505

Zafeiropoulos NE, Vickers PE, Baillie CA, Watts JF (2003) An experimental investigation of modified and unmodified flax fibres with XPS, ToF–SIMS and ATR–FTIR. J. Mat Sci 38:3903–3914

Zhang LL, Zhu RY, Chen JY, Chen JM, Feng XX (2008) Seawater–retting treatment of hemp and characterization of bacterial strains involved in the retting process. Process Biochem 43:1195–1201

Zhou Z, Wang J, Huang X, Zhang L, Moyo S, Sun S, Qiu Y (2012) Influence of absorbed moisture on surface hydrophobization of ethanol pretreated and plasma treated ramie fibers. Appl Surf Sci 258:4411–4416

Zhou M, Li Y, He C, Jin T, Wang K, Fu Q (2014) Interfacial crystallization enhanced interfacial interaction of Poly (butylene succinate)/ramie fiber biocomposites using dopamine as a modifier. Compos Sci Technol 91:22–29