SPRINGER BRIEFS IN MOLECULAR SCIENCE
BIOBASED POLYMERS

Nicolas Le Moigne
Belkacem Otazaghine
Stéphane Corn
Hélène Angellier-Coussy
Anne Bergeret

Surfaces and Interfaces in Natural Fibre Reinforced Composites

Fundamentals, Modifications and Characterization

epnoe

Springer

SpringerBriefs in Molecular Science

Biobased Polymers

Published under the auspices of EPNOE**Springerbriefs in Biobased polymers* covers all aspects of biobased polymer science, from the basis of this field starting from the living species in which they are synthetized (such as genetics, agronomy, plant biology) to the many applications they are used in (such as food, feed, engineering, construction, health, …) through to isolation and characterization, biosynthesis, biodegradation, chemical modifications, physical, chemical, mechanical and structural characterizations or biomimetic applications. All biobased polymers in all application sectors are welcome, either those produced in living species (like polysaccharides, proteins, lignin, …) or those that are rebuilt by chemists as in the case of many bioplastics.

Under the editorship of Patrick Navard and a panel of experts, the series will include contributions from many of the world's most authoritative biobased polymer scientists and professionals. Readers will gain an understanding of how given biobased polymers are made and what they can be used for. They will also be able to widen their knowledge and find new opportunities due to the multidisciplinary contributions.

This series is aimed at advanced undergraduates, academic and industrial researchers and professionals studying or using biobased polymers. Each brief will bear a general introduction enabling any reader to understand its topic.

**EPNOE The European Polysaccharide Network of Excellence (www.epnoe.eu) is a research and education network connecting academic, research institutions and companies focusing on polysaccharides and polysaccharide-related research and business.*

More information about this series at http://www.springer.com/series/15056

Nicolas Le Moigne · Belkacem Otazaghine
Stéphane Corn · Hélène Angellier-Coussy
Anne Bergeret

Surfaces and Interfaces in Natural Fibre Reinforced Composites

Fundamentals, Modifications and Characterization

Springer

Nicolas Le Moigne
Centre des Matériaux des Mines d'Alès (C2MA)
IMT Mines Alès
Alès
France

Belkacem Otazaghine
Centre des Matériaux des Mines d'Alès (C2MA)
IMT Mines Alès
Alès
France

Stéphane Corn
Centre des Matériaux des Mines d'Alès (C2MA)
IMT Mines Alès
Alès
France

Hélène Angellier-Coussy
UMR IATE
Université de Montpellier
Montpellier
France

Anne Bergeret
Centre des Matériaux des Mines d'Alès (C2MA)
IMT Mines Alès
Alès
France

ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISSN 2510-3407 ISSN 2510-3415 (electronic)
Biobased Polymers
ISBN 978-3-319-71409-7 ISBN 978-3-319-71410-3 (eBook)
https://doi.org/10.1007/978-3-319-71410-3

Library of Congress Control Number: 2017960918

© The Author(s) 2018
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Foreword

The society expectations drive towards developing sustainable, biodegradable light materials. In this context, renewable (sustainability) organic (both in terms of biodegradability and the low density to compare with other families, i.e. inorganic and metals) materials are excellent candidates. One of the biggest limitation of organic materials is their low mechanical strength and their low resistance to temperature. The first drawback is generally overcome by the preparation of biphasic composites in which the combination of reinforcing phase and a continuous polymeric matrix gives high performant materials. In composite materials, the quality of the fibre–matrix interface is crucial. In fact, under mechanical constraints, the matrix will tend to transfer the stress to the reinforcing phase, therefore, this load transfer should be efficient in order to allow the material to stand up the external solicitation.

In this context, the exploitation of lignocellulosic fibres is increasing, as they possess several potential advantages in addition to the fact that they meet perfectly the society expectations. These elements are ubiquitously available, inexpensive; they could be supplied in a variety of forms, they possess modest abrasivity and finally, they are easy to recycle in the energy recovery stream of the materials made thereof. The last advantage should be opposed to glass-fibre-based composites. In fact, natural fibre based composites do not leave any solid residue after their combustion at the end of their life cycle, which is not the case when using glass fibre, as reinforcing agent.

Unfortunately, natural fibres also have some drawbacks because they possess a strong polar character, which gives rise to two major limitations when used as reinforcing elements in composite materials. The first one is associated with their strong sensitivity to water and even moisture, which induces a loss of the mechanical properties of the composite under ageing conditions, and (ii) their poor compatibility with the hydrophobic macromolecular matrices generally used, which causes weak interfacial adhesion. The challenge is then to protect them from water uptake and release (or at least to slow down their sensitivity to water) without affecting their integrity.

In this context, cellulosic fibres are generally submitted to various surface modifications aiming at minimizing the interfacial energy between the fibres and the non-polar polymer matrix, which yields a better adhesion between the two phases and therefore gives rise to a performant composite. A lot of work was already done in the contexts of using superficial modifications of the fibres and of that related to the investigation of the interfacial quality, but a lot of work is still needed to ascertain better these materials. Several areas should be developed in parallel, namely: (i) looking for greener ways of modifying cellulose fibres and particularly water-based or solvent-less procedure; (ii) investigating new systems with improving the kinetics of the modification reactions and (iii) developing innovative techniques of characterization of the fibres and the composites.

New laboratories have started working in this area, which is an excellent sign to progress in understanding the complexity of such an area of research. Even though, I believe that in the near future more people will shift to the area of natural fibres-based composites. This tendency has also induced an increase of the number of publications, conferences, book chapters and books. This book illustrates very well the necessity of the required efforts and has the merit of summarizing the most recent advances in the fields of (i) natural fibre morphology at different levels; (ii) interfacial phenomena in natural fibre reinforced composites; (iii) modification of these interfaces; (iv) characterization of the fibre modifications and (v) characterization of the interface/interphase in these composites. I believe that researchers working in this area will find here an updated state of the art of the hottest tendencies and I am sure about the success of this book.

Grenoble, France
September 2017

Prof. Mohamed Naceur Belgacem
CNRS, Grenoble INP, LGP2
Université Grenoble Alpes

Contents

About the Authors

Dr. Ing. Nicolas Le Moigne is Associate Professor at IMT Mines Alès. His current research areas include the processing of bio-based polymers and (nano)composites and the characterization of their physical chemical and rheological properties, with emphasis on reinforcement/matrix interactions. Since 2005, he is involved in research projects aiming at studying and improving the selection, physical and chemical treatment, and processing of biomass (lignocellulosic fibres and microalgae) for the development of bio-based polymeric materials in packaging and structural applications.

Dr. Belkacem Otazaghine is Associate Professor at IMT Mines Alès. He obtained his Ph.D. in 2003 working on molecular and macromolecular synthesis in the field of the controlled radical polymerization of fluorinated monomers. His main research projects are in the field of the chemical modification of mineral and organic nanoparticles and natural fibres for the control of composites structure and properties.

Dr. Ing. Stéphane Corn is Associate Professor at IMT Mines Alès. His research interests relate to the mechanical behaviour of composite materials and especially the assessment of their properties from multiscale numerical modelling. He is also a lecturer in the area of structural dynamics. He is involved in research projects dedicated to the improvement of natural fibre reinforced composites.

Dr. Ing. HDR Hélène Angellier-Coussy is Associate Professor at the Technical Institute of the University of Montpellier. She is working on the development of sustainable materials for food packaging applications. Her research activities are focused on the formalization of structure/properties relationships in bio(nano)composites, with a particular attention to better understand the impact of the interphase on mass transfer properties. She is particularly involved in projects dealing with the conversion of lignocellulosic agro-residues for the production of eco-efficient fillers.

Prof. Anne Bergeret holds a Chemical Engineering Diploma and a Ph.D. in Polymer and Composite Materials. She worked as expert in glass fibre sizing for composite materials at Owens Corning Co. before being hired at IMT Mines Alès. Currently, she manages the Advanced Polymer Materials department at Centre des Matériaux des Mines d'Alès. In the field of polymer composite materials, she has experience in surface treatments of glass and natural fibres and in the improvement of composite performances in severe in-service conditions.

Abbreviations

AE	Acoustic Emission
AFM	Atomic Force Microscopy
AGU	Anhydroglucose Units
AKD	Alkyl ketene dimers
APS	γ-aminopropyl triethoxy silane
ASA	Alkenyl succinic acid anhydrides
ATRP	Atom Transfer Radical Polymerization
CA	Contact Angle
CESA	Cellulose Synthase proteins
CFM	Chemical Force Microscopy
CHNS	Elemental Combustion Analyses
CP-MAS	Cross-Polarization Magic Angle Spinning NMR
CSCs	Cellulose Synthase Complexes
DAP	Dihydrogen ammonium phosphate
DCP	Dicumyl peroxide
DEA	Dielectric Thermal Analysis
DMA	Dynamic Mechanical Analysis
DMTA	Dynamic Mechanical Thermal Analysis
DP	Degree of Polymerization
DS	Degree of Substitution
DSC	Differential Scanning Calorimetry
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive analysis of X-rays
ESEM	Environmental Scanning Electron Microscopy
FTIR	Fourier Transform Infrared spectroscopy
GPS	γ-glycidoxypropyl trimethoxy silane
GRP	Glycine-rich
HCl	Hydrogen Chloride
HDPE	High-density poly (ethylene)
HG	Homogalacturonans

HRPG	Hydroxylamine-rich
HRR	Heat Release Rate
ICP AES	Inductively Coupled Plasma Atoms Emission Spectroscopy
IFSS	Interfacial Shear Strength
IGC	Inverse Gas Chromatography
ILSS	Interfacial Laminar Shear Strength
LDPE	Low-density poly (ethylene)
MA	Maleic anhydride
MAPC1	Dimethyl (methacryloyloxy) methyl phosphonate
MAPE	Maleic anhydride grafted polyethylene
MAPP	Maleic anhydride grafted polypropylene
MDF	Medium-Density Fibreboard
MDI	Methylene-bis-diphenyl diisocyanate
MFA	Microfibrillar Angle
ML	Middle Lamella
MPS	γ-methacryloxypropyl trimethoxy silane
MVP	Dimethylvinyl phosphonate
NaOH	Sodium hydroxide
NIR	Near Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
ODPA	Octadecylphosphonic acid
OWRK	Owens, Wendt, Rabel and Kaelble
P(3HB-co-3HH)	Poly (3-hydroxybutyrate-co-3-hydroxyhexanoate)
PBAT	Poly (butyrate adipate terephthalate)
PBS	Poly (butylene succinate)
PBSA	Poly (butylene-succinate-co-adipate)
PCFC	Pyrolysis Combustion Flow Calorimetry
PE	Poly (ethylene)
PEG	Poly (ethylene glycol)
PHB	Poly (hydroxybutyrate)
PHBV	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly (lactic acid)
POM	Polarized Optical Microscopy
PP	Poly (propylene)
PPDI	1,4-phenylene diisocyanate
PPG	Poly (propylene glycol)
PRP	Proline-rich
PVC	Poly (vinyl chloride)
PVDF	Poly (vinylidene fluoride)
Py-GC/MS	Pyrolysis coupled with Gas Chromatography and Mass Spectrometry
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RG type I and II	Branched rhamnogalacturonans
SAXS	Small-angle X-ray Scattering

sc-CO_2	Supercritical carbon dioxide
SEM	Scanning Electron Microscopy
SiAn	3-(triethoxysilyl)propylsuccinic anhydride silane
SThM	Scanning Thermal Microscopy
TCMS	Trichloromethyl silane
TD	Thermodilatometry
TDI	Toluene-2,4-diisocyanate
TGA	Thermogravimetric Analysis
THF	Tetrahydrofurane
TL	Thermoluminescence
TMA	Thermomechanical Analysis
ToF-SIMS	Time-Of-Flight Secondary Ion Mass Spectrometry
VTMO	Vinyl trimethoxy silane
VTS	Vinyl trimethoxy silane
W_A	Work of Adhesion
WVP	Water Vapour Permeability
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Introduction: Aim and Scope

Natural fibres are fascinating hierarchical bio-assemblies that are perfectly designed to fulfil a specific role in Nature (plants structures, sheep wool, spider web…) and able to adapt in an evolutive environment. Thought being used since several thousand years for human needs (single-storey houses, textile…), natural fibres, especially plant fibres, show a growing interest for their use in technical and high performance applications as in automotive, building or sports and leisure. Indeed, natural fibre reinforced composites are considered as a promising alternative to synthetic fibre reinforced composites due to their advantageous specific mechanical properties as well as their interesting viscoelastic damping and acoustic and thermal insulation properties. In order to enhance their performances and better implement this new class of biocomposites at an industrial scale, various strategies are currently conducted regarding the selection and processing of the raw materials and the improvement of the fibre/matrix interface quality.

The interfacial adhesion is primarily governed by the chemical coupling and mechanical interlocking between the polymer matrix and the fibres. In this regard, various enzymatic, chemical and physical treatments have been developed to *(i)* better disperse the fibres and enhance the specific interfacial area, and to *(ii)* favour the wettability and the (physico-)chemical interactions at the fibre/matrix interface. Besides, fibre and interface modifications are also an opportunity to introduce new functionalities in natural fibre based composites, such as enhanced hydrophobicity, flame retardancy or controlled barrier properties.

This book is addressed to Master and Ph.D. students as well as researchers from academia and industry. It aims to provide the key definitions to understand the issues related to interface modifications in natural fibre based composites considering the particular supramolecular and micro-structures encountered in plant fibres. A particular emphasis is given to the modification and functionalization strategies of natural fibres and their impact on biocomposites behaviour and properties. Commonly used and newly developed treatment processes are described in view of scaling-up natural fibre treatments for their implementation in industry. Finally, a detailed and comprehensive description of the tools and methodologies developed to investigate and characterize surfaces and interfaces in natural fibre based composites is reviewed and discussed.

Chapter 1
Introduction on Natural Fibre Structure: From the Molecular to the Macrostructural Level

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.

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3_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	1.3–1.7	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	0.7–3	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	0.4–0.8	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	0.3–1.2	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	2–6	–	–	–	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	–	9.5–11.2	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 fat/wax	% wt ash	MFA (S2 wall) °	Crystallinity index I_c%	Plant cells length mm/width µm	References
											Silva et al. (2011, 2012), Le Digabel et al. (2004), Müssig et al. (2010)
Leaf fibres	Piassava	29	26	45–48	–	–	–	–	–	–	Ferreira et al. (2014), John and Anandjiwala (2008)
	Sisal	43–88	10–15	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	4–28	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	0.8–2	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 synthetized 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 HRPG, 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 Paredez et al. (2006). In fact, the authors were able to obtain an *in vivo*

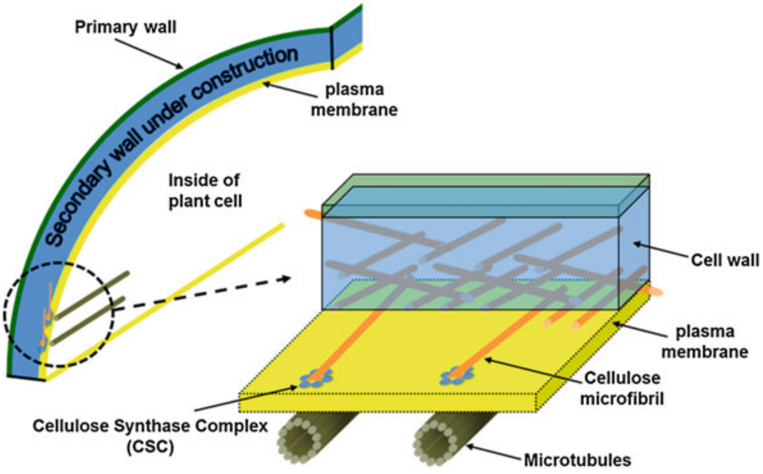


Fig. 1.1 Building of the cell walls. The CSCs localized in the plasma membrane synthesize and depose the cellulose microfibrils along the cell wall. Several distinct cell wall layers in terms of composition and orientation are produced by this mechanism

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

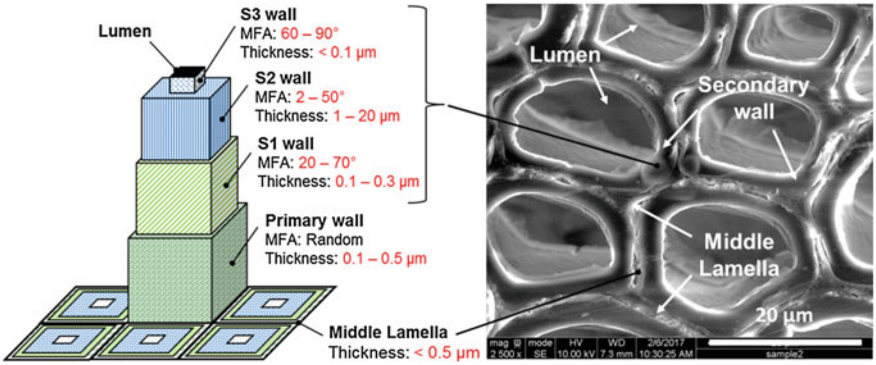


Fig. 1.2 **a** General cell wall structure of natural fibres, with: middle lamella (ML), primary P wall, secondary S1 wall, secondary S2 wall (main body), secondary S3 wall, lumen. For each wall, indications about their thickness and overall microfibrillar angle (MFA) are given according to (Klemm et 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 (<0.1 µm). 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

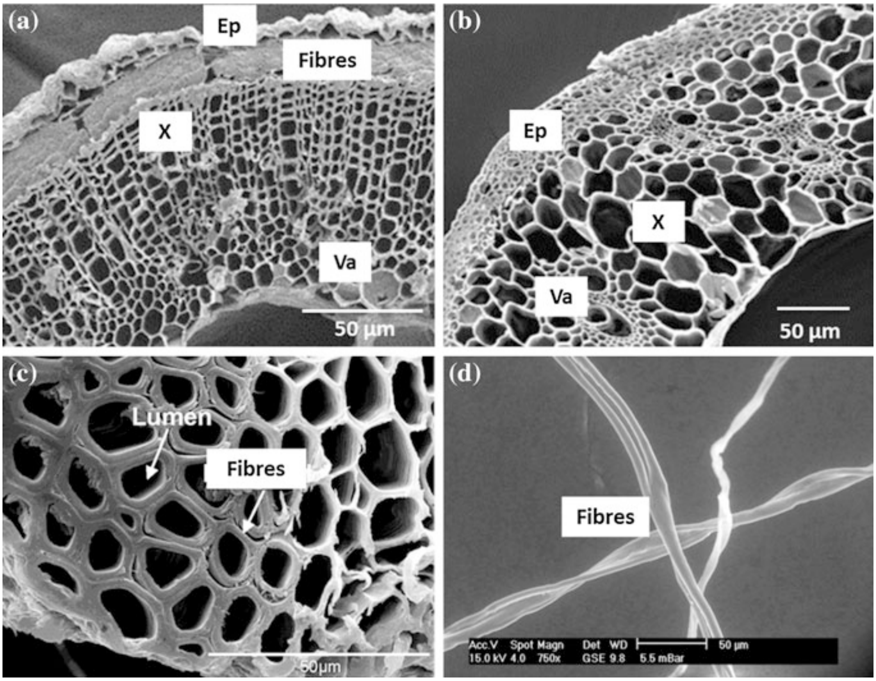


Fig. 1.3 SEM pictures of plant cells from various origins. **a** flax (stem); **b** wheat straw (stem); **c** sisal (leaf); **d** cotton (seed). Ep : epidermis; Fibres; X : xylem; Va : vascular bundles. SEM pictures reprinted from Akin et al. (2007), Fig. 1a; Yu et al. (2008), Fig. 1 Fidelis et al. (2013), 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 Walls 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/m^2 to 40.3–43.1 mJ/m^2 and from 0.7–2.9 mJ/m^2 to 2.7–5.5 mJ/m^2, 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 (ξ)-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 Walls 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	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
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	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
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).

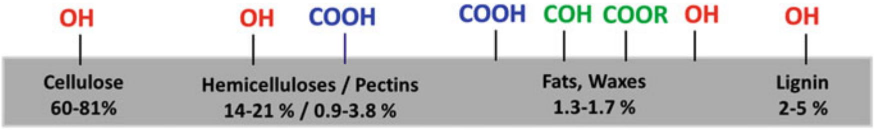


Fig. 1.4 Overall biochemical composition of flax fibres and possible reactive functional groups at their surface

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 weigth 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 macrofibrillar 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 m^2/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).

References

Abdelmouleh M, Boufi S, Belgacem MN, Duarte AP, Salah AB, Gandini A (2004) Modification of cellulosic fibres with functionalised silanes: development of surface properties. Int J Adhes Adhes 24(1):43–54

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

Agarwal UP, Reiner RR, Ralph SA (2011) Cellulose crystallinity of woods, wood pulps, and agricultural fibers by FT–Raman Spectroscopy. Red 19:67–69

Akin DE, Condon B, Sohn M, Foulk JA, Dodd RB, Rigsby LL (2007) Optimization for enzyme–retting of flax with pectate lyase. Ind Crops Prod 25(2):136–146

Akin DE (2010) Chemistry of Plant Fibres. In: Müssig J (ed) Industrial applications of natural fibres: structure, properties and technical applications, John Wiley & Sons Ltd. West Sussex, United Kingdom, pp 13–22

Aranberri-Askargorta I, Lampke T, Bismarck A (2003) Wetting behaviour of flax fibers as reinforcement for polypropylene. J Colloid Interf Sci 263(2):580–589

Argyropoulos DS, Menachem SB (1998) Lignin. In: Kaplan DL (ed) Biopolymers from renewable resources. Springer, Berlin Heidelberg, pp 292–322

Atchison JE (1983) Data on non–wood plant fibers. In: Kocurek MJ (ed) Pulp and Paper Manufacture, vol 1. Properties of fibrous raw materials and their preparation for pulping, Tappi Press, Atlanta, GA, XVII

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 S 37:1626–1637

Baltazar-y-Jimenez A, Bismarck A (2007) Wetting behaviour, moisture up–take and electrokinetic properties of lignocellulosic fibres. Cellulose 14:115–127

Bartell FE, Zuidema HH (1936) Wetting characteristics of solids of low surface tension such as talc, waxes and resins. J Am Chem Soc 58(8):1449–1454

Beaugrand J, Chabbert B, Kurek B (2017) Production, transformation et critères de qualité des fibres de lin et de chanvre pour un usage dans les matériaux composites. In: Berzin F (ed.) Composites polymères et fibres lignocellulosiques: Propriétés, transformation et caractérisation, Lavoisier, Hermes, pp 1–40

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

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

Berthet MA, Commandré JM, Rouau X, Gontard N, Angellier-Coussy H (2016) Torrefaction treatment of lignocellulosic fibres for improving fibre/matrix adhesion in a biocomposites. Mater Design 92:223–232

Bismarck A, Aranberry-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, Shenderovich I, Limbach HH (2002) Surface characterization of flax, hemp and cellulose fibers surface properties and the water uptake behaviour. Polym Composite 23:872–894

Boudet AM (2002) L'amélioration des plantes, base de l'agriculture. Rapport de communication, Institut Fédératif de Recherche Signalisation Cellulaire et Biotechnologie Végétale (IFR 40), Toulouse

Bourmaud A, Morvan C, Baley C (2010) Importance of fiber preparation to optimize the surface and mechanical properties of unitary flax fiber. Ind Crops Prod 32:662–667

Brosse N, El Hage R, Sannigrahi P, Ragauskas A (2010) Dilute sulfuric acid and ethanol organosolv pretreatment of Miscanthus x Giganteus. Cell Chem Technol 44:71–78

Brosse N, Dufour A, Meng X, Sun Q, Ragauskas A (2012) Miscanthus: a fast–growing crop for biofuels and chemicals production. Biofuels Bioprod Bioref 6:580–598

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

Cassie ABD, Baxter S (1944) Wettability of porous surfaces. Trans Faraday Soc 40:546–550

Castellano M, Gandini A, Fabbri P, Belgacem MN (2004) Modification of cellulose fibres with organosilanes: under what conditions does coupling occur? J Colloid Interface Sci 273:505–511

CELL division (2017) Cellulose structure & biosynthesis symposium. In: Papers presented at the 253rd ACS national meeting (vol. 253), San Francisco, CA, 2–6 April 2017

Choi H, Han S, Lee J (2009) The effects of morphological properties of henequen fiber irradiated by eb on the mechanical and thermal properties of henequen fiber/PP composites. Compos Interface 16:751–768

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

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

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

Driscoll M, Stipanovic A, Winter W, Cheng K, Manning M, Spiese J, Galloway RA, Cleland MR (2009) Electron beam irradiation of cellulose. Radiat Phys Chem 78:539–542

El Hage R, Chrusciel L, Desharnais L, Brosse N (2010a) Effect of autohydrolysis of Miscanthus x giganteus on lignin structure and organosolv delignification. Bioresour Technol 101:9321–9329

El Hage R, Brosse N, Sannigrahi P, Ragauskas A (2010b) Effects of process severity on the chemical structure of Miscanthus ethanol organosolv lignin. Polym Degrad Stabil 95:997–1003

Eriksson M, Notley SM, Wågberg L (2007) Cellulose thin films: degree of cellulose ordering and its influence on adhesion. Biomacromol 8:912–919

Fengel D, Wegener G (1989) Wood chemistry, ultrastructure and reactions. Walter de Gruyter, Berlin

Ferreira M, Sartori M, Oliveira R, Guven O, Moura EAB (2014) Short vegetal–fiber reinforced HDPE – A study of electron–beam radiation treatment effects on mechanical and morphological properties. Appl Surf Sci 310:325–330

Fidelis MEA, Pereira TVC, Gomes ODFM, de Andrade Silva F, Toledo Filho RD (2013) The effect of fiber morphology on the tensile strength of natural fibers. J Mater Res Technol 2(2):149–157

Fink HP, Philipp B, Zschunke C, Hayn M (1992) Structural changes of LOPD cellulose in the original and mercerized state during enzymatic hydrolysis. Acta Polym 43:270–274

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

George M, Mussone PG, Abboud Z, Bressler DC (2014) Characterization of chemically and enzymatically treated hemp fibres using atomic force microscopy and spectroscopy. Appl Surf Sci 314:1019–1025

Gorshkova T, Salnikov VV, Pogodina NM, Chemikosova SB, Yablokova EV, Ulanov AV, Ageeva MV, Van Dam JEG, Lozovaya VV (2000) Composition and distribution of cell wall phenolic compounds in flax (*Linum usitatissimum L.*) stem tissues. Ann Bot 85:477–486

Gu Y (2017) Does cortical microtubule array guide the orientation of cellulose deposition or not? In: Papers presented at the 253rd ACS national meeting (vol. 253), San Francisco, CA, 2–6 April 2017

Gutierrez A, Rodrıguez IM, del Rio JC (2008) Chemical composition of lipophilic extractives from sisal (Agave sisalana) fibers. Ind Crops Prod 28:81–87

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

Han Y, Han S, Cho D, Kim H (2006b) Henequen/unsaturated polyester biocomposites: electron beam irradiation treatment and alkali treatment effects on the henequen fiber. Macromol Symp 245–246:539–546

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

Heinze T, Petzold-Welcke K, van Dam JEG (2012) Polysaccharides: Molecular and supramolecular structures. Terminology. In: Navard P (ed) The European polysaccharide network of excellence (EPNOE), Springer, Wien, pp 23–64

Hon DNS (1994) Cellulose: a random walk along its historical path. Cellulose 1:1–25

Jain S, Kumar R, Jindal UC (1992) Mechanical behaviour of bamboo and bamboo composite. J Mater Sci 27:4598–4604

Jarvis MC (1984) Structure and properties of pectin gels in plant cell walls. Plant, Cell Environ 7:153–164

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

Joseph S, Sreekala M, Oommen Z, Koshy P, Thomas S (2002) A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres. Compos Sci Technol 62:1857–1868

Kaack K, Schwarz KU, Brander PE (2003) Variation in morphology, anatomy and chemistry of stems of miscanthus genotypes differing in mechanical properties. Ind Crops Prod 17:131–141

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

Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998) Comprehensive cellulose chemistry. Wiley–VCH, Weinheim

Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem Int Ed 44:3358–3393

Krässig HA (1993) Cellulose —structure, accessibility and reactivity. In: Huglin MB (ed) Polymer monographs, vol 11. Gordon and Breach Science Publishers, Amsterdam

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 J–M, Bénézet J–C, 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

Lefeuvre A, Le Duigou A, Bourmaud A, Kervoelen A, Morvan C, Baley C (2015) Analysis of the role of the main constitutive polysaccharides in the flax fibre mechanical behaviour. Ind Crops Prod 76:1039–1048

Legras A, Kondor A, Heitzmann MT, Truss RW (2015) Inverse gas chromatography for natural fibre characterisation: Identification of the critical parameters to determine the Brunauer–Emmett–Teller specific surface area. J Chromatogr A 1425:273–279

Lerouxel O, Cavalier DM, Liepman AH, Keegstra K (2006) Biosynthesis of plant cell wall polysaccharides – a complex process. Curr Opin Plant Biol 9:1–10

Lilholt H, Lawther JM (2000) Natural organic fibres. In: Kelly A, Zweben C (eds) Comprehensive composite materials. Pergamon, Oxford, pp 303–325

Luner and Sandell (1969) The wetting of cellulose and wood hemicelluloses. J Polym Sci Pol Sym 28:115–142

Marques G, del Rio J, Gutierrez A (2010) Lipophilic extractives from several non woody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching. Bioresour Technol 101:260–267

Misra MK, Ragland KW, Baker AJ (1993) Wood ash composition as a function of furnace temperature. Biomass Bioenerg 4:103–116

Montane D, Farriol X, Salvado J, Jollez P, Chornet E (1998) Fractionation of wheat straw by steam–explosion pre–treatment and alkali delignification. J Wood Chem Technol 18:171–191

Morvan C, Andème-Onzighi C, Girault R, Himmelsbach DS, Driouich A, Akin DE (2003) Building flax fibres: more than one brick in the walls. Plant Physiol Bioch 41:935–944

Müssig J, Fischer H, Graupner N, Drieling A (2010) Testing methods for measuring physical and mechanical fibre properties (plant and animal fibres). In: Müssig J (ed) Industrial applications of natural fibres: structure, properties and technical applications. Wiley, West Sussex, UK, pp 269–309

Notley SM, Norgren M (2010) Surface energy and wettability of spin–coated thin films of lignin isolated from wood. Langmuir 26(8):5484–5490

Orue A, Jauregi A, Peña-Rodriguez C, Labidi J, Eceiza A, Arbelaiz A (2015) The effect of surface modifications on sisal fiber properties and sisal/poly (lactic acid) interface adhesion. Compos Part B Eng 73:132−138

O'Sullivan AC (1997) Cellulose: the structure slowly unravels. Cellulose 4:173–207

Ozdal T, Capanoglu E, Altay F (2013) A review on protein–phenolic interactions and associated changes. Food Res Int 51:954–970

Paredez AR, Somerville CR, Ehrhardt DW (2006) Visualization of cellulose synthase demonstrates functional association with microtubules. Science 312:1491–1495

Park JM, Quang ST, Hwang BS, DeVries KL (2006a) Interfacial evaluation of modified Jute and Hemp fibers/polypropylene (PP)–maleic anhydride polypropylene co–polymers (PP–MAPP) composites using micromechanical technique and nondestructive acoustic emission. Compos Sci Technol 66(15):2686–2699

Park S, Venditti RA, Jameel H, Pawlak JJ (2006b) Changes in pore size distribution during the drying of cellulose fibres as measured by differential scanning calorimetry. Carbohydr Polym 66:97–103

Prat R, Mosiniak M, Roland JC (2004) Architecture moléculaire de la paroi. In: La paroi primaire de la cellule végétale. Université Pierre & Marie Curie. http://www.snv.jussieu.fr/bmedia/paroi/architecture.htm. Accessed 22 Aug 2017

Qi X, Behrens BX, West PR, Mort AJ (1995) Solubilization and partial characterization of extensin fragments from cell walls of cotton suspension cultures (Evidence for a covalent cross–Link between extensin and pectin). Plant Physiol 108:1691–1701

Saxena IM, Brown RM Jr (2005) Cellulose biosynthesis: current views and evolving concepts. Ann Bot 96:9–21

Shahzad A (2013) A study in physical and mechanical properties of hemp fibres. Adv Mater Sci Eng: 325085. https://doi.org/10.1155/2013/325085

Shen Q, Liu DS, Gao Y, Chen Y (2004) Surface properties of bamboo fiber and a comparison with cotton linter fibers. Colloid Surf B 35:193–195

Silva GGD, Guilbert S, Rouau X (2011) Successive centrifugal grinding and sieving of wheat straw. Powder Technol 208:266–270

Silva GGD, Couturier M, Berrin JG, Buléon A, Rouau X (2012) Effects of grinding processes on enzymatic degradation of wheat straw. Bioresour Technol 103:192–200

Sjöström E (1981) Wood polysaccharides. In: Wood chemistry: fundamentals and applications. Academic Press, New York, p 51

Sjöström E (1993) Wood polysaccharides. In: Wood chemistry: fundamentals and applications, 2nd edn. Academic press, San Diego, pp 51–70, 292

Sørensen A, Teller PJ, Hilstrom T, Ahring BK (2008) Hydrolysis of miscanthus for bioethanol production using dilute acid presoaking combined with wet explosion pre–treatment and enzymatic treatment. Bioresour Technol 99:6602–6607

Takács E, Wojnárovits L, Borsa J, Cs Földváry, Hargittai P, Zöld O (1999) Effect of γ–irradiation on cotton–cellulose. Radiat Phys Chem 55:663–666

Takács E, Wojnárovits L, Cs Földváry, Hargittai P, Borsa J, Sajó I (2000) Effect of combined gamma–irradiation and alkali treatment on cotton–cellulose. Radiat Phys Chem 57:399–403

Terinte N, Ibbett R, Schuster KC (2011) Overview on native cellulose and microcrystalline cellulose I structure studied by X–ray diffraction (WAXD): comparison between measurement techniques. Lenzinger Ber 89:118–131

Thakur R, Sarkar CR, Sarmah R (1999) Chemical composition of some varieties of ramie and their fibre characteristics. Indian J Fibre Text 24:276–278

Thygesen A, Oddershede J, Lilholt H, Thomsen AB, Stahl K (2005) On the determination of crystallinity and cellulose content in plant fibres. Cellulose 12:563–576

Van de Velde K, Kiekens P (1999) Wettability of natural fibres used as reinforcement for composites. Angew Makromol Chem 272:87–93

Van Hazendonka JM, van der Putten JC, Keurentjes JTF, Prins A (1993) A simple experimental method for the measurement of the surface tension of cellulosic fibres and its relation with chemical composition. Colloid Surface A 81:251–261

Van Oss CJ (2006) Interfacial forces in aqueous media. CRC Press, New York

Varghese S, Kuriakose B, Thomas S (1994) Short sisal fibre reinforced natural rubber composites: high energy radiation, thermal and ozone degradation. Polym Degrad Stabil 44:55–61

Wahab R, Mustafa MT, Sudin M, Mohamed A, Rahman S, Samsi HW, Khalid I (2013) Extractives, holocellulose, α–cellulose, lignin and ash contents in cultivated tropical bamboo Gigantochloa brang, G. levis, G. scortechinii and G. wrayi. J Biol Sci 5:266–272

Wang X, li X, Ren H (2010) Variation of microfibril angle and density in moso bamboo (Phyllostachys pubescens). J Trop Forest Sci 22(1):88–96

Warwicker JO, Jeffries R, Colbran RL, Robinson RN (1996) A review of the literature on the effect of caustic soda and other swelling agents on the fine structure of cotton. Shirley Institute Pamphlet 93, St Ann's Press, England

Wenzel RN (1936) Resistance of solid surfaces to wetting by water. Ind Eng Chem 28:988−994

Westerlind BS, Berg JC (1988) Surface energy of untreated and surface-modified cellulose fibers. J Appl Polym Sci 36(3):523–534

Yan L, Chouw N, Jayaraman K (2014) Flax fibre and its composites—A review. Compos Part B-Eng 56:296–317

Yu Y, Fei B, Zhang B, Yu X (2007) Cell–wall mechanical properties of bamboo investigated by in–situ imaging nanoindentation. Wood Fiber Sci 39:527–535

Yu H, Liu R, Shen D, Wu Z, Huang Y (2008) Arrangement of cellulose microfibrils in the wheat straw cell wall. Carbohyd Polym 72:122–127

Zhao H, Kwak JH, Zhang ZC, Brown HM, Arey BW, Holladay JE (2007) Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis. Carbohydr Polym 68:235–241

Zhuang RC, Burghardt T, Mäder E (2010) Study on interfacial adhesion strength of single glass fibre/polypropylene model composites by altering the nature of the surface of sized glass fibres. Compos Sci Technol 70:1523–1529

Chapter 2
Interfaces in Natural Fibre Reinforced Composites: Definitions and Roles

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

2.1 Multiple and Multi-scale Interfaces Systems

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

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3_2

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

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

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

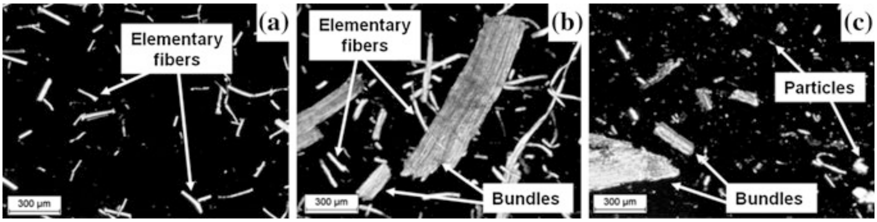


Fig. 2.1 Optical microscopy images obtained in light transmission mode between crossed polarizers of composites diluted with Decalin®: **a** PP/4% MAPP/40% flax; **b** PP/4% MAPP/40% sisal and **c** PP/4% MAPP/40% wheat straw. Three entities are found: elementary fibres, bundles and particles. Reprinted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

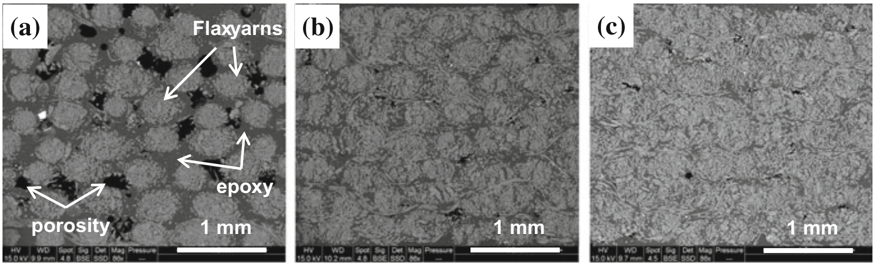


Fig. 2.2 SEM micrographs of transverse cross section of flax tow fabrics reinforced epoxy composites for different extraction treatments: **a** untreated, **b** ethanol, **c**NaOH 1%

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

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

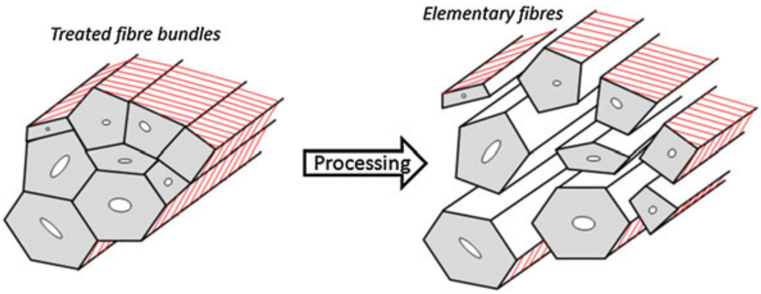


Fig. 2.3 Illustration of treated fibre surfaces (dashed zones) before processing and the ones exposed to the matrix after processing. Reprinted from Le Moigne et al. (2014), Fig. 6 with permission from Elsevier

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

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

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

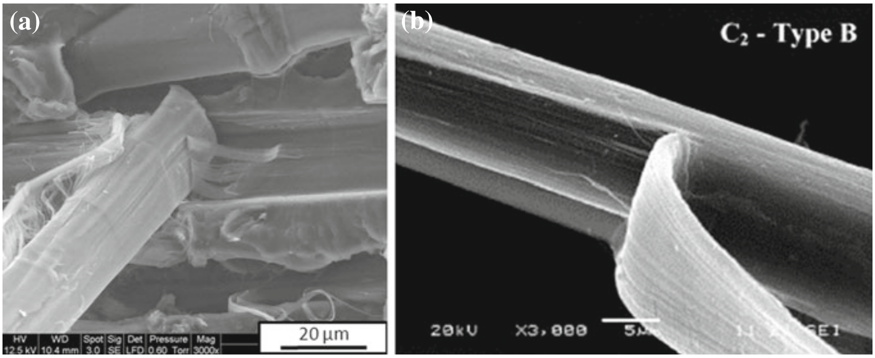


Fig. 2.4 Evidence of cell wall decohesion after **a** tensile and **b** debonding tests. Reprinted from **a** Le Moigne et al. (2014), Fig. 13 and **b** Le Duigou et al. (2012), Fig. 6 with permission from Elsevier

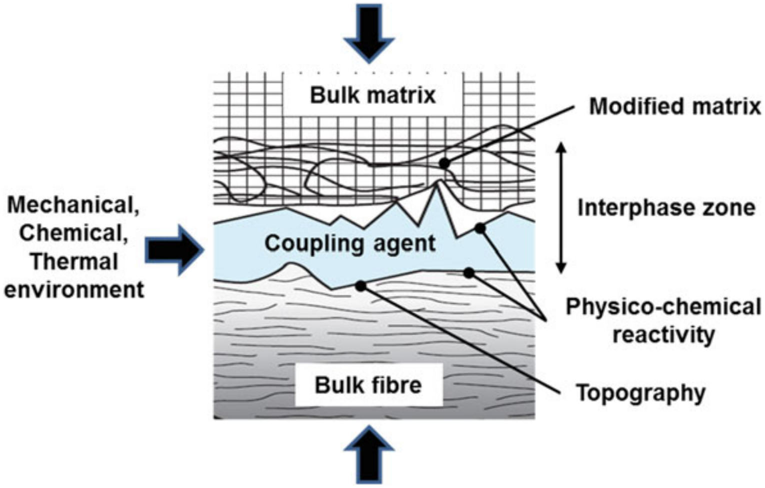


Fig. 2.5 Fibre/matrix interphase in a composite material. Adapted from Bergeret and Krawczak (2006)

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

2.2 Importance and Role of the Fibre/Matrix Interface

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

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

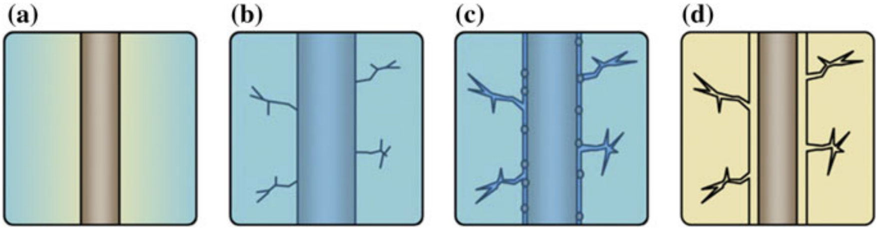


Fig. 2.6 Damage mechanisms likely to occur in lignocellulosic fibres reinforced composites during hydrothermal ageing: **a** Water diffusion into the composite, **b** Swelling of fibres leading to microcracks within the matrix, **c** diffusion of water and possible leaching of water-soluble substances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

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

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

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

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

2.3 Strategies to Control Interfacial Adhesion in Natural Fibre Reinforced Composites

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

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

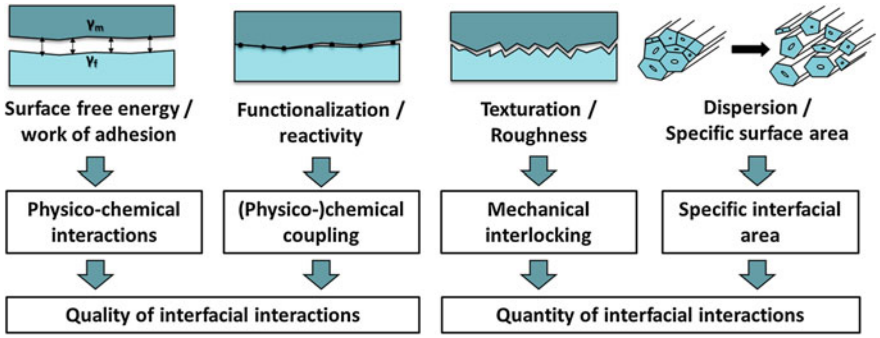


Fig. 2.7 Strategies to control interfacial adhesion in natural fibres based composites

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

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

Concluding, natural fibre reinforced composites are multiple and multi-scale interfaces systems originating from the inter- and intra-cellular cohesion in plant cells and the dispersion state of natural fibres in the polymer matrix. Improving the quantity and the quality of fibre/matrix interface could be achieved by developing specific treatments and processes that would promote fibre dispersion while offering an optimum exposure of reactive and/or functionalized fibre surfaces to the matrix without weakening fibres structure. This constitutes one of the main challenges for the industrial implementation of natural fibre reinforced composites with advanced structural properties. Chapter 3 provides a comprehensive overview of the pre-treatments and functionalization treatments that are used to control the interfacial adhesion in natural fibre reinforced composites.

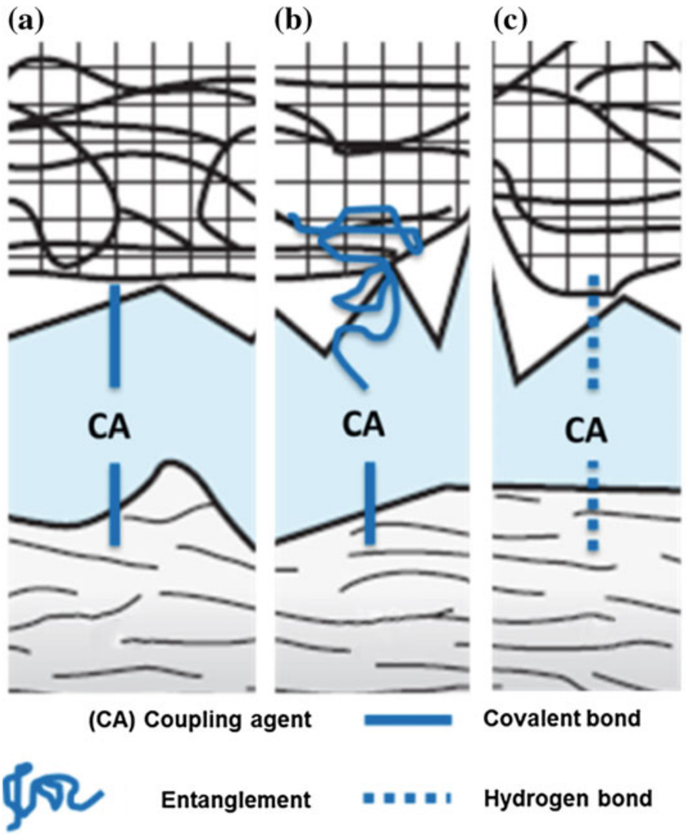


Fig. 2.8 Functionalization strategies to control the physico-chemical coupling between natural fibres and polymer matrices

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

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

One original approach is the surface modification of natural fibres to enhance their electrical conductivity. Razak et al. (2012) modified kenaf fibres by conducting polyaniline via an in situ polymerization approach. The obtained coated fibres achieved new electrical properties, without sacrificing their mechanical properties and natural fibre characteristics. Using another strategy, Trihotri et al. (2013) reported the modification of sisal fibres for the control of electrical properties in epoxy composites. The authors used a silver conducting paint to coat sisal fibres and showed that incorporation of the modified natural fibres in epoxy based composites can significantly enhance their dielectric properties.

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

As concerns the mass transfer properties, it is worth noting that lignocellulosic fibres were rarely used in membrane or food packaging applications to modulate mass transfers of composites. Till now, only a few laboratories are closely interested in the understanding and modelling of the structure/mass transfer properties relationships in composite materials, with the majority of the studies devoted to layered silicate nanocomposites, polymers from fossil resources and/or separating membrane applications. It clearly emerges from this context a need for fundamental researches turned towards the analysis of mass transfers in biocomposites and the development of modelling approaches that consider an increasing complexity of microstructures involving in particular the interfaces. Existing models currently used to predict mass transfers in (nano)composites primarily aim at predicting permeability or diffusivity of the (nano)-composite material from the permeability or diffusivity of each single component (matrix and particle), the particle content and its in situ aspect ratio and orientation within the composites structure. These models usually consider two compartments, i.e. the matrix and the filler, and the three following hypotheses: (i) impermeable (tortuosity-based models) or permeable particles (models for mix of polymers for instance), (ii) perfect adhesion between the filler and the matrix, and (iii) no modification of the mass transfer properties of the matrix induced by the presence of fillers. But in most cases, the third assumption is incompatible with the second one, since the establishment of a strong filler/matrix interphase inevitably induces structural changes of the polymer matrix (cross-linking degree for thermosets, crystallinity degree for semi-crystalline thermoplastics, molecular weight, free volume, etc.). For all aforementioned models, when a deviation between experimental values and values predicted by “two-phase” models is noted, it is generally attributed to the existence of a third phase at the filler/matrix interface, called interphase or interfacial zone, that generally displays different mass transfer properties than the ones of the fillers and the matrix (Wolf et al. 2016). The deviation between experimental and predicted values could also be attributed to changes in mass transfer properties of each individual constituent. Finally, in the case of biocomposites, tortuosity models based on the hypothesis that fillers are impermeable obstacles increasing the diffusion pathway cannot be validated anymore since lignocellulosic particles could be permeable to gases or solutes (and even more than the matrix). As an example, it was shown for PHBV/wheat straw composites that changes in interfacial adhesion induced by the torrefaction of fibres allowed to modulate the water vapour permeability (WVP) of materials. Higher WVP was observed in the case of untreated fibres as compared to torrefied fibres (Berthet et al. 2016a). This was ascribed to the more hydrophobic character of torrefied fibres concomitantly to a tortuosity effect favoured by a better dispersion of fibres and an improved interfacial adhesion with the PHBV. A good knowledge of the fibre/matrix interface is thus fundamental to choose the most appropriate strategy able to modulate the compatibility between the two constituents and the resulting mass transfer properties of the composite material depending on the targeted application. In the field of food packaging, a strong filler/matrix adhesion is not necessary targeted. For example, an increase in gas and water vapour permeability could be preferred in the case of respiring food products such as fresh fruits and vegetable while a barrier material would be required in the case of sandwiches (Berthet et al. 2016b).

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

References

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

Bergeret A, Krawczak P (2006) Liaison renfort/matrice: définition et caractérisation. Techniques de l’ingénieur. Plast Compos AM5305:1–19

Berthet MA, Commandré JM, Rouau X, Gontard N, Angellier-Coussy H (2016a) Torrefaction treatment of lignocellulosic fibres for improving fibre/matrix adhesion in a composite. Mater Design 92:223–232

Berthet MA, Angellier–Coussy H, Guillard V, Gontard (2016b) Vegetal fibre–based biocomposites: which stakes for food packaging applications? J Appl Polym Sci 133:42528

Bismarck A, Aranberry-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, Shenderovich I, Limbach HH (2002) Surface characterization of flax, hemp and cellulose fibers surface properties and the water uptake behaviour. Polym composite 23:872–894

Castellani R, Di Giuseppe E, Beaugrand J, Dobosz S, Berzin F, Vergnes B, Budtova T (2016) Lignocellulosic fiber breakage in a molten polymer. Part 1. Qualitative analysis using rheo–optical observations. Compos Part A Appl S 91:229–237

Cech V, Palesch E, Lukes J (2013) The glass fiber–polymer matrix interface/interphase characterized by nanoscale imaging techniques. Compos Sci Technol 83:22–26

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

Heman MB (2008) Contribution à l'étude des interphases et de leur comportement au vieillissement hygrothermique dans les systèmes à matrice thermodurcissable renforcés de fibres de verre. Thèse de doctorat, Université du sud Toulon–Var, France. http://tel.archives-ouvertes.fr/tel-00348059

Herrera-Franco PJ, Drzal LT (1992) Comparison of methods for the measurement of fibre/matrix adhesion in composites. Composites 23(1):2–27

Hu L, Pasta M, La Mantia FL, Cui L, Jeong S, Deshazer HD, Choi JW, Han SM, Cui Y (2010) Stretchable, porous, and conductive energy textiles. Nano Lett 10:708–714

Ikuta N, Suzuki Y, Maekawa ZI, Hamada H (1993) Investigation of the interphase of a silane-finished glass fibre/vinylester resin using a microscopic. FTi.r. spectrometer. Polymer 34:2445–2446

Kim JK, Sham ML, Wu J (2001) Nanoscale characterisation of interphase in silane treated glass fibre composites. Compos Part A Appl S 32:607–618

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, Van Den Oever M, Budtova T (2011) A statistical analysis of fibre size and shape distribution after compounding in composites reinforced by natural fibres. Compos Part A Appl S 42:1542–1550

Le Moigne N, Longerey M, Taulemesse JM, Bénézet 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

Lvov Y, Wang W, Zhang L, Fakhrullin R (2016) Halloysite clay nanotubes for loading and sustained release of functional compounds. Adv Mater 28:1227–1250

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

Oksman K, Mathew AP, Långström R, Nyström B, Joseph K (2009) The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene. Compos Sci Technol 69:1847–1853

Raj G, Balnois E, Baley C, Grohens Y (2011) Role of polysaccharides on mechanical and adhesion properties of flax fibres in flax/PLA biocomposite. Int J Polym Sci, Article ID, p 503940

Razak SIA, Rahman WAWA, Hashim S, Yahya MY (2012) In situ surface modification of natural fiber by conducting polyaniline. Compos Interfaces 19:365–376

Regazzi A, Corn S, Ienny P, Bénézet JC, Bergeret A (2016) Reversible and irreversible changes in physical and mechanical properties of biocomposites during hydrothermal aging. Ind Crops Prod 84:358–365

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

Trihotri M, Jain D, Dwivedi UK, Khan FH, Malik MM, Qureshi MS (2013) Effect of silver coating on electrical properties of sisal fibre-epoxy composites. Polym Bull 70:3501–3517

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 S 42:66–74

Wolf C, Guillard V, Angellier-Coussy H, Ghizzi D Silva G, Gontard N (2016) Water vapour sorption and diffusion in wheat straw particles and impact on mass transfer properties of biocomposites. J Appl Polym Sci 133:43329

Xia C, Garcia AC, Shi SQ et al (2016) Hybrid boron nitride–natural fiber composites for enhanced thermal conductivity. Sci Rep 6:34726

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

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

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

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

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3_3

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

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

3.1 Pre-treatments of Natural Fibres

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

3.1.1 Retting Treatments

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

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

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

---

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

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

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

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

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

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

3.1.2 Chemical Treatments

Considering the complex structure of natural fibres which is made of various biopolymers and oligomers of varying polarity, they are likely to be sensitive to aqueous and organic solvents. Indeed, changes in the biochemical composition and physico-chemical properties of natural fibres can be observed when they are treated with solvents due the solubilization and partial or total extraction of various intra and inter-cellular components. Even water treatments can induce significant chemical modifications in natural fibres. Bourmaud et al. (2010) studied the influence of water pre-treatments at different temperatures onto flax fibres. The authors showed the extraction of several polysaccharides from the middle lamella even at ambient temperature for long treatment times (72 h). They also found that when the fibres are treated with water at high temperature (105 °C), pectins undergo partial hydrolysis. Based on these results, Le Duigou et al. (2012) showed that a water treatment at ambient temperature (72 h at 23 °C) results in small decrease of fibre properties but a significant improvement in interfacial shear strength (IFSS) with poly(acide L-lactique), due to the removal of weaky bonded components from the fibre surface. Truss et al. (2016) studied the impact of water washing on the evolution of biochemical composition of hemp fibres. The authors found a modification of the surface chemistry of the fibres due to the elimination of cuticle components loosely attached to the surface. Water washing also removed inorganic material and large amounts of nitrogen containing polymers, probably proteins. The analysis of the recovered washing water suggested that the water treatment also removed products from the bulk of the fibres that were not originally on the surface.

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

Among all the chemical pre-treatments, the alkali pre-treatment, also called mercerization, is widely used in the textile industry and consists in treating natural fibres and man-made cellulosic fibres with basic aqueous solutions, generally NaOH. The study of the effect of alkali pre-treatments on natural fibres for polymer composite applications has been widely studied (Chandrasekar et al. 2017). Alkali pre-treatments modify the biochemical composition of natural fibres by the extraction of the different non-cellulosic components from the fibres, such as lignin, pectins or hemicelluloses. The extraction of these components can induce a separation of fibre bundles into elementary fibres or even promote the defibrillation of the latter into cellulose microfibrils. The alkali treatment is also likely to modify the cellulose crystalline structure in natural fibres, depending on the alkali concentration but also on the duration of the treatment and the nature of the alkali reagent used. If the NaOH concentration is high enough (>15–20%w/w in water), the crystalline structure of native cellulose recombines from cellulose I to a more stable crystalline form, called cellulose II, in which the cellulose chains are organized anti-parallel involving changes in the inter- and intra-molecular hydrogen bonding network. This is accompagnied by a significant swelling of the fibres due the diffusion of water molecules into their crystalline structure. Altough being less pronounced as with ethanol or toluene (Acera Fernandez et al. 2016), the removal of some hydrophobic components (waxes, oils…) by alkali pre-treatments can also increase the hydrophylic character of the fibres. It should be pointed out that at very high alkali concentrations (~ 30%w/w in water), a decrease of the cellulose crystallinity and polymerization degrees for jute and flax fibres were observed (Gassan and Bledzki 2001).

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

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

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

3.1.3 Thermal Treatments

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

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

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

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

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

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

3.2 Functionalization of Natural Fibres

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

3.2.1 Chemical Functionalization

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

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

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

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

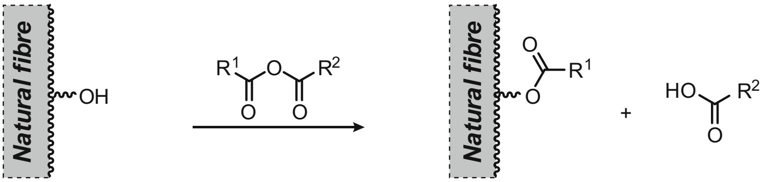


Fig. 3.1 Esterification reaction of lignocellulosic fibres with anhydride

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

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

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

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

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

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

(continued)

Table 3.1 (continued)

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

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

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

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

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

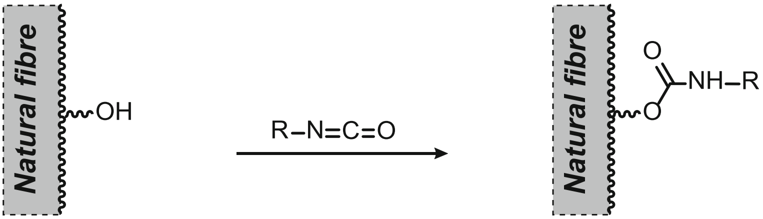


Fig. 3.2 Chemical reaction of isocyanates with hydroxyl groups of natural fibres

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

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

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

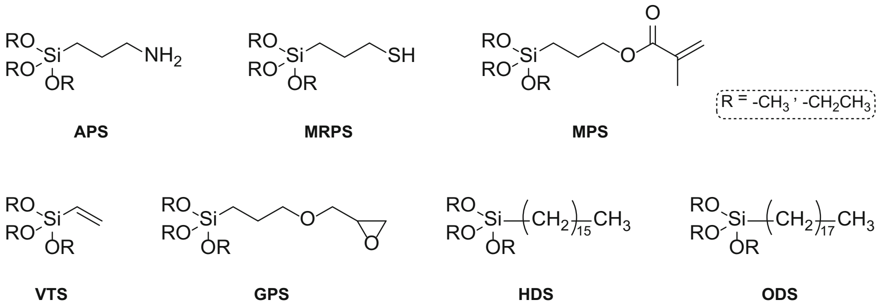


Fig. 3.3 Chemical structure of various organosilanes. APS: γ-aminopropyl trialkoxy silane; MRPS: γ-mercaptopropyl trialkoxy silane; MPS: γ-methacryloxypropyl trialkoxy silane; VTS: vinyl trialkoxy silane; GPS: γ-glycidylpropyl trialkoxy silane; HDS: hexadecyl trialkoxy silane; ODS: octadecyl trialkoxy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

3.2.2 Physical Treatments and Physical–Activated Chemical Functionalization

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

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

Gassan and Gutowski (2000) studied the possibility to increase the polarity of jute fibres by corona treatment (sometimes referred to as air plasma), so as to improve the interfacial adhesion with epoxy matrices. The authors showed that a balance must be found between the increased polarity and the inherent degradation of the fibres under corona discharge. Indeed, corona proved to considerably improve the polar component of the surface tension of jute fibres, but a gradual decrease of their toughness was measured according to the duration and the power corona discharge. Kafi et al. (2011) also showed that an optimal treatment time can be determined for jute fibres treated by atmospheric plasma under helium and mixtures of helium/nitrogen and helium/acetylene. Indeed, the authors showed that the removal of waxes and pectins at the fibre surface by plasma treatment can increase their hydrophilicity and kinetics of water absorption up to 10 s of exposure, longer exposure times having no more effect due to the total removal of waxes. Flexural strength and modulus as well as interfacial laminar shear strength (ILSS) of polyester/jute composite laminates were also significantly improved due to changes in the surface chemistry and roughness of the fibres. According to Pizzi et al. (2009), the mechanical properties of lignin-based matrices reinforced by non-woven flax and hemp fabrics can be significantly enhanced if exposing the fabrics to corona treatments during 5 to 15 min. This was explained by the increased roughness of the fibres, and so enhanced mechanical interlocking with the matrix. However, longer treatment times led to a severe degradation of the fibres and a reduction in tensile strength of the composites. Bozaci et al. (2013) modified flax fabrics by plasma treatments under air and argon. The authors also observed changes in surface physico-chemistry as well as an increased fibre surface roughness after treatment. Despite a gradual decrease of fabric strength related to an etching effect with increasing plasma power, the interfacial adhesion with high density polyethylene (HDPE) and an unsaturated polyester resin was improved as demonstrated by micromechanical pull-out tests. An increase in IFSS of 26 and 40% with HDPE and 47 and 30% with unsaturated polyester was obtained for plasma treatments under air and argon, respectively. This highlights the critical role of processing gases that should be tailored according to the matrix. In this study, the modification of O/C ratio resulting from the oxydation of the fibres under air plasma was found as being a key factor in the case of unsaturated polyester, while the greater surface roughness obtained with argon plasma was more beneficial in the case of HDPE due to enhanced mechanical interlocking. A study on ramie/polypropylene composites showed that fibre roughness can be increased with the time of exposure to atmospheric helium plasma, thus significantly improving their specific surface area and mechanical interlocking with the matrix (Li et al. 2013). Similarly, Ragoubi et al. (2010) also assumed that the increase in mechanical properties (13% on Young's modulus and 32% on maximum strength) observed for PP/20% hemp fibres treated with corona was related to an enhanced fibre roughness and improvement in mechanical interlocking. In another study, comparing PLA/miscanthus and PP/miscanthus composites, the authors showed that this increase in roughness observed by Scanning Electron Microscopy (SEM) was accompanied by a surface oxidation of the fibres. Indeed, X-ray Photoelectron Spectroscopy (XPS) analyzes showed an increase in the concentration of functional groups, i.e. carbonyl, hydroxyl, carboxyl, at the fibre surface, likely to favour the physico-chemical interactions with the PLA matrix (Ragoubi et al. 2012). The work of Li et al. (2013) suggested that the pre-treatment of ramie fibres with ethanol could act in synergy with an atmospheric helium plasma treatment by grafting CH_3 groups at fibre surface, and results in a reduced hydrophilicity of the fibres. Better compatibility with polypropylene matrix and improved tensile properties of the composites were achieved due to improved mechanical and physico-chemical interactions between the fibres and the matrix. Other works were conducted on the effect of atmospheric pressure plasma in cellulose–acetate–butyrate reinforced with lignocellulosic fibres (abaca, flax, hemp and sisal) and led to the same conclusions (Baltazar-y-Jimenez et al. 2008a, b).

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

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

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

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

3.2.3 Incorporation of Amphoteric Compatibilizers

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

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

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

3.3 Treatment Processes

One of the major challenges in the treatment of natural fibres for composite applications is the development of efficient and reliable treatment processes taking into account industrial feasibility. Several issues must thus be considered as the scale-up of the process, the development of discontinuous or continuous processes, compatibility with REACH policy, the use of bio-based resources, investments, running costs…. The search for clean, solvent-free processes that use minimal energy and water is also a critical issue. These treatment processes must allow the fast and homogeneous functionalization of natural fibres so as to control their surface morphological and physico-chemical properties, and thus to decrease the variability in physical properties often blamed to biocomposites while improving their performances. Widely explored and optimized for technical glass fibres, various wet and dry processes have been developed on an industrial scale. In the remainder of this chapter, attention will be devoted to the various wet (liquid and vapour phase, supercritical fluids) and dry (reactive extrusion, dry-blending and powder impregnation) treatment processes that have been studied at lab-scale or even at pilot-scale in the case of natural fibres. It is worth noted that these treatment processes use for applying functionalizing molecules on natural fibres could be combined with physical treatments such as plasma or irradiation in order to promote an efficient and fast grafting of molecules.

3.3.1 Wet Treatment Processes

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

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

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

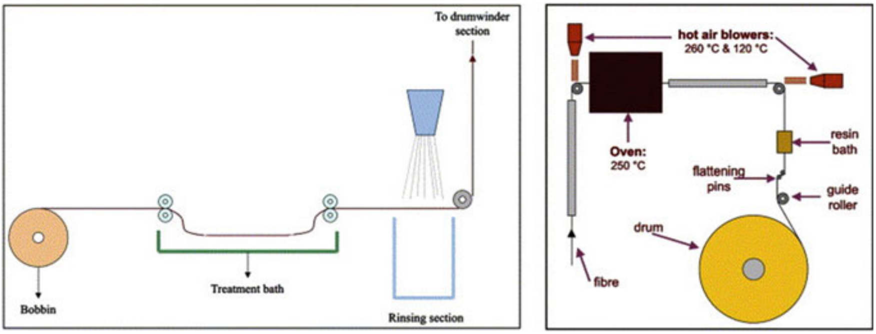


Fig. 3.4 Sketch of the treatment section and the successive drying section in the fully continuous production set-up. Reprinted from Van de Weyenberg et al. (2006), Fig. 5 with permission from Elsevier

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

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

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

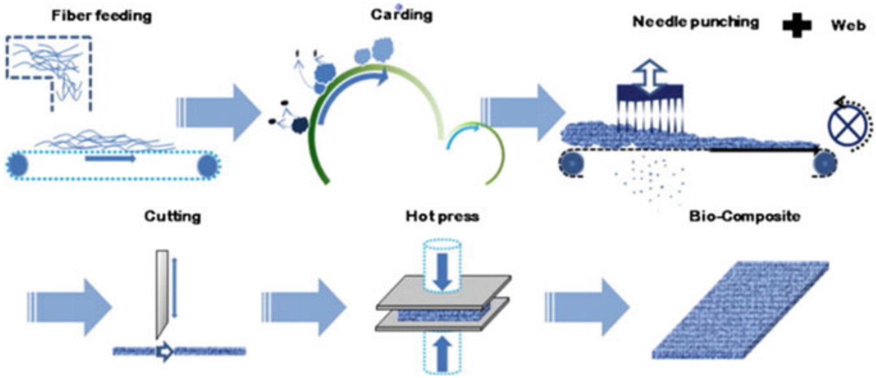


Fig. 3.5 Carding process for the manufacturing of PLA/Kenaf bio-composite panels. Reprinted from Lee et al. (2009), Fig. 1 with permission from Elsevier

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

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

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

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

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

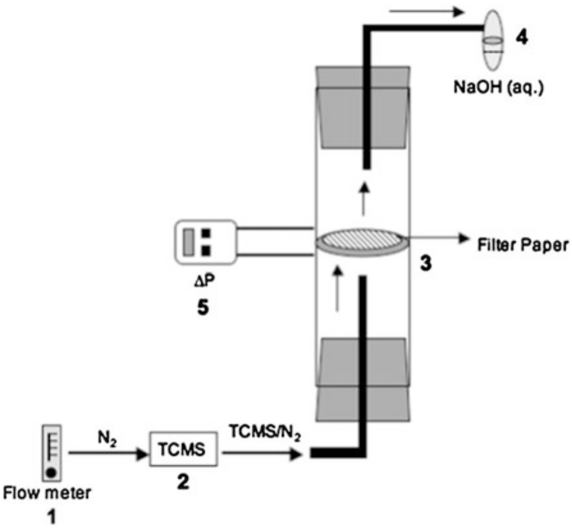


Fig. 3.6 Schematic representation of the vapour deposition process assisted by nitrogen gas used to treat cellulose substrate with TCMS. Reprinted from Cunha et al. (2010), Fig. 2 with permission from Elsevier

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

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

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

3.3.2 Dry Treatment Processes

Dry treatment processes consist in functionalizing and compatibilizing natural fibres with the matrix during the composites preparation, either by means of reactive processes, in particular reactive extrusion used for the compounding of short natural fibres based composites, or by the pre-impregnation of natural fibres with the polymer matrix and the coupling agent using dry-blending or powder impregnation processes.

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

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

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

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

Dry-blending consists in the preparation of pre-mixes of natural fibres, polymer matrix and additives in powder form. One simple method is to use a high-speed mixer at controlled temperature to prepare a pre-compound of polymer-coated fibres in view of its subsequent processing. This technique is often used for the production of PVC/wood fibres mixtures (Sombatsompop et al. 2003; Matuana et al. 2001), before they are melt-blended in an extruder. Besides the incorporation of several additives during dry-blending (stabilizers, lubricants, $CaCO_3$, TiO_2), Matuana et al. (2001) reported the possibility to add an aminosilane coupling agent (APS) in the formulation so as to improve interfacial adhesion between PVC matrix and wood fibres. Ayrilmis et al. (2011b) have also used this process to prepare pre-compounds of PP/coconut fibres compatibilized with different amounts of MAPP powders, and manufacture mats that were thermocompressed to obtain composite panels for automotive interior applications. The authors emphasized the industrial benefit to combine dry-blending and thermocompression in terms of costs and productivity compared to conventional extrusion and injection processes. Ayrilmis et al. (2011b) and Mohanty et al. (2002) also argued that dry-blending is less degrading for natural fibres structure, since they do not undergo high shearing during processing as in extrusion and injection moulding.

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

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

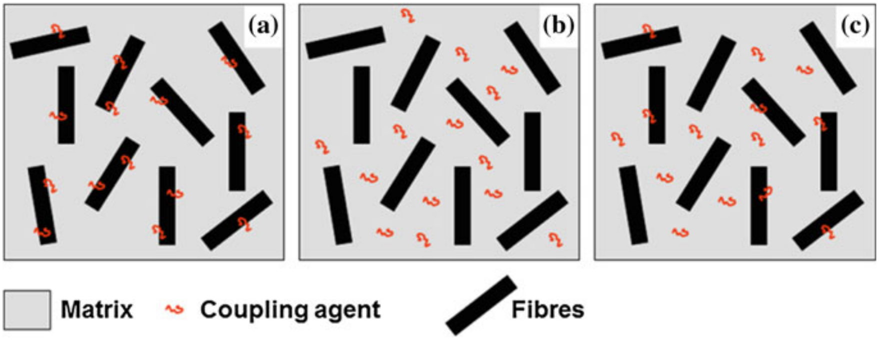


Fig. 3.7 Possible localization of the coupling agent molecules within the composite microstructure after reactive compounding. **a** All the molecules diffuse at the interface and are grafted on the fibres; **b** all the molecules stay free in the matrix; **c** only a part of the molecules diffuse at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

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

3.4 Concluding Remarks

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

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

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

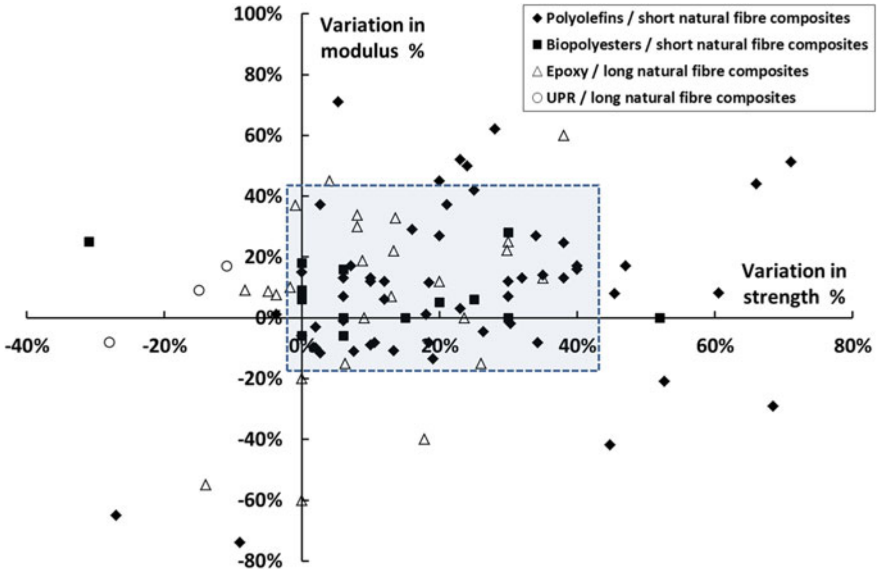


Fig. 3.8 Ashby plot—variation in modulus versus variation in strength of natural fibre reinforced composites consecutive to pre-treatments and/or functionalization of natural fibres. Non-exhaustive set of data taken from literature for polyolefins and biopolyesters/short fibre composites (tensile properties) and epoxy and unsaturated polyester (UPR) resins/long fibre composites (flexural or tensile properties)

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

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

References

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

Akin DE, Gamble GR, Morrison WH III, Rigsby LL, Dodd RB (1996) Chemical and structural analysis of fibre and core tissues from flax. J Sci Food Agric 72:155–165

Arbelaiz A, Fernandez B, Cantero G, Llano-Ponte R, Valea A, Mondragon I (2005) Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization. Compos Part A Appl S 36:1637–1644

Arputharaj A, Raja ASM, Saxena S (2016) Developments in Sustainable Chemical Processing of Textiles. In: Muthu SS, Gardetti MA (eds) Green fashion, environmental footprints and eco–design of products and processes. Springer, Singapore, pp 217–252

Arthur JC (1971) Reactions Induced by High-Energy Radiation. In: Bikales NM, Segal L (eds) High polymers: cellulose and cellulose derivatives. Wiley-Interscience, New York, pp 937–975

Ayrilmis N, Jarusombuti S, Fueangvivat V, Bauchongkol P (2011a) Effect of thermal–treatment of wood fibres on properties of flat–pressed wood plastic composites. Polym Degrad Stabil 96:818–822

Ayrilmis N, Jarusombuti S, Fueangvivat V, Bauchongkol P, White RH (2011b) Coir fiber reinforced polypropylene composite panel for automotive interior applications. Fiber Polym 12:919–926

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

Baiardo M, Zini E, Scandola M (2004) Flax fibre–polyester composites. Comp Part A– Appl Sci 35:703–710

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

Baltazar-y-Jimenez A, Juntaro J, Bismarck A (2008a) Effect of atmospheric air pressure plasma treatment on the thermal behaviour of natural fibres and dynamical mechanical properties of randomly–oriented short fibre composites. J Biobased Mater Bioenergy 2(3):264–272

Baltazar-y-Jimenez A, Bistritz M, Schulz E, Bismarck A (2008b) Atmospheric air pressure plasma treatment of lignocellulosic fibres: impact on mechanical properties and adhesion to cellulose acetate butyrate. Compos Sci Technol 68(1):215–227

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

Bergeret A, Krawczak P (2006) Liaison renfort/matrice: définition et caractérisation. Techniques de l'Ingénieur, Plastiques et Composites AM 5305:1–19

Berlioz S, Stinga C, Condoret J, Samain D (2008) Novel principle of chemical grafting for cellulose. Int J Chem React Eng 6(1):1542–6580

Berthet MA, Commandré JM, Rouau X, Gontard N, Angellier-Coussy H (2016) Torrefaction treatment of lignocellulosic fibres for improving fibre/matrix adhesion in a biocomposites. Mater Design 92:223–232

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

Bouchard J, Méthot M, Jordan B (2006) The effects of ionizing radiation on the cellulose of woodfree paper. Cellulose 13:601–610

Bourmaud A, Riviere J, Le Duigou A, Raj G, Baley C (2009) Investigations of the use of a mussel-inspired compatibilizer to improve the matrix-fiber adhesion of a biocomposite. Polym Test 28:668–672

Bourmaud A, Morvan C, Baley C (2010) Importance of fiber preparation to optimize the surface and mechanical properties of unitary flax fiber. Ind Crops Prod 32:662–667

Bouzouita S, Salvia M, Ben Daly H, Dogui A, Forest E (2010) Effect of fiber treatment on fiber strength and fiber/matrix interface of hemp reinforced polypropylene composites. Adv Mater Res 112:1–8

Bouzouita S (2011) Optimisation des interfaces fibre–matrice de composites à renfort naturel. Thèse de doctorat, Ecole Centrale de Lyon (France) – Ecole Nationale d'Ingénieurs de Monastir (Tunisia)

Bozaci 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 adhesion between fiber–matrix for composite materials. Compos Part B Eng 45:565–572

Brown AE, Sharma HSS, Black DLR (1986) Relationship between pectin content of stems of flax cultivars, fungal cell wall–degrading enzymes and pre–harvest retting. Ann Appl Biol 109:345–351

Calabia BP, Ninomiya F, Yagi H, Oishi A, Taguchi K, Kunioka M, Funabashi M (2013) Biodegradable Poly(butylene succinate) composites reinforced by cotton fiber with silane coupling agent. Polymer 5(1):128–141

Chandrasekar M, Ishak MR, Sapuan SM, Leman Z, Jawaid M (2017) A review on the characterisation of natural fibres and their composites after alkali treatment and water absorption. Plast, Rubber Compos 46:119–136

Choi H, Han S, Lee J (2009) The effects of morphological properties of henequen fiber irradiated by EB on the mechanical and thermal properties of henequen fiber/PP composites. Compos Interfaces 16:751–768

Credou J, Berthelot T (2014) Cellulose: from biocompatible to bioactive material. J Mater Chem B 2:4767–4788

Cunha AG, Freire C, Silvestre A, Pascoal Neto C, Gandini A, Belgacem MN, Chaussy D, Beneventi D (2010) Preparation of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas–solid reaction. J Colloid Interf Sci 344:588–595

Cunha AG, Gandini A (2010) Turning polysaccharides into hydrophobic materials: a critical review. Part 1. Cellulose. Cellulose 17:875–889

Dogan SD, Tayfun U, Dogan M (2016) New route for modifying cellulosic fibres with fatty acids and its application to polyethylene/jute fibre composites. J Compos Mater 50(18):2477–2485

Driscoll M, Stipanovic A, Winter W, Cheng K, Manning M, Spiese J, Galloway RA, Cleland MR (2009) Electron beam irradiation of cellulose. Radiat Phys Chem 78:539–542

Fages J (2003) Powder processing using supercritical fluids. In: Bonnaudin N, Cansell F, Fouassier O (eds) Supercritical fluids & materials, ISASF, pp 33–85

Faruk O, Bledzki A, Fink HP, Sain M (2012) Biocomposites reinforced with natural fibers: 2000–2010. Prog Polym Sci 37:1552–1596

Faruk O, Bledzki A, Fink HP, Sain M (2014) Progress report on natural fiber reinforced composites. Macromol Mater Eng 299:9–26

Flax Technic® (2017) TwinFlax products. http://www.flaxtechnic.fr/en/products/twinflax/. Accessed 6 Feb 2017

Freire CSR, Silvestre AJD, Neto CP, Belgacem MN, Gandini A (2006) Controlled heterogeneous modification of cellulose fibers with fatty acids: effect of reaction conditions on the extent of esterification and fiber properties. J Appl Polym Sci 100:1093–1102

Freire CSR, Silvestre AJD, Neto CP, Gandini A, Martin L, Mondragon I (2008) Composites based on acylated cellulose fibers and low–density polyethylene: Effect of the fiber content, degree of substitution and fatty acid chain length on final properties. Compos Sci Technol 68:3358–3364

Gaiolas C, Amaral ME, Costa AP, Silva MJS, Belgacem MN (2012) Cold–plasma assisted grafting of cellulose fibres by acrylic monomers. AIP Conf Proc 1459:296–299

Gassan J, Gutowski VS (2000) Effects of corona discharge and UV treatment on the properties of jute–fibre expoxy composites. Compos Sci Technol 60:2857–2863

Gassan J, Bledzki AK (2001) Thermal degradation of flax and jute fibers. J Appl Polym Sci 82:1417–1422

George J, Ivens J, Verpoest I (1999) Mechanical properties of flax fibre reinforced epoxy composites. Angew Makromol Chem 272:41–45

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

Gironès J, Pimenta MTB, Vilaseca F, Carvalho AJF, Mutjé P, Curvelo AAS (2008) Blocked diisocyanates as reactive coupling agents: application to pine fiber polypropylene composites. Carbohydr Polym 74:106–113

González D, Santos V, Parajo JC (2012) Silane–treated lignocellulosic fibers as reinforcement material in polylactic acid biocomposites. J Thermoplastic Compos Mater 25(8):1005–1022

Gourier C, Le Duigou A, Bourmaud A, Baley C (2014) Mechanical analysis of elementary flax fibre tensile properties after different thermal cycles. Compos Part A Appl S 64:159–166

Graupner N (2008) Application of lignin as natural adhesion promoter in cotton fibre–reinforced poly(lactic acid) (PLA) composites. J Mater Sci 43:5222–5229

Graupner N, Fischer H, Ziegmann G, Müssig J (2014) Improvement and analysis of fi–bre/matrix adhesion of regenerated cellulose fibre reinforced PP-, MAPP- and PLA-composites by the use of Eucalyptus globulus lignin. Compos Part B Eng 66:117–125

Hakkou M, Pétrissans M, Gérardin P, Zoulalian A (2005a) Wettability of heat–treated wood. Holzforschung 59:35–37

Hakkou M, Pétrissans M, Gérardin P, Zoulalian A (2005b) Investigations of the reasons for fungal durability of heat–treated beech wood. Polym Degrad Stabil 91:393–397

Hakkou M, Pétrissans M, Zoulalian A, Gérardin P (2005c) Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. Polym Degrad Stabil 89:1–5

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

Han Y, Han S, Cho D, Kim H (2006b) Henequen/unsaturated polyester biocomposites: electron beam irradiation treatment and alkali treatment effects on the henequen fiber. Macromol Symp 245–246:539–546

Han Y, Han S, Cho D, Kim H (2007) Kenaf/polypropylene biocomposites: effects of electron beam irradiation and alkali treatment on kenaf natural fibers. Compos Interface 14:559–578

Hassaini L, Kaci M, Touati N, Pillin I, Kervoelen A, Bruzaud S (2017) Valorization of olive husk flour as filler for biocomposites based on poly(3–hydroxybutyrate–co–3–hydrixyvalerate): Effects of silane treatment. Polym Testing 59:430–440

Hijazi N (2014) Développement de composites nanostructurés à base de biopolyesters et de nanoparticules de chitosane générées par des procédés assistés par CO_2 supercritique. Thèse de doctorat, Ecole des Mines Albi-Carmaux, France

Hil CAS, Abdul Khalil HPS, Hale MD (1998) A study of the potential of acetylation to improve the properties of plant fibres. Ind Crops Prod 8:53–63

Hill CAS (2006) Thermal Modification of Wood. Wood modification: chemical, thermal and other processes. John Wiley & Sons Ltd, Chichester, UK, pp 99–127

Hutton BH, Parker IH (2009) A surface study of cellulose fibres impregnated with alkyl ketene dimers via subcritical and supercritical carbon dioxide. Colloids Surface A 334:59–65

Hutton BH, Shen W (2005) Sizing effects via AKD vaporization. Appita J 58:367–373

Iller E, Kukiełka A, Stupińska H, Mikołajczykc W (2002) Electron–beam stimulation of the reactivity of cellulose pulps for production of derivatives. Radiat Phys Chem 63:253–257

Javadi A, Srithep Y, Pilla S, Lee J, Gong S, Turng LS (2010) Processing and characterization of solid and microcellular PHBV/coir fiber composites. Mater Sci Eng C30:749–757

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

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

Kalia S, Kaith BS, Kaur I (2009) Pretreatments of natural fibers and their application as reinforcing material in polymer composites—a review. Polym Eng Sci 49:1253–1272

Kazayawoko M, Balatinecz JJ, Matuana LM (1999) Surface modification and adhesion mechanisms in woodfiber–polypropylene composites. J Mater Sci 34:6189–6199

Khan F (2005) Characterization of methyl methacrylate grafting onto preirradiated biodegradable lignocellulose fiber by γ–radiation. Macromol Biosci 5:78–89

Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998) Comprehensive cellulose chemistry. Wiley–VCH, Weinheim

Kodama Y, Barsbay M, Güven O (2014) Radiation–induced and RAFT–mediated grafting of poly (hydroxylethyl methacrylate) (PHEMA) from cellulose surfaces. Radiat Phys Chem 94:98–104

Kuzuya M, Matsuno Y, Yamashiro T, Tsuiki M (1997) Electron spin resonance study on plasma Induced surface radicals of pol(ethylene naphthalate). Plasmas Polym 2:79–89

Kuzuya M, Niwa J, Ito H (1993) Nature of plasma–induced surface radicals of powdered polyethylene studied by electron spin resonance. Macromolecules 26:1990–1995

Kuzuya M, Yamashiro T, Kondo SI, Sugito M, Mouri M (1998) Plasma–induced surface radicals of low–density polyethylene studied by electron spin resonance. Macromolecules 31:3225–3229

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

Lefeuvre A, Le Duigou A, Bourmaud A, Kervoelen A, Morvan C, Baley C (2015) Analysis of the role of the main constitutive polysaccharides in the flax fibre mechanical behaviour. Ind Crops Prod 76:1039–1048

Le Moigne N, Budtova T, Van den Oever M (2013) Dynamic and capillary shear rheology of natural fiber–reinforced composites. Polym Eng Sci 53(12):2582–2593

Le Moigne N, Longerey M, Taulemesse JM, Bénézet 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

Le Moigne N, Sonnier R, El Hage R (2017) Radiation–induced modifications in natural fibres and their biocomposites: Opportunities for controlled physico–chemical modification pathways? Indus Crop Prod 109:199–213

Lee SH, Wang S (2006) Biodegradable polymers/bamboo fiber biocomposites with bio-based coupling agent. Compos Part A Appl Sci 37(1):80–91

Lee BH, Kim HS, Lee S, Kim HJ, Dorgan JR (2009) Bio-composites of kenaf fibers in polylactide: role of improved interfacial adhesion in the carding process. Compos Sci Technol 69:2573–2579

Li Y, Hu C, Yu Y (2008) Interfacial studies of sisal fiber reinforced high density polyethylene (HDPE) composites. Compos Part A– Appl Sci 39:570–578

Li Y, Pickering KL (2008) Hemp fibre reinforced composites using chelator and enzyme treatments. Compos Sci Technol 68:3293–3298

Li Y (2009) Processing of hemp fibre using enzyme/fungal treatment for composites. PhD dissertation, University of Waikato, New–Zealand

Li Y, Pickering KL, Farrell RL (2009) Analysis of green hemp fibre reinforced composites using bag retting and white rot fungal treatments. Ind Crops Prod 29:420–426

Li Y, Moyo S, Ding Z, Shan Z, Qiu Y (2013) Helium plasma treatment of ethanol–pretreated ramie fabrics for improving the mechanical properties of ramie/polypropylene composites. Ind Crops Prod 51:299–305

Loow YL, Wu TY, Yang GH, Jahim JMd, Teoh WH, Mohammad AW (2016) Role of energy irradiation in aiding pretreatment of lignocellulosic biomass for improving reducing sugar recovery. Cellulose 23:2761–2789

Lu JZ, Qing Lin W, McNabb HS (2000) Chemical coupling in wood fibre and polymer composites: a review of coupling agents and treatments. Wood Fibre Sci 32(1):88–104

Lu T, Liu S, Jiang M, Xu X, Wang Y, Wang Z, Gou Jan, Hui D, Zhou Z (2014) Effects of modifications of bamboo cellulose fibers on the improved mechanical properties of cellulose reinforced poly (lactic acid) composites. Comp Part B Eng 62:191–197

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

Majeed K, Jawaid M, Hassan A, Bakar AA, Khalil HA, Salema AA, Inuwa I (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Design 46:391–410

Marduel J (2003) Procédé et dispositif d'imprégnation d'un réseau fibreux par de la poudre utilisant un champ électrostatique alternatif. Brevet EP 1526214:A1

Martin N, Mouret N, Davies P, Baley C (2013) Influence of the degree of retting of flax fibers on the tensile properties of single fibers and short fiber/polypropylene composites. Ind Crops Prod 49:755–767

Matuana LM, Kamdem DP, Zhang J (2001) Photoaging and stabilization of rigid PVC/Wood–Fiber composites. J Appl Polym Sci 80:1943–1950

Meijer WJM, Vertregt N, Rutgers B, Van de Waart M (1995) The pectin content as a measure of the retting and rettability of flax. Ind Crops Prod 4:273–284

Moczo J, Pukanszky B (2008) Polymer micro and nanocomposites: structure, interactions, properties. J Ind Eng Chem 14:535–563

Mohanty AK, Drzal LT, Misra M (2002) Novel hybrid coupling agent as an adhesion promoter in natural fiber reinforced powder polypropylene composites. J Mater Sci Lett 21:1885–1888

Mohanty S, Nayak SK, Verma SK, Tripathy SS (2004) Effect of MAPP as a coupling agent on the performance of jute–PP composites. J Reinforced Plastics Compos 23:625–637

Mohanty S, Verma SK, Nayak SK (2006) Rheological characterization of HDPE/jute composite melts. J Appl Polym Sci 99:1476–1484

Nachtigall SMB, Cerveira GS, Rosa SML (2007) New polymeric–coupling agent for polypropylene/wood–flour composites. Polym Test 26:619–628

Nguila–Inari G (2008) Contribution à la compréhension des modifications moléculaires et macromoléculaires intervenant lors du traitement thermique du bois– Effet sur la réactivité chimique et sur la durabilité du matériau. Thèse de doctorat, Université Henri–Poincaré, Nancy–I, France

Ohkita T, Lee SH (2004) Effect of aliphatic isocyanates (HDI and LDI) as coupling agents on the properties of eco–composites from biodegradable polymers and corn starch. J Adhes Sci Technol 18:905–924

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

Paridah MT, Amel BA, Syeed OASA, Zakiah A (2011) Review of bast fiber retting. Bioresources 6:5260–5281

Paridah MT, Khalina A (2009) Effect of soda retting on the tensile strength of kenaf (*Hibiscus cannabinus* L.) bast fibres. Project Report Kenaf EPU

Petinakis E, Yu L, Edward G, Dean K, Liu H, Scully A (2009) Effect of matrix-particle interfacial adhesion on the mechanical properties of poly (lactic acid)/wood–flour micro-composites. J Polym Environ 17:83–94

Pickering KL, Abdalla A, Ji C, McDonald AG, Franich RA (2003) The effect of silane coupling agents on radiata pine fibre for use in thermoplastic matrix composites. Compos Part A Appl Sci 34(10):915–926

Pizzi A, Kueny R, Lecoanet F, Massetau B, Carpentier D, Krebs A, Loiseau F, Molina S, Ragoubi M (2009) High resin content natural matrix–natural fibre biocomposites. Ind Crops Prod 30:235–240

Placet V (2009) Characterization of the thermo–mechanical behaviour of Hemp fibres intended for the manufacturing of high performance composites. Compos Part A Appl S 40:1111–1118

Ponomarev AV, Ershov BG (2014) Radiation-induced high–temperature conversion of cellulose. Molecules 19:16877–16908

Popescu MC, Totolin M, Tibirna CM, Sdrobis A, Stevanovic T, Vasile C (2011) Grafting of softwood kraft pulps fibers with fatty acids under cold plasma conditions. Int J Biol Macromol 48:326–335

Rachini A, Mougin G, Delalande S, Charmeau JY, Barrès C, Fleury E (2012) Hemp fibers/polypropylene composites by reactive compounding: Improvement of physical properties promoted by selective coupling chemistry. Polym Degrad Stabil 97:1988–1995

Ragoubi M, Bienaim D, Molina S, George B, Merlin A (2010) Impact of corona treated hemp fibres onto mechanical properties of polypropylene composites made thereof. Ind Crops Prod 31:344–349

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 S 43:675–685

Reulier M, Perrin R, Averous L (2016) Biocomposites based on chemically modified cellulose fibers with renewable fatty–acid–based thermoplastic systems: Effect of different fiber treatments. J Appl Polym Sci Article number 43878

Reux F, Verpoest I (eds) (2012) Flax and hemp fibres: a natural solution for the composite industry. JEC Composites, Paris

Rozman HD, Tay GS, Kumar RN, Abusamah A, Ismail H, Mohd Ishak ZA (2001) Polypropylene–oil palm empty fruit bunch–glass fibre hybrid composites : a preliminary study on the flexural and tensile properties. Eur Polym J 37:1283–1291

Saba N, Tahir PM, Jawaid M (2014) A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. Polymers 6(8):2247–2273

Sahoo S, Misra M, Mohanty AK (2011) Enhanced properties of lignin–based biodegradable polymer composites using injection moulding process. Compos Part A Appl S 42:1710–1718

Sahoo S, Misra M, Mohanty AK (2013) Effect of compatibilizer and fillers on the properties of injection molded lignin–based hydrid green composites. J Appl Polym Sci 4110–4121

Sahoo S, Misra M, Mohanty AK (2014) Biocomposites from switchgrass and lignin hydrid and poly(butylene succinate) bioplastic: Studies on reactive compatibilisation and performance evaluation. Macromol Mater Eng 299:178–189

Schmid M, Benz A, Stinga C, Samain D (2012) Zeyer KP (2012) Fundamental investigations regarding barrier properties of grafted PVOH layers. Int J Polym Sci 637837(1–637837):6

Scrubar WV, Pilla S, Wright ZC, Ryan CA, Greene JP (2012) Mechanisms and impact of fiber–matrix compatibilization techniques on the material characterization of PHBV/oak wood flour engineered biobased composites. Compos Sci Technol 72:708–715

Sharif J, Mohamad S, Othman N, Bakaruddin N, Osman H, Güven O (2013) Graft copolymerization of glycidyl methacrylate onto delignified kenaf fibers through pre–irradiation technique. Radiat Phys Chem 91:125–131

Sharma HSS (1987) Studies on chemical and enzyme retting of flax on a semi–industrial scale and analysis of the effluents for their physico–chemical components. Int Biodeterior 23:329–342

Sivonen H, Maunu SL, Sundholm F, Jamsa S, Viitaniemi P (2002) Magnetic resonance studies of thermally modified wood. Holzforschung 56:648–654

Snijder MHB, Bos HL (2000) Reinforcement of polypropylene by annual plant fibers: optimisation of the coupling agent efficiency. Compos Interface 7:69–75

Sombatsompop N, Chaochanchaikul K, Phromchirasuk C, Thongsang S (2003) Effect of wood sawdust content on rheological and structural changes, and thermo–mechanical properties of PVC/sawdust composites. Polym Int 52:1847–1855

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

Stinga NC (2008) Utilisation de la chimie chromatogénique pour la conception et la réalisation de matériaux cellulosiques barrières à l’eau, aux graisses et aux gaz. Thèse de doctorat, Université Joseph Fourier – Grenoble 1, France

Takács E, Wojnárovits L, Borsa J, Cs Földváry, Hargittai P, Zöld O (1999) Effect of γ–irradiation on cotton–cellulose. Radiat Phys Chem 55:663–666

Takács E, Wojnarovits L, Borsa J, Papp J, Hargittai P, Korecz L (2005) Modification of cotton–cellulose by preirradiation grafting. Nucl Instr and Meth in Phys Res B 236:259–265

Thomason JL (ed) (2013) Glass fibre sizings. a review of the scientific literature. Self–published

Torres FG, Cubillas ML (2005) Study of the interfacial properties of natural fibre reinforced polyethylene. Polym Test 24:694–698

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

Tserki V, Matzinos P, Zafeiropoulos NE, Panayiotou C (2006) Development of biodegradable composites with treated and compatibilized lignocellulosic fibres. J Appl Polym Sci 100 (6):4703–4710

Twite-Kabamba E, Mechraoui A, Rodrigue D (2009) Rheological properties of polypropylene/ hemp fiber composites. Polym Compos 30:1401–1407

Van de Velde K, Baetens E (2001) Thermal and mechanical properties of flax fibres as potential composite reinforcement. Macromol Mat Eng 286:342–349

Van de Weyenberg I, Ivens J, De Coster A, Kino B, Baetens E, Verpoest I (2003) Influence of processing and chemical treatment of flax fibres on their composites. Compos Sci Technol 63:1241–1246

Van de Weyenberg I, Chi Truong T, Vangrimde B, Verpoest I (2006) Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment. Compos Part A Appl S 37:1368–1376

Van Sumere CF (1992) Retting of flax with special reference to enzyme retting. Sharma HSS. The biology and processing of flax. M Publications, Belfast, pp 157–198

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

Yan L, Chouw N, Yuan X (2012) Improving the mechanical properties of natural fibre fabric reinforced epoxy composites by alkali treatment. J Reinf Plast Compos 31:425–437

Yildiz S (2002) Physical, mechanical, technological and chemical properties of beech and spruce wood treated by heating. PhD dissertation, Karadeniz Technical University, Turkey

Yildiz S, Gümüskaya E (2007) The effects of thermal modification on crystalline structure of cellulose in soft and hardwood. Build Environ 42:62–67

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. Compos Part A Appl Sci 41(4):499–505

Zafeiropoulos NE (ed) (2011) Interface engineering of natural fibre composites for maximum performance. Woodhead Publishing Limited

Zafeiropoulos NE, Williams DR, Baillie CA, Matthews FL (2002a) Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part I. Development and investigation of surface treatments. Compos Part A Appl S 33:1083–1093

Zafeiropoulos NE, Baillie CA, Hodgkinson JM (2002b) Engineering and characterisation of the interface in flax fibre/polypropylene composite materials, Part II. The effect of surface treatments on the interface, Compos Part A Appl Science 33:1185–1190

Zhang H, Kannangara D, Hilder M, Ettl R, Shen W (2007) The role of vapour deposition in the hydrophobization treatment of cellulose fibres using alkyl ketene dimers and alkenyl succinic acid anhydrides. Colloid Surface A 297:203–210

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 Q, Greffe L, Baumann MJ, Malmstro E, Teeri TT, Brumer H III (2005) Use of xyloglucan as a molecular anchor for the elaboration of polymers from cellulose surfaces: a general route for the design of biocomposites. Macromolecules 38:3547–3549

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

Zini E, Baiardo M, Armelao L, Scandola M (2004) Biodegradable polyesters reinforced with surface-modified vegetable fibers. Macromolecul Biosci 4:286–295

Zini E, Focarete ML, Noda I, Scandola M (2007) Bio-composite of bacterial poly(3–hydroxybutyrate–co–3–hydroxyhexanoate) reinforced with vegetable fibers. Compos Sci Technol 67:2085–2094

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

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3_4

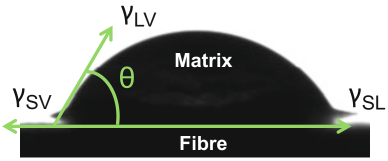


Fig. 4.1 Schematic representation of the contact angle θ, the surface free energy γ_{SV} of the solid, the surface tension γ_{LV} of the reference liquid and the interfacial tension γ_{SL} between solid and liquid on a sessile drop

(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

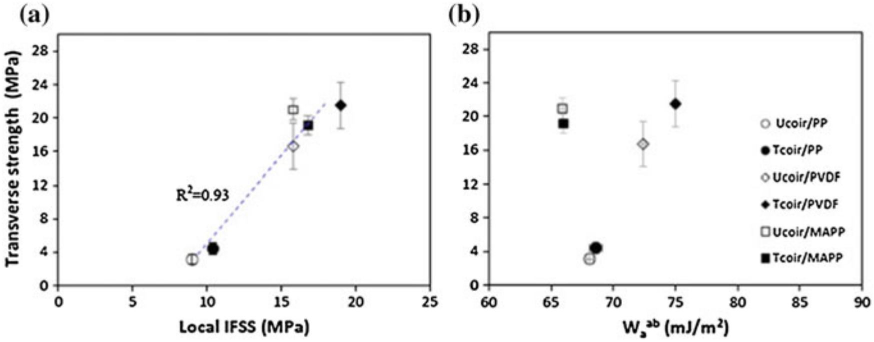


Fig. 4.2 **a** The correlation between local IFSS from the single fibre pull-out test and transverse strength from the three point bending test of unidirectional composite for different fibre–matrix composites, and **b** the transverse strength of unidirectional composites as function of the work of 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

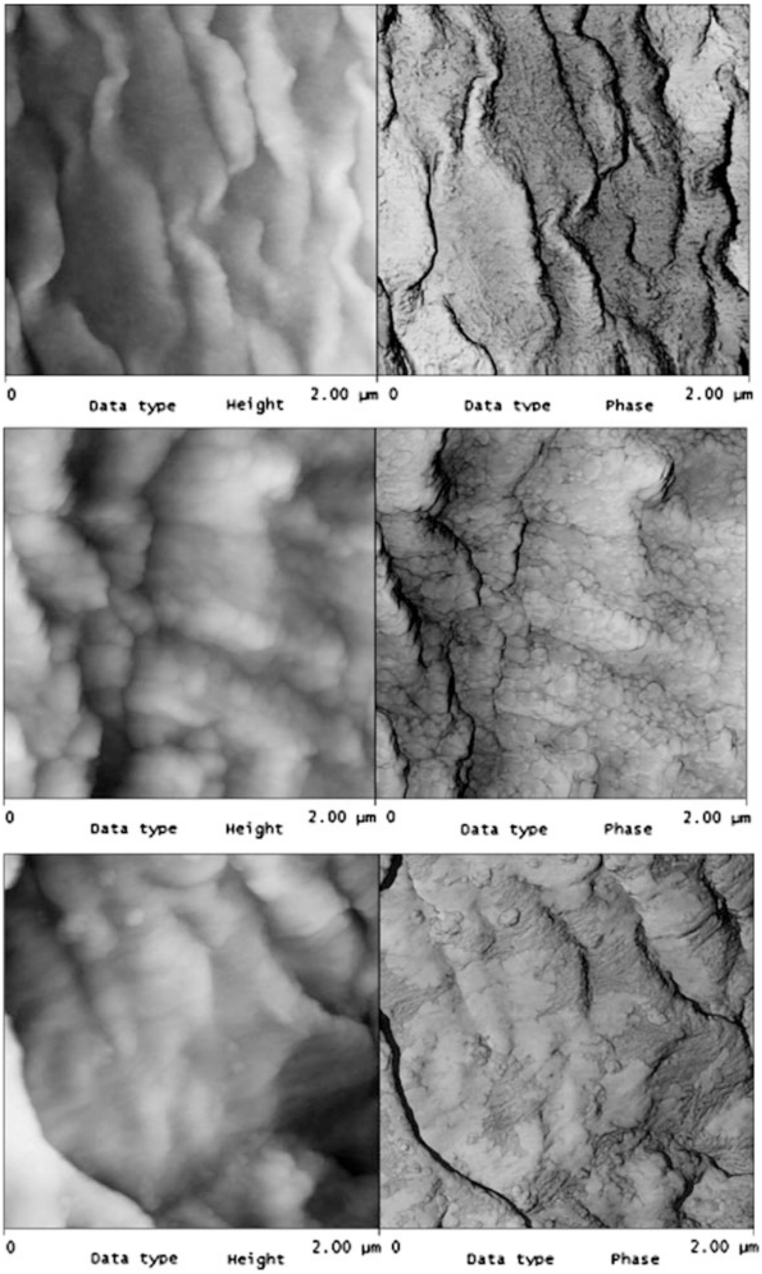


Fig. 4.3 AFM topography (left) and phase images (right) of (top) untreated jute, (middle) NaOH and (bottom) NaOH/(APS + epoxy dispersion) treated jute surfaces. Reproduced from Doan et al. 2012, Fig. 2 with permission from Elsevier

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).

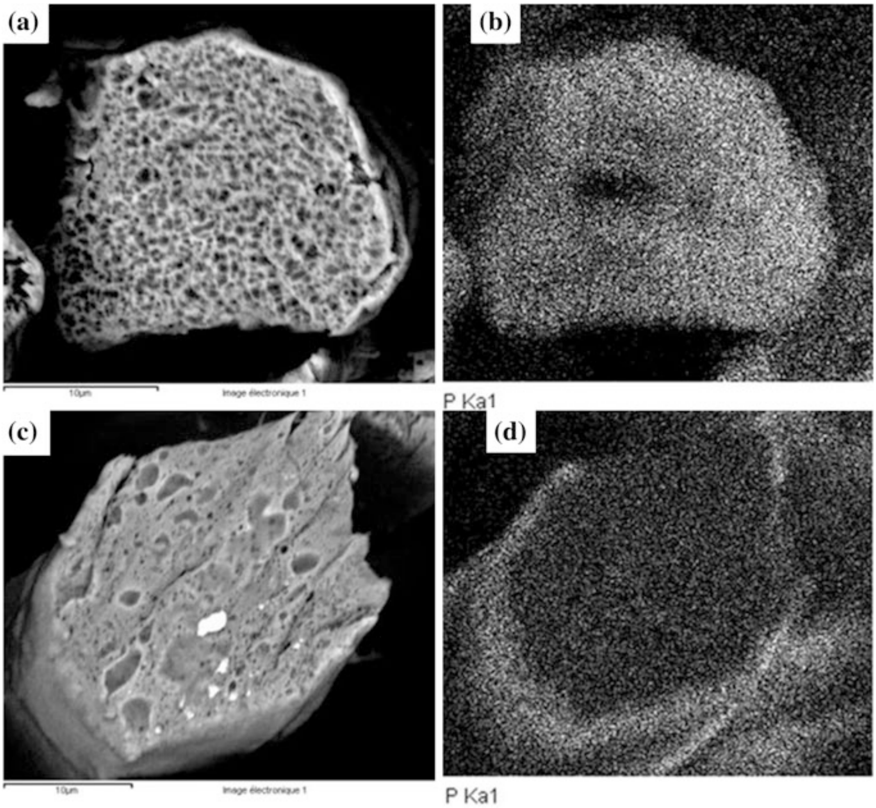


Fig. 4.4 SEM observations of flax fibres grafted by **a** dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) and **c** dimethylvinyl phosphonate (MVP). Phosphorus imaging using EDX analysis of flax fibres grafted by **b** MAPC1 and **d** MVP. Reproduced from Sonnier et al. (2015) with permission from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

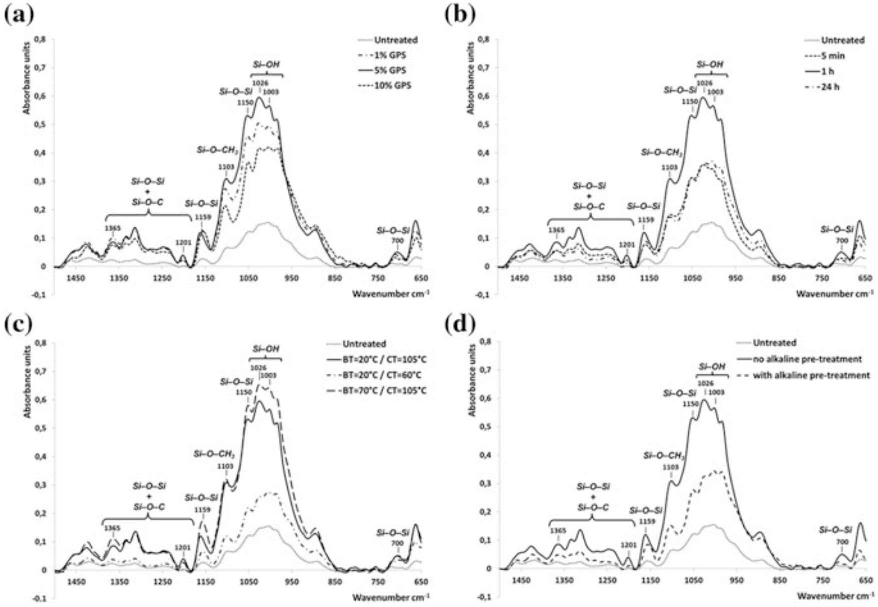


Fig. 4.5 IR spectra of untreated and treated flax fibre bundles. Influence of **a** GPS concentration (soaking time = 1 h; BT = 20 °C; CT = 105 °C; no alkaline pre-treatment), **b** soaking time (5% GPS; BT = 20 °C; CT = 105 °C; no alkaline pre-treatment), **c** bath and curing temperatures (5% GPS;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

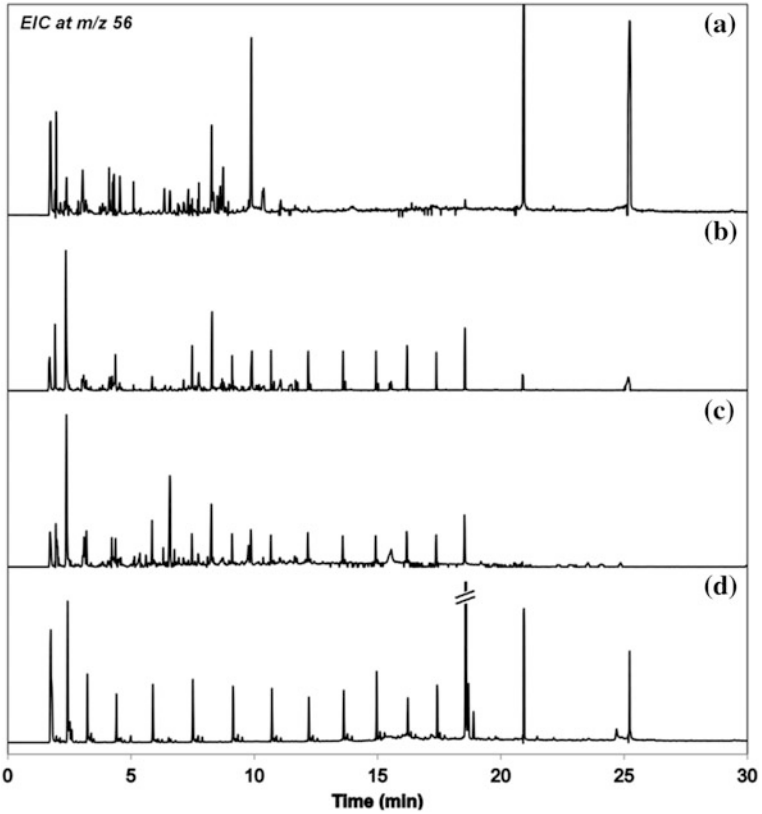


Fig. 4.6 EIC at m/z 56 of pyrograms of **a** flax treated with ethanol, **b** flax grafted by ODPA, **c** flax grafted by ODPA and treated by soxhlet extraction (Tfl/ODPAsox) and **d** ODPA. Reprinted from Dorez et al. (2014b) with permission from Elsevier

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

Chapter 5
Characterization of the Interface/Interphase in Natural Fibre Based Composites

There are currently no standardized methods to assess the quality of the interface/interphase in natural fibre reinforced composites. Nevertheless different approaches have been developed and are widely used by the scientific and industrial communities. These include microscopic and physico-chemical analyzes as well as micromechanical tests on model microcomposites and macroscopic mechanical tests on composite specimens. This last chapter proposes a review of the experimental techniques modelling approaches used to investigate the interface/interphase in natural fibres composites and quantify the interfacial adhesion.

5.1 Microstructural Analysis of the Interphase

5.1.1 Microscopic Analysis

Scanning Electron Microscopy (SEM) has proved to be a key tool for investigating the microstructure of composites made of lignocellulosic fibres and polymer matrix. SEM analyses provide direct visualization of the morphology at the filler/matrix interface. The qualitative criteria are mainly the occurrence of failure surfaces, fibre pull-outs, interfacial gaps around the fibres and debonding, or wetting of fibres by the polymer (Fig. 5.1). As observed for example for wood fibre-reinforced polyurethane composites (Rials et al. 2001), strong interfacial adhesion between the two phases was deduced from the observation of failure surfaces with a distinct fibre fracture without pull-out which is characteristic of a cohesive interfacial failure. In contrast, mostly fibre pull-out would be observed in the case of an adhesive interfacial failure. SEM observations are generally performed on manually cryo-fractured surfaces, which can induce bias in the observation of the morphology of surface failures. Indeed, the material is violently cooled, which might generate gaps between fibres and matrix, due to differences of thermal shrinkage between both components (Berthet et al. 2015). As

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3_5

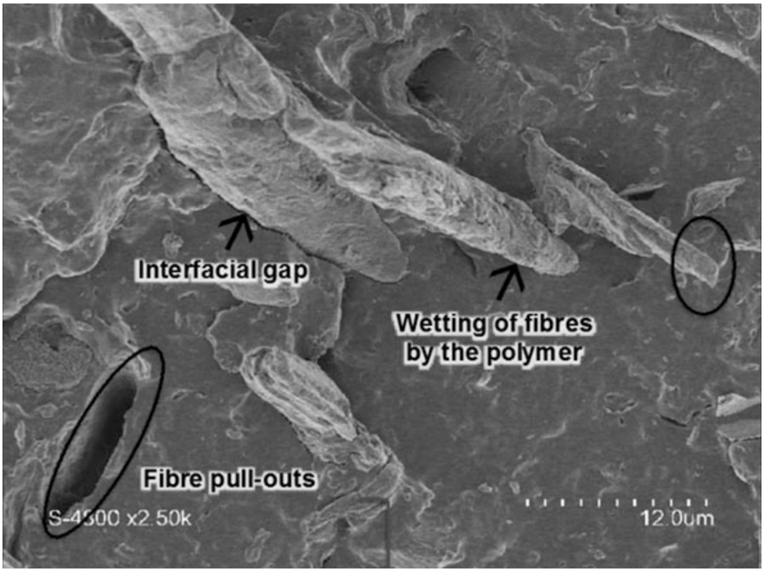


Fig. 5.1 SEM picture of cryo-fractured surface of PHBV/wheat straw fibres (20wt%) composites

performed by Bledzki and Jaszkiewick (2010), it sounds reasonable to only use SEM as a qualitative mean to compare the fibre/matrix interfacial adhesion in different formulations and to discriminate different failure surface morphologies. As compared to "classical" SEM analysis, the advantage of environmental scanning electron microscopy (ESEM) is the possibility to characterize wet, oily or electrically non-conductive samples without preliminary preparation and operating at relatively high pressures (George et al. 2001; Wright and Mathias 1993; Singh et al. 2013).

In situ observations of crack propagation by ESEM (equipped with an in situ tensile apparatus) could be useful to monitor failure mechanisms at the interface of biocomposites (see also Chap. 5, Sect. 2.1) and thus, provide qualitative information on the quality of the fibre/matrix interface. As showed for polylactic acid (PLA)/flax fibres composites (Le Moigne et al. 2014), this technique allows discriminating adhesive interfacial failure (due to the decohesion of the fibres and characterized by a clean break of the matrix) from cohesive interfacial failure (characterized by the tearing of the matrix and the breaking of the fibres). When ESEM is combined with X-ray energy analysis, the elemental composition of the surface can be determined using energy dispersive analysis of X-rays (EDX). The principle of ESEM-EDX consists in bombarding a specimen with an electron beam of sufficient energy with the emission of X-rays characteristics of each element present. Based on its specific energy and intensity, the atomic number and relative concentration of a particular element can then be determined. For example, Wright and Mathias (1993) used EDX to evidence that poly(EHMA) (homopolymer of ethyl alpha-hydroxymethylacrylate) and wood fibres were strongly bonded, through the presence of poly (EHMA) and its copolymers within the wood cell walls.

Polarized Optical Microscopy (POM) and transcrystallization. In the case of semi-crystalline polymers, POM observations of the crystallization phenomenon from the melt can be used to highlight the occurrence (or not) of interfacial transcrystallization and/or particle nucleating effect, both indicators of filler/matrix interactions (Wurm et al. 2010). Transcrystallization may reduce the final crystallinity degree of the matrix due to the reduced mobility of polymer chains as a consequence of the fast formation of high density nuclei on the filler surface (Luduena et al. 2012). As reported by Luduena et al. (2012), several parameters affect this process: the nature of the fibre, their surface roughness and surface treatment, the thermal conductivity of the fibre, and the processing conditions of composites.

As showed by Wang et al. (2011) for sisal/PLA systems, sisal fibres un-treated or treated with alkali or aminosilane (APS) have a nucleating ability and induce transcrystallinity in PLA matrix. When placed under isothermal crystallization conditions between 123 and 130 °C, first nuclei appeared preferentially at the fibres surface. Based on the theory of heterogeneous nucleation, the authors found that interfacial free energy difference functions of PLA for untreated and treated fibres were similar, suggesting that fibre surface modifications by using alkali or APS silane has no significant influence on the nucleation ability of sisal fibres in PLA matrix. Based on these results, the authors assumed that, although being influenced by fibre treatments, the surface energy of the fibre is not a critical factor for the development of transcrystallinity. They also pointed out that surface topography rather than surface chemistry might induce the nucleation process. Indeed, treated and untreated sisal fibres all had rough surfaces, providing abundant nucleation sites to induce transcrystallinity in PLA.

Joseph et al. (2003) also found that the surfaces of sisal fibre act as nucleating sites for the crystallisation of PP, promoting the growth of spherulites perpendicular to the fibres surface and forming a transcrystalline region around the fibre. Depending on the crystallization conditions (temperature, time and stress), the thickness of the transcrystalline layer varied from about 5 µm to more than 11 µm. The authors found that longer crystallization time and higher crystallization temperature, as well as stress induced crystallisation favour the formation of a thicker transcrystalline layer. As observed by Wang et al. (2011), fibre surface treatment with toluene-2, 4-diisocyanate (TDI)/polypropylene glycol (PPG) had limited effect on the nucleating ability of sisal fibres and transcrystallization of PP.

It is worth noting that POM samples are generally prepared between two glass slides, which constraints the material to crystallize with a limited mobility, possibility favouring the occurrence of cracks at the fibre/matrix interface and in the polymer phase during the crystallization process (Berthet et al. 2015).

Atomic force microscopy (AFM). Non-destructive methods such as AFM in tapping or force modulation modes could be used to characterize the physical properties (i.e. mainly the stiffness and visco-elastic behaviour) of composite interphases depending on the interaction forces between a sharp tip suspended on a very soft spring called cantilever and the sample surface, allowing to deduce interphase thickness (Mai et al. 1998). The lateral resolution of the AFM (related to the curvature radius of the probe) is typically of the order of 10 to 30 nm even if it is still possible to identify and localize objects with dimensions down to the nanometre (e.g. carbon nanotubes). The depth resolution is of the order of the ångström. The sizes of analysed zones can vary from 1 μm × 1 μm to 100 μm × 100 μm. The development of scanning thermal microscopy (SThM), combined to AFM, allowed researchers to evaluate the thermal properties of materials (such as the glass transition temperature) at the microscopic scale (Tillman et al. 2000). AFM is also able to provide 3D images of topography, various interaction forces with molecular resolution within a thin layer of material and therefore gives an indication of the interfacial adhesive forces, as shown on wood-plastic composites (Effah et al. 2015). This is based on the knowledge of the depth of analysis, which is system dependent. AFM is not limited to topographic images; it can also be used to identify and discriminate surfaces that differ from their chemical properties by using modified AFM probes. In that case, called chemical force microscopy (CFM), the instrument detects the chemical interactions between the functionalized tip and the material surface. Among the constraints that have to be taken into account in the case of lignocellulosic fibre based composites, the surface roughness must be in the order of 100 nm or lower than the imaged zones, which imposes an adequate method of cutting and/or polishing of samples. The size of analysed particles must be compatible with the lateral resolution of the AFM (related to the radius of the probe), typically of the order of 10 nm. Finally, the respective hardness of the matrix and the particles will determine the maximal depth of analysis.

X-ray computed tomography. A visual analysis of the 3D structure, including the 3D porosity and distributed voids, can be done by X-ray computed tomography, as already done for glass fibre/polypropylene (Kastner et al. 2012) or carbon fibre/epoxy composites (Nikishkov et al. 2013; Yang and Elhajjar 2014). X-ray computed tomography is a non-destructive, powerful technique that provides a volumetric map of a specimen in three dimensions, generated from a series of X-ray projections of the samples recorded at different angles. It allows to quantitatively analyze the filler dispersion on macroscopic length scales. Continuous improvements in the quality and performance of X-ray tubes, detectors and devices have led to cone beam X-ray computed tomography systems, which can now achieve spatial resolutions down to 1 μm and even below, *i.e.* 50 nm in the case of nano-tomographs. Applications of high-resolution X-ray computed tomography are possible even when the density differences between the constituents are rather low, as recently reported for carbon fiber reinforced polymers (Kastner et al. 2012). By applying various 3D-filters, authors succeeded in extracting from the X-ray computed tomography data the following quantitative information and values: filler percentage, 3D-geometry of the fillers (diameter, surface, volume), fibre length distribution, filler orientation, 3D filler distribution, filler interconnectivity, porosity. In the case of biocomposite materials, the main limit will be the difference of density between the lignocellulosic fibres and the polymer matrix that may be too low to obtain exploitable images.

Alemdar et al. (2008) were among the first authors to use X-ray micro-tomography to study the effect of fibre separation techniques (enzyme treated and carded hemp fibres) and coupling agent (MAPP) on the microstructure and fibre size distribution in wood and hemp fibre reinforced PP composites. It was shown that the use of MAPP coupling agent in wood/PP composites resulted in a significant decrease of fibre breakage during processing, and hence higher fibre length and width, possibly due to the lubricant effect of low molecular MAPP contributing to the shear stress reduction during processing. Smaller width distribution, higher aspect ratio and more uniform fibre distribution were observed for carded and enzyme treated hemp fibres/PP composites, highlighting the interest of these fibre separation techniques for composites applications. Some other interesting results were found by Martin et al. (2013) on PP/flax fibres biocomposites. X-ray micro-tomography observations of injection molded samples revealed greater fibre bundle splitting for higher retting degree of flax fibres. The authors also found a relatively low porosity content which decreases with the degree of retting, voids being mostly located in the core of samples in a plane parallel to the flow direction. Di Giuseppe et al. (2016) compared X-ray micro-tomography to 2D scanner and an automated fibre analyzer for determining natural fibre length and diameter distributions in PP/miscanthus and PP/hemp biocomposites. The authors concluded that the analysis of lignocellulosic fibers' dimensions in composite materials is complex and that the three techniques used do not allow an unbiased estimation of fibre sizes. Besides, their study highlighted the complementarity of these techniques in terms of length scale.

5.1.2 Nano-mechanical Analysis

Nano-mechanical analysis, which is largely used in polymer tribology,[1] could be useful to characterize the filler/matrix interphase region and evaluate its thickness. Nano-mechanical analysis includes nano-indentation, nano-scratch tests or nano-mechanical imaging techniques, possibly coupled with AFM. All these techniques require the polishing of materials to reduce surface roughness as much as possible.

Nano-indentation tests are able to produce indents of few nanometers in order to measure differences in nano-hardness and Young modulus in the cross-section of composite materials, and thus to highlight the fiber/matrix interphase region. This technique consists in indenting a rigid tip of known geometry, perpendicularly to the material surface and measuring the depth of penetration as a function of the applied load (Downing et al. 2000). Berkvich indenters, i.e. a three-sided triangular-based pyramidal diamond, are commonly used for measurements of mechanical properties at the nanometric scale. This technique has already been applied to wood-reinforced polypropylene composites (Jakes et al. 2007). Authors did not discriminate changes in mechanical properties in the interphase, probably due to the fact that there was no difference. However, they concluded on the need of improving the surface preparation technique. Lee et al. (2007) investigated the hardness and elastic modulus in interphase region of PP/cellulose fibres using

---

[1] Tribology is the science and engineering of interacting surfaces in relative motion, including the study and application of the principles of friction, lubrication and wear—to characterize the surface properties of polymer films or coatings.

different indentation depths and spacings. The authors showed that nano-indents need to be as small as possible to reduce the zone of analysis and limit the influence of neighbouring material properties.

For nano-scratch tests, the indenter tip is replaced by a scratch tip that scratches the surface in a straight line, crossing matrix and fillers areas. Nano-scratch technique involves moving a sample while it is in contact with a diamond tip. The depth of the indenter is also recorded, thus indicating the hardness of the surface being scratched. The coefficient of friction is determined from the fraction of the lateral and the normal force (this latter being maintained constant). Therefore, the coefficient of friction indicates the resistance of the materials to the tip penetration in the tangential direction. Nano-indentation and nano-scratch techniques can be successfully used if the interface thickness is higher than the penetrating width of the tip, as demonstrated for polymer/glass fibres composites (Hodzic et al. 2000a, b). In the case of nanometric interphases, their thickness can be quantitatively evaluated by mapping the dynamic mechanical property around the interphase region through the use of nano-mechanical imaging techniques. The experimental results show that this method can determine the width and topography of the interphase with nanoscale lateral resolution, as it is for example the case for carbon fibre reinforced polymer composites for which an interface thickness of about 120 nm was evaluated, based on the storage modulus profile on the cross section of the composite (Gu et al. 2010). For the moment, it has only been applied to the characterization of interfaces in polymer micro-composites reinforced with either glass (Kim et al. 2001) or carbon fibres (Gu et al. 2010). Thus, the characterization of polymer/lignocellulosic fibres still remains a challenge.

Finally, abrasion (or scratching) experiments using AFM in contact mode coupled with a simple tribological model could also be a promising way to evaluate differences in nano-mechanical properties between the different phases and at the interface in composite materials (Ahimou et al. 2007, Chichti et al. 2013). This method consists in progressively abrading the surface of the material and simultaneously measuring the shear force. The volume of the material removed by the tip is estimated from the analysis of successive topographic images of the surface, and the shear force is measured by keeping a constant normal force. As previously mentioned, AFM is also a highly useful tool for probing the interphase, because it involves much lower interaction forces between the probe and the sample than nano-indentation (Downing et al. 2000). Thereby, AFM imaging and nano-mechanical measurements are commonly combined (Gao and Mäder 2002; Lee et al. 2007; Young et al. 2013; Cech et al. 2013).

5.2 Mechanical Characterization of the Interphase

5.2.1 Micromechanical Analysis

Among the experimental techniques used for assessing the fibre/matrix interfacial adhesion in composites, micromechanical analyses rely on the study of the mechanical behaviour of a model microcomposite composed of a single fibre (or a bundle of fibres) embedded in a small volume of the matrix. These analyses allow understanding the interfacial failure mechanisms that occur at the local scale when a fibre undergoes mechanical loads. They are thus relevant to provide quantitative information about the interfacial strength.

Pull-out test is a micromechanical analysis technique that has been widely used for glass fibre reinforced composites and is being adapted to natural fibres. It consists in pulling a fibre out of the matrix which can be a block, a small cylinder or a micro-droplet (case of microbond test) of polymer held by a microvise or blades (Fig. 5.2). The pulling force, which is applied axially by a mechanical testing machine, induces mainly tensile stresses in the fibre and shear stresses at the fibre/matrix interface. The force is monitored while the displacement at the end of the fibre is increased at a constant speed until either pull-out occurs or the fibre breaks. The typical force–displacement curve (Fig. 5.2) exhibits an increase of the force up to a maximum (F_{max}) which corresponds to the total debonding of the fibre, followed by the force drop associated to the release of the adherence and the frictional sliding of the fibre (Miller et al. 1987).

Figure 5.3 shows a typical SEM image of a flax fibre/polyester matrix microbond specimen after debonding. The polyester droplet of 50 µL was deposited on the fibre with a calibrated micro-syringe (Baley et al. 2006).

Based on the measurements of the pull-out force F_{max} and the area A of the embedded length L of fibre within the matrix, the apparent interfacial shear strength τ_{app} (IFSS) is calculated from the Eq. 5.1:

$$\tau_{app} = \frac{F_{max}}{A} \tag{5.1}$$

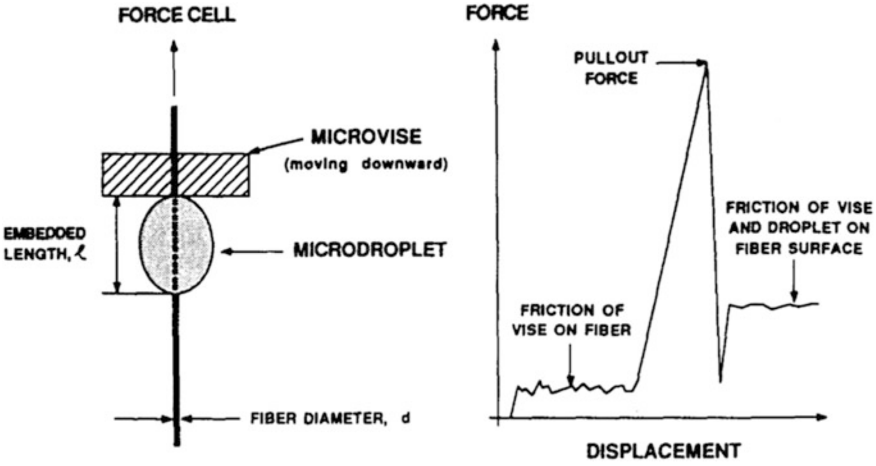


Fig. 5.2 The microbond arrangement (left) and a typical force-displacement record (right). Reprinted from (Miller et al. 1991), Fig. 2. with permission from Elsevier

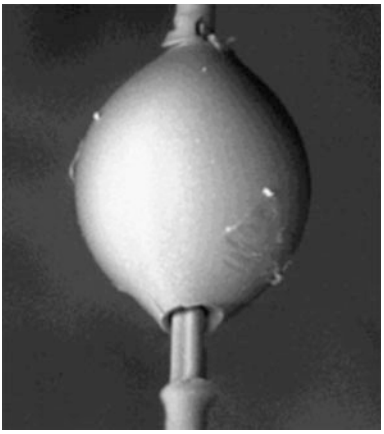


Fig. 5.3 Example of a microdrop of polyester on flax fibre after debonding (fibre diameter: 16 µm). Reprinted from (Baley et al. 2006), Fig. 5. with permission from Elsevier

For a straight fibre with a uniform cross-section, A is the product of the embedded length *L* by the cross-sectional perimeter. Thus, for a cylindrical fibre with a diameter *D*, Eq. 5.1 leads to the following expression of the IFSS:

$$\tau_{app} = \frac{F_{max}}{\pi DL} \tag{5.2}$$

Because the cross-section of natural fibres can differ a lot from a regular circular shape (Fig. 5.4), the assessment of the cross-sectional perimeter deduced from the side optical measurement of the fibre can be a major source of error in the IFSS measurement. For IFSS evaluations of flax fibres/unsaturated polyester, (Zhang et al. 2014) demonstrated that the error could reach a factor of three. The authors were able to improve the reliability of the IFSS values thanks to direct measurements of the perimeter from images of the fibre cross-section.

Since the fibre undergoes tensile stress during pull-out, the IFSS measurement requires that the fibre does not break before debonding occurs, thus limiting the embedded length below a specific value. For a cylindrical fibre with a given tensile strength σ, the theoretical limit of the embedded length is given by:

$$L < \frac{D\sigma}{4\tau} \tag{5.3}$$

The definition of apparent interfacial shear strength relies on the assumption that the shear stress distribution is uniform along the embedded length. Several authors proposed advanced models able to account for a realistic stress distribution in the case of regular fibres like glass and carbon fibres (Zhandarov and Mäder 2005; Bergeret and Krawczak 2012). However, their application to fibres with variable shape and roughness along their length like natural fibres is not straightforward. Moreover, studies on natural fibres/polymer matrix systems highlighted the

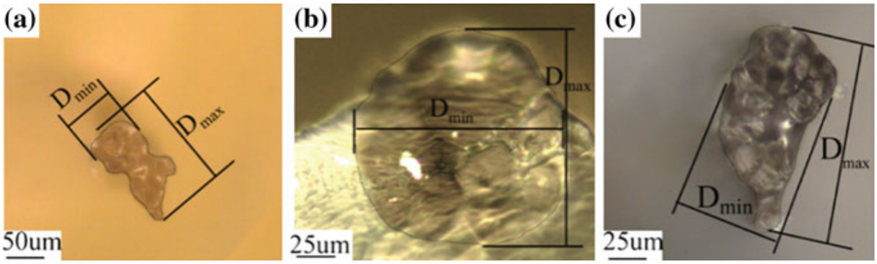


Fig. 5.4 Cross section dimensions of three flax fibres. Reprinted from (Zhang et al. 2014), Fig. 7. with permission from Elsevier

relevance of the post-debonding friction regime in the analysis of the interfacial adhesion (Le Duigou et al. 2013; Yang and Thomason 2010, 2012). It is stated that the corresponding friction strength $\tau_{friction}$ can be related to the residual stresses induced by processing conditions.

A comparison between flax/PLLA and glass/PLLA microbond measurements proposed by (Le Duigou et al. 2012) showed that both systems exhibit similar pull-out force-displacement curves and that the apparent shear strength of the flax/PLLA interface is around twice as high as those of de-sized glass/PLLA (Fig. 5.5 left). It was demonstrated that this discrepancy is the concomitant result of the physico-chemical interactions between the flax surface and PLLA on the one hand and the lower roughness of the de-sized glass fibres (as measured by AFM) on the other hand. In addition, debonding tests performed on single flax fibres treated with release agent in order to weaken the interfacial adhesion confirmed that in that case the only resistance is due to friction (Fig. 5.5 right). This study draws an illustration of the relationship between typical pull-out responses and the behaviour of systems with tailored interfacial adhesion.

The many studies using the pull-out and microbond techniques for natural fibres/polymer matrix systems provide quantitative information relative to the interfacial adhesion and trends about the strategies to enhance it. Thereafter are summarized a few representative examples.

The study of short hemp fibres/PP-MAPP composites highlighted the beneficial effect of a white rot fungi treatment on the IFSS assessed from pull-out measurements (Li et al. 2009). This enzymatic fibre treatment led to an 80% increase of the IFSS, which was clearly visible from the force-displacement curves. It is worth noting that, despite a 28% reduction of the fibres tensile strength and almost no variation of their stiffness, the improvement of the interfacial bonding allowed increasing up to 28% the strength and 62% the stiffness of corresponding tensile composite specimens. The authors correlated the better IFSS to the removal of non-cellulosic compounds (wax, pectin, and lignin) as well as the increased roughness of the fibre surface.

Micromechanical analyses have also been carried out for the interfacial strength of jute and hemp fibres with various polymer matrix composites (Park et al. 2006). The authors proved that the IFSS of the natural fibres/PP significantly increases

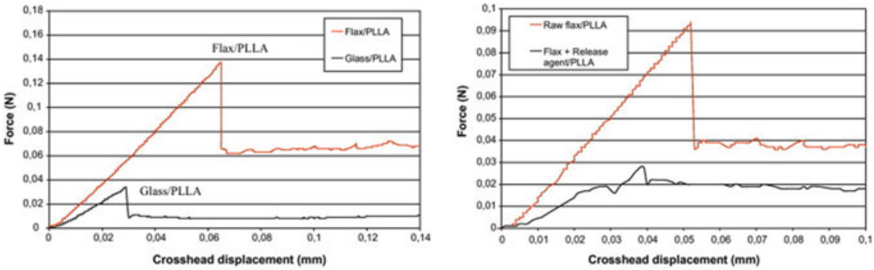


Fig. 5.5 Typical microdroplet test plots for flax/PLLA and de-sized E-glass/PLLA (left); Influence of release agent on microdroplet test for flax/PLLA (right). Reprinted from (Le Duigou et al. 2012) with permission from Elsevier

with increasing the content of MAPP coupling agent within the matrix as well as after treating fibres with alkaline solution and silane coupling agent (Fig. 5.6).

As a comparison, Table 5.1 presents values of the apparent shear stress from debonding tests on single fibre for different natural fibre/polymer matrix systems. Several supplementary results about the IFSS of biocomposites can be found in the literature. For thermoplastic or thermoset matrices associated to different short or long natural fibres: flax (Baley et al. 2006; Le Duigou et al. 2012, 2013; Fuentes et al. 2016), hemp (Li et al. 2009), jute (Park et al. 2008), coir (Tran et al. 2013), bamboo (Fuentes et al. 2015). As discussed in Chap. 4, IFSS is often related to the work of adhesion determined from the surface energies of fibres and matrix. As the interfacial strength can be greatly enhanced by fibre roughness, chemical bonding between the matrix and the fibres, IFSS is not necessarily correlated to the work of adhesion (see Fig. 4.2). Furthermore, Le Duigou et al. (2017) proposed a multiscale analysis of the influence of hygroscopic radial expansion of natural fibres on IFSS in the case of PP/flax biocomposites. They demonstrated that a variation of water content in the composite and thus in flax fibres can be much more influent on the interfacial shear strength than residual stresses induced by the thermomechanical history related to the manufacturing process. Therefore, the processing and design of natural fibre/polymer systems should better take into account their moisture sensitivity that should not only be considered as a drawback, and could play a positive role on interfacial properties if radial stresses are controlled.

Fragmentation test is a technique dedicated to the evaluation of the fibre-matrix adherence inside a composite. It involves the application of increasing axial load to a specimen that contains a single fibre (or bundle or yarn) embedded in the polymer matrix. Load is transferred through the matrix to the fibre by means of the shear stress at the interface. The fibre breakage occurs when this transferred stress reaches locally the tensile strength of the fibre. Kelly and Tyson (1965) reported that when the composite is strained, brittle regular fibres embedded in polymers tend to fracture at the locations of the defects along their length. As the load increases, the fibre continues to fracture into shorter length fragments (Fig. 5.7). The interfacial shear stresses is unable to induce failure stresses in fragments having a length lower

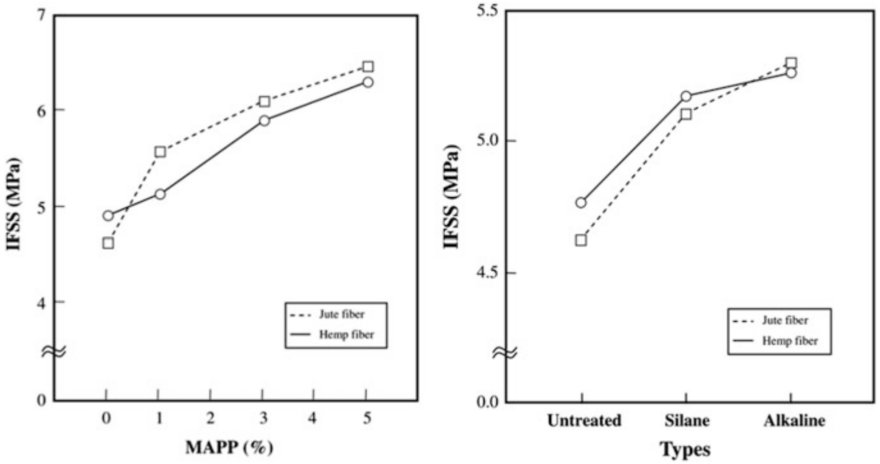


Fig. 5.6 IFSS of jute and hemp fibres/PP with various contents of MAPP coupling agent (left) and fibre treatments (right). Reprinted from (Park et al. 2006) with permission from Elsevier

Table 5.1 Apparent shear stresses (IFSS) determined from debonding tests. Adapted from review tables in (Le Duigou et al. 2012) and (Graupner et al. 2014b)

Fibre type	Matrix	**IFSS** (MPa)	References
Glass	PP	3.3	Le Duigou et al. (2012)
	Epoxy	29.3	
Ananas	PHBV	8.2	Graupner et al. (2014b)
Flax	PLLA (Natureworks)	16.4	Le Duigou et al. (2012)
	PLLA (Biomer)	15.3	
	Epoxy	22.7–23	
	Unsatured polyester	14.2	
	PP	3.4	Graupner et al. (2014b)
	PLA	9–22.2	
	Mater-Bi (Novamont)	4.2	
	PHB	8.8	
Hemp	PP	4.7–9	Le Duigou et al. (2012)
	PP	5.1	Graupner et al. (2014b)
	PLA	11.3	
	Mater-Bi (Novamont)	3	
Henequen	MAPP	4.1	
Jute	PLA	4.6–5.5	
Kenaf	PLA	5.4–10.7	
Lyocell	LDPE	6	
	PP	4.2–5.3	
Ramie	LDPE	10	
	PP	4.9–6	
Sisal	PP	4.6	
	PLA	14.3	
	Mater-Bi (Novamont)	3.2	

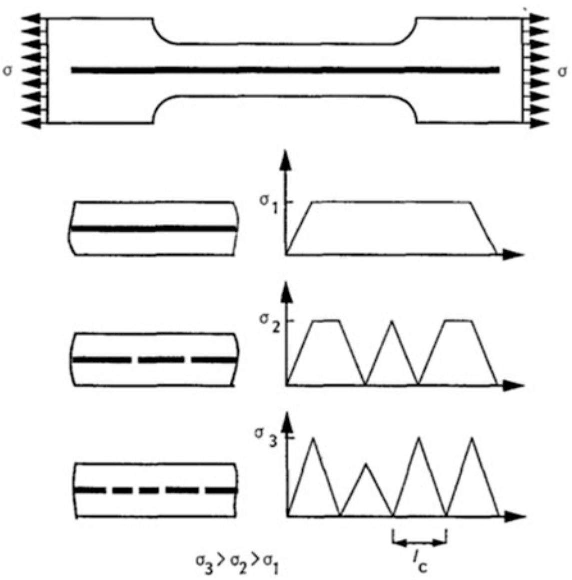


Fig. 5.7 Schematic representation of the single fibre fragmentation test. Reprinted from (Herrera-Franco and Drzal 1992), Fig. 12 with permission from Elsevier

than a specific value L_c, referred as the critical length and considered as an indicator of the interfacial strength. Thus, a decrease of L_c reflects an improvement of the interfacial adhesion and hence the IFSS.

In order to experimentally interpret the failure modes during a fragmentation test, the lengths of the fibre fragments are usually measured using an optical microscope, requiring that the matrix is transparent (Herrera-Franco and Drzal 1992). Theoretically, fragments longer than L_c have been broken into two, yielding a random distribution of fragment lengths between $L_c/2$ and L_c at the end of the fragmentation process. Thereby, the critical length L_c can be deduced from the evaluation of the average $\overline{L}$ of the experimental fragments lengths distribution:

$$L_c = \frac{4}{3}\overline{L} \tag{5.4}$$

Then, according to Kelly and Tyson (1965), the interfacial shear strength τ (IFSS) is calculated from the Eq. 5.5:

$$\tau = \frac{\sigma}{2}\frac{D}{L_c} \tag{5.5}$$

where σ is the fibre tensile strength, D its diameter and L_c the critical length.

To complete the understanding of the complex mechanisms occurring during the fragmentation process, experimental fragmentation testing can be coupled with numerical predictions (Guillebaud-Bonnafous et al. 2012). In that study, a finite element model was developed to simulate the fragmentation process of single hemp

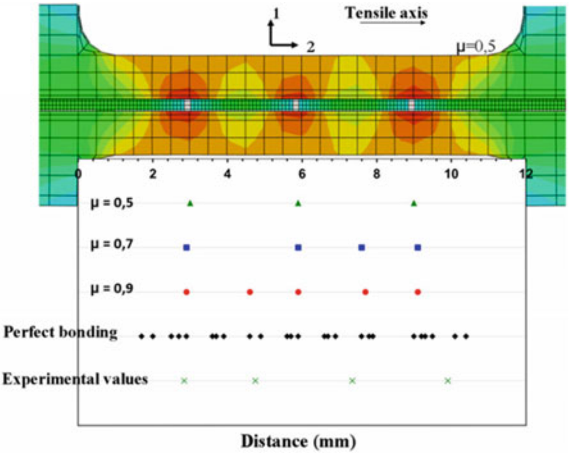


Fig. 5.8 Finite element analysis of the yarn fragmentation locations for different values of the friction coefficient μ and comparison with experimental results. Reprinted from (Guillebaud-Bonnafous et al. 2012) with permission from Elsevier

yarn composite specimens. These simulations, which allowed assessing the sensitivity to the frictional contact coefficient μ (at the fibre/matrix interface), led to results close to the experimental fragmentation patterns and to a comprehensive analysis of the fragmentation test results (Fig. 5.8).

Several studies have provided results about the interfacial properties of natural fibre reinforced thermoplastics. The interfacial shear strength of PE-sisal composites was measured using the single fibre fragmentation test (Torres and Cubillas 2005). Fibre treatment with stearic acid increased the interfacial shear strength by 23% with respect to untreated fibres, which was consistent with SEM observations of failure surfaces. However, the authors discussed the difficulties in obtaining accurate measurements due to the opacity of the matrix and the irregular shape of the natural fibres.

In another study, the interfacial shear strength of a hemp fibre/PP-MAPP composite was evaluated by means of fragmentation testing (Beckermann and Pickering 2009). Based on a mathematical modeling, it was demonstrated that the reinforcing fibres need to be axially aligned in the composite and equal to or longer than 4 L_c in order to achieve the maximum theoretical composite strength.

The mechanical behavior of HDPE reinforced with henequen fibres was studied (Herrera-Franco and Valadez-González 2004). Based on the IFSS measurements of the fragmentation test, the authors showed that fibre-matrix adhesion was improved by the use of a silane coupling agent. It was found that the resulting strength and stiffness of the composite depended on the amount of silane deposited on the fibres. Good correlation was found between the IFSS and the composite tensile strength and an optimal silane concentration was found (Fig. 5.9). From the failure surfaces, it was additionally observed that with increasing fibre-matrix interactions the failure mode changed from adhesive interfacial failure to cohesive interfacial failure occurring in the matrix.

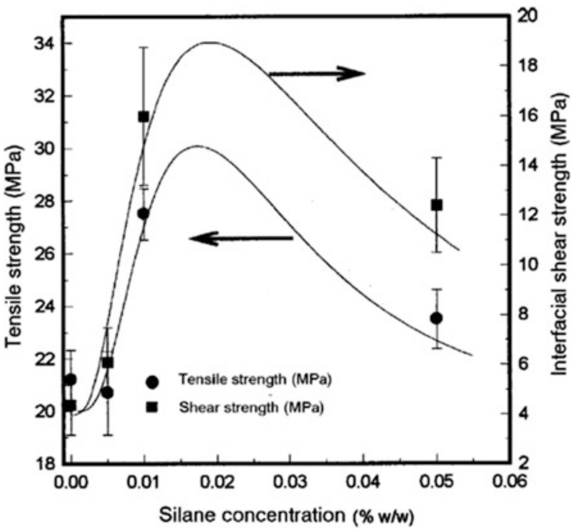


Fig. 5.9 Effect of the concentration of the silane coupling agent solution on the tensile strength and IFSS of henequen–fibre composites. Reprinted from (Herrera-Franco and Valadez-González 2004) with permission from Elsevier

For different thermoplastic matrices (PLA, PP, MAPP) reinforced with Lyocell cellulose fibres, Graupner et al. (2014a) investigated the influence of eucalyptus lignin as a bio-based coupling agent. Lyocell fibres were treated with a lignin-ethanol solution. Fibre/matrix adhesion was assessed using single fibre pull-out and single fibre fragmentation tests. Both testing procedures evidenced the increase of the interfacial shear strength for the lignin-treated fibres (compared with untreated fibres) for all investigated matrices (Fig. 5.10). This improvement was attributed to better chemical interactions between the fibre and matrix and a rougher and larger fibre surface with lignin particles which was revealed by AFM investigations.

In situ tensile test by SEM is a micromechanical characterization technique of composite materials which consists in submitting a coupon to a tensile mechanical loading while observing it by SEM. There have been many studies that deal with the mechanical testing of biocomposites at the macro scale, but very few have reported testing on composites at a micro scale.

The damage mechanisms under stress of flax/PP composite have been studied by in situ SEM observations (Bourmaud et al. 2013). The authors highlighted the influence of the fibre bundles during a tensile experiment. Figure 5.11 shows the occurrence of micro cracks through the transversely oriented fibre bundles, which induce a dislocation between the elementary fibres. This observation evidences that the weakness of natural fibres composites was mainly located at the bundles middle lamellas rather than at the fibre/matrix interface. As a result, the authors postulated that a decrease of the amount of bundles in favour of well dispersed and individualized fibres leads to better mechanical properties of the composite, which can be achieved thanks to an efficient retting of the flax stems.

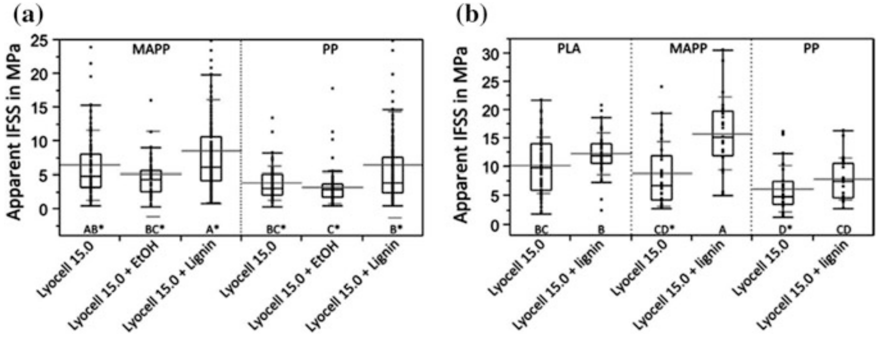
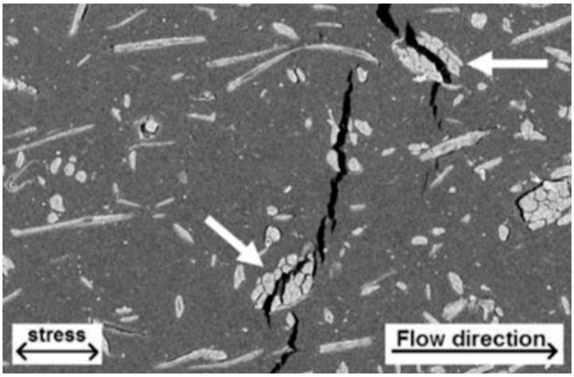


Fig. 5.10 IFSS of untreated, ethanol-treated and ethanol/lignin-treated Lyocell fibres in different matrices measured with the fragmentation (**a**) and pull-out (**b**) tests. Reprinted from Graupner et al. (2014a) with permission from Elsevier

Fig. 5.11 SEM micrograph in the core of PP/flax sample under loading, Reprinted from (Bourmaud et al. 2013) with permission from Elsevier



In a study of the interface in flax/PLA composites modified by organosilane treatments, Le Moigne et al. (2014) conducted SEM observations of crack propagation during tensile test while force-elongation responses were recorded. In order to pick out a region of interest, the coupon was notched on one edge, which induces stress concentrations during the force increments and thus localizes the occurrence of a macrocrack. The SEM observation of the crack tip and margins during its propagation gave access to the analysis of the fibres behaviour under stress within the matrix (Fig. 5.12). Due to the notched, the breakage of the samples occurs by tearing and is not brittle. This experiment could be assimilated to a pull-out test at a larger scale, i.e. several fibres are progressively extracted from the matrix during the crack propagation. Results expressed clearly that the alkaline/GPS silane-treated biocomposites showed a cohesive interfacial failure at much higher loads, as confirmed by the force-elongation curves (Fig. 5.13), which brings out the higher

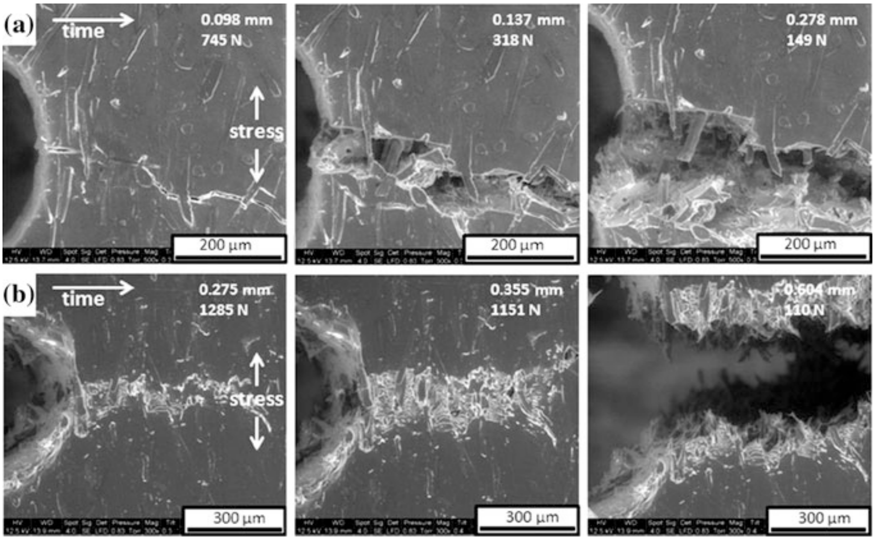


Fig. 5.12 SEM observations during crack propagation in notched specimens for PLA/20% flax **a** non-treated **b** alkaline/GPS silane-treated. Reprinted from Le Moigne et al. (2014) with permission from Elsevier

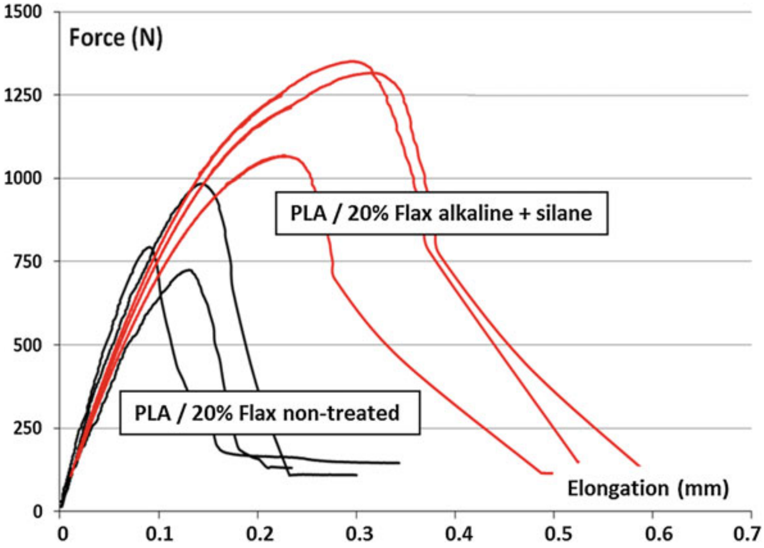


Fig. 5.13 Tensile force-elongation curves recorded during in situ tensile test by SEM for PLA/20% flax non-treated and alkaline/silane-treated (three tests per biocomposites). Reprinted from Le Moigne et al. (2014) with permission from Elsevier

load transfer from the PLA to the treated flax fibres, and hence the greater interfacial adhesion.

5.2.2 *Static Mechanical Analysis*

Static mechanical testing of coupons at the macroscopic scale is the most common technique used for assessing the mechanical performances of composite materials. The shape and dimensions of the coupons are usually imposed by the loading conditions and the eventual corresponding standards. However, the sensitivity of the static mechanical properties to the interfacial adhesion is highly variable between the different possible loading conditions, the nature of the induced stresses and the microstructure of the composite.

In a review of the properties of unidirectional fibre composites, Agarwal et al. (2006) established a qualitative summary of the typical influence of fibres, matrix and interface on the properties of these composites. The results, which are compiled in Table 5.2, are applicable provided that the Young's modulus of the fibres is at least ten times higher than that of the matrix. This summary highlights that the mechanical properties which prove to be actually sensitive to the interfacial adhesion are the tensile transverse strength, the in-plane shear strength and the interlaminar shear strength (Fig. 5.14). The influence of the interface on the other mechanical properties is found to be weak or negligible. Thus, the choice of mechanical tests that are likely to evidence these interface-influenced properties should be prefered in order to assess the interfacial adhesion in unidirectional polymer composites.

As mentioned by Marrot et al. (2014) in a study of the interfacial adhesion between flax fibres and biobased thermoset matrices, several macroscopic

Table 5.2 Summary of the typical influence of constituents on properties of unidirectional polymer composites. S = strong influence, W = weak influence, N = negligible influence. Adapted from (Agarwal et al. 2006)

Composite property	Fibres	Matrix	Interface
Tensile properties			
Longitudinal modulus	S	W	N
Longitudinal strength	S	W	N
Transverse modulus	W	S	N
Transverse strength	W	S	**S**
Compression properties			
Longitudinal modulus	S	W	N
Longitudinal strength	S	S	N
Transverse modulus	W	S	N
Transverse strength	W	S	N
Shear properties			
In-plane shear modulus	W	S	N
In-plane shear strength	W	S	**S**
Interlaminar shear strength	N	S	**S**

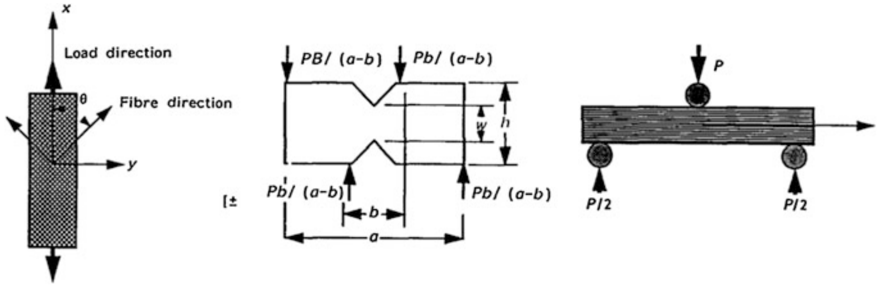
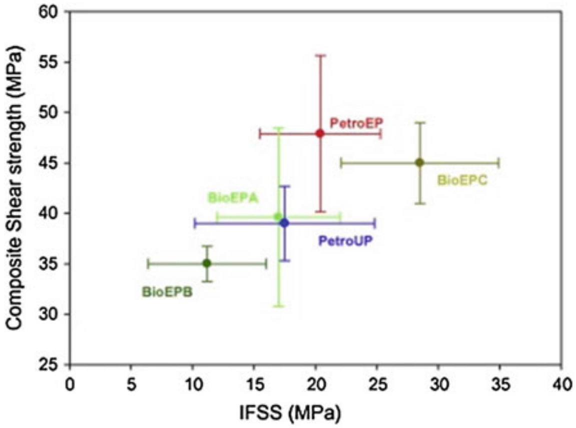


Fig. 5.14 Schematic representation of several shear tests: ±45 tension, Iosipescu and short beam shear (from left to right), Reprinted from (Herrera-Franco and Drzal 1992) with permission from Elsevier

mechanical tests are sensitive to the interfacial properties: transverse tensile, in-plane ±45 tension, Iosipescu and short-beam shear tests (Fig. 5.14), which are still not widely used for biocomposites. In that study, the interlaminar shear strength (ILSS) was assessed using in-plane tension shear test on ±45 flax laminates manufactured with the different petrochemical and biobased matrices, and the ILSS results were compared to IFSS measurements determined via the debonding test. A strong positive correlation between the ILSS and the IFSS was highlighted (Fig. 5.15). In parallel, tensile mechanical properties of unidirectional (UD) flax fibres composites based on the same matrices were measured. As expected, the Young's modulus of the UD composites was primarily determined by the fibres and matrices stiffness and the fibre volume fraction according to the mixing rule, showing virtually no relationship with the interlaminar shear strength.

Among the possible methods that allow evaluating the ILSS of composites, the **short-beam shear test** is performed with a three-points bending specimen (Fig. 5.14) with a low span-to-thickness ratio, typically in the range 4 to 5, in order to induce interlaminar failure due to shear stresses. The interlaminar shear strength τ of the specimen is calculated from the Eq. 5.6:

Fig. 5.15 Shear strength (ILSS) of the ±45 laminates versus microscopic IFSS given by the microbond test. Reprinted from Marrot et al. (2014) with permission from Elsevier



$$\tau = \frac{3}{4}\frac{F_{max}}{A} \tag{5.6}$$

where F_{max} is the load at failure and A the transverse cross-sectional area.

The main advantage of the short-beam test is its simplicity comparatively to other current ILSS test methods, which involve complex setups or special sample machining.

In a study about jute/polyester composites, Sever et al. (2012) proposed several fabrics surface treatments in order to enhance the interfacial adhesion. Jute fabrics were modified by alkali, micro-emulsion silicon and fluorocarbon based agents. ILSS were evaluated by short-beam shear tests and IFSS from pull-out tests. All surface treatments improved both the IFSS and ILSS of the composites, the maximum improvement being obtained with the fluorocarbon based agents. Tensile measurements evidenced that the proposed treatments improved the modulus and strength of the composites, accordingly.

Acoustic emission (AE) is a non-destructive method based on the statistical analysis of the elastic waves produced by the different failures in a coupon during a tensile test and measured at its surface by high sensitivity piezoelectric (PZT) sensors. AE allows monitoring the types of fracture sources and their progress during the test by analyzing parameters such as energy, amplitude, and frequency emitted from fibre failures, matrix cracking, and fibres debonding. Moreover, the combination of several PZT sensors enables the localization of the different events inside the coupon. Acoustic emission real-time monitoring has been successfully used on traditional polymer composites reinforced with carbon or glass fibres. However, experimental difficulties may arise in the case of natural fibres composites, mainly because of the scattering in fibres properties and the less pronounced acoustic emission activity than in traditional composites.

As reviewed by Romhány et al. (2003) and De Rosa et al. (2009) and other authors, acoustic emission was used to monitor the failure modes in flax bundles during a single fibre fracture test, showing that an AE range of amplitudes can be assigned to the main failure mechanisms (Fig. 5.16). The authors also showed that AE can be used to identify the failure mode sequence of flax fibre reinforced thermoplastic composites during a tensile test, and that the AE amplitudes of the different failure events follows the subsequent ranking: (i) fibre/matrix debonding, as well as the axial split of the pectin boundary layer between the elementary flax fibres (ii) fibre pull-out, as well as formation of microcracks within the elementary flax fibres (iii) fibre breakage.

Assarar et al. (2011) used the acoustic emission technique to study the influence of water ageing on tensile mechanical properties and damage events in flax–fibre/epoxy composites (compared with glass–fibre/epoxy composites). In this study, the AE signals analysis was based on several parameters: the amplitude, the energy, the duration, the rise time and the events counts. These collected parameters were used as input descriptors in a specific classification method which allows identifying each damage mechanisms and to follow their progress until the final global failure of the tensile sample. For the aged flax composite samples, it was shown that the AE activities start from the beginning of the tensile test (Fig. 5.17), which was not

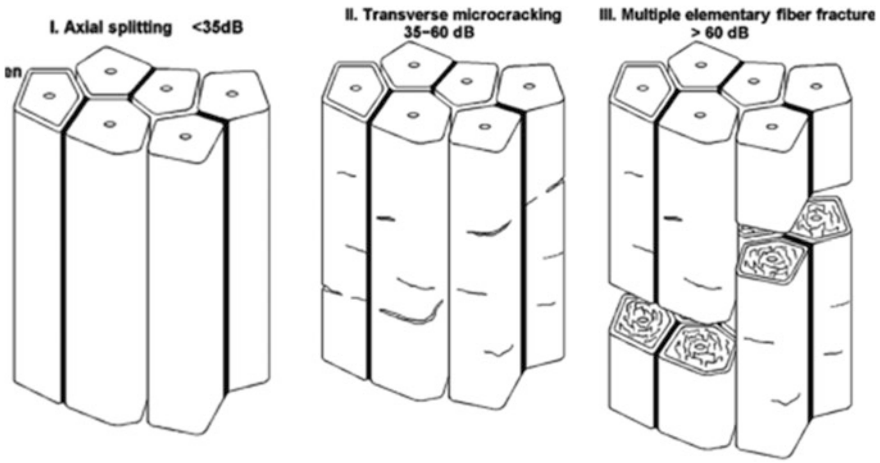


Fig. 5.16 Schematic lay-up of the failure sequence along flax bundle with the related AE amplitude ranges (from left to right): (I) axial splitting of elementary fibres (AE amplitude <35 dB), (II) transverse microcracking of elementary fibres (AE amplitude 35–60 dB), (III) multiple fracture of flax bundle (AE amplitude >60 dB). Adapted from De Rosa et al. (2009) with permission from Elsevier

noticed for unaged samples or for the glass–fibres reinforced composite. Combined with the absence of fibre-matrix debonding signals after ageing, this led the authors to the conclusion that fibre/matrix interface weakening was the main damage mechanism induced by water ageing for flax composites.

5.2.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) also called **dynamic mechanical thermal analysis** (DMTA), is a technique dedicated to the assessment of the viscoelastic behaviour of materials, mainly polymers and composites. A specimen is submitted to sinusoidal stress in tension, bending, shearing or torsion and the resulting strain is measured, allowing determining the stress/strain ratio as a complex modulus. The temperature of the specimen or the loading frequency is swept in order to investigate the resulting variations of the complex modulus. The real part *E'* of the complex modulus, known as the *storage modulus*, is a measure of the elastic character of the material, while the imaginary part *E"*, known as the *loss modulus*, is a measure of its viscous character. The ratio of the loss and storage moduli, defined as the *damping factor* (or loss factor) $\tan\delta = E''/E'$, is related to internal frictions and is sensitive to different kinds of molecular motions, relaxation processes, thermal transitions and structural heterogeneities. A typical DMA graph of the evolution of storage modulus, loss modulus and $\tan\delta$ versus temperature is shown in Fig. 5.18. The maximum values of the damping factor are located at

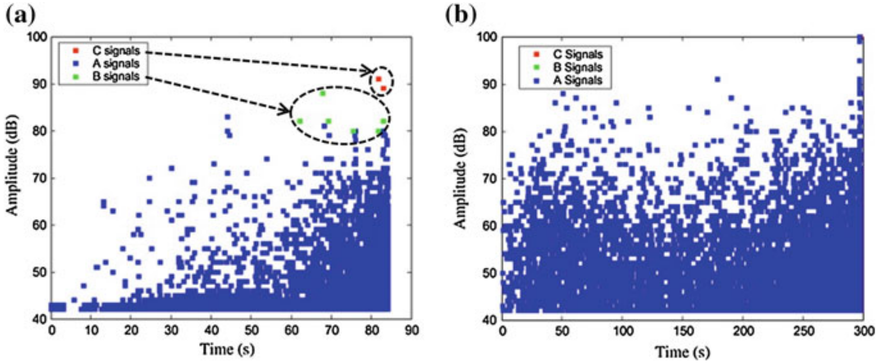
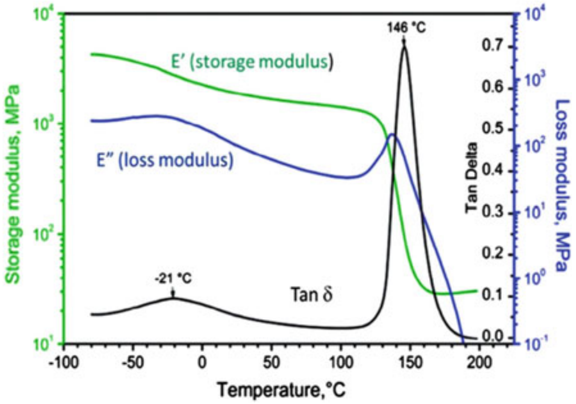


Fig. 5.17 AE signals versus tensile tests time for flax–fibre reinforced composites, unaged (**a**) and after 20 days of immersion into a water bath at room temperature (**e**). A signals: matrix cracking, B signals: fibre–matrix debonding and C signals: fibre failure. Adapted from Assarar et al. (2011) with permission from Elsevier

specific temperatures associated to polymer chains relaxations such as the glass transition *Tg*. In the vinicity of the *Tg*, the α transition is usually characterized by a prominent peak, being more pronounced with increasing amorphous polymer fraction. Other transitions associated to smaller molecular motions are visible at lower temperatures, i.e. β and γ transitions.

Energy dissipation in composites, which is expressed by the damping factor measured by DMA, depends on the intrinsic viscoelastic properties of the individual components, their volume fractions and arrangement in the composite and also the interfacial adhesion between the fibre and the matrix. A poorly bonded interface potentially leads to local sliding-friction mechanisms and thus to additional global dissipation which tends to increase the damping factor while a strong interface cohesion tends to decrease it. Thus, the variations of the damping factor can be used as an indication of the interfacial adhesion in composites.

Fig. 5.18 Typical DMA graph of the evolution of storage modulus, loss modulus and tan δ versus temperature. Reprinted from Saba et al. (2016), with permission from Elsevier



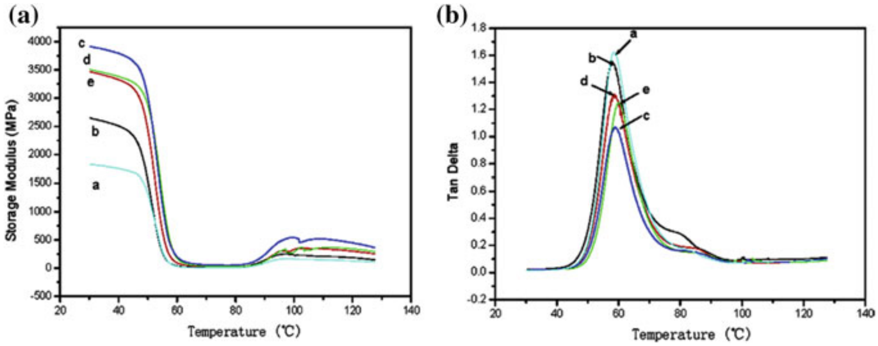


Fig. 5.19 Temperature dependence of storage modulus (A) and damping factor (B) of PLA and PLA-based composites: neat PLA (a), composite with untreated fibres (b), composite with alkali treated fibres (c), composite with APS silane treated fibres (d), composite with GPS silane treated fibres (e). Reprinted from Yu et al. (2010), Fig. 5 with permission from Elsevier

In a study about PLA/ramie composites, Yu et al. (2010) conducted dynamic mechanical analyses which highlight the effect of fibre surface treatments on the viscoelastic properties of the composites. Figure 5.19 displays the comparison of the temperature dependence of the storage modulus and the damping factor for neat PLA and PLA-based composites (with untreated fibres and with fibres treated by alkali and silanes). The increase of the storage modulus at ambient temperature with the presence of the ramie fibres confirms their reinforcement capability which is additionally improved by the tested fibre treatments, especially the alkali one. The storage modulus of all samples drops at around 60 °C. The damping factor exhibits a maximum for this temperature, which can be associated to the glass transition temperature of the system. The amplitude of the damping peak of the treated composites decreases in comparison to neat PLA and untreated composites, which indicates that the treatments decreased the molecular mobility of macromolecular chains at the fibre/matrix interface due to an improved compatibility between PLA matrix and ramie fibres. The strength of the same materials, which was measured by flexural tests, resulted in the same ranking, confirming the efficiency of the alkali and silane treatments to enhance interfacial adhesion and hence the composites' performances.

Many other studies about natural fibre reinforced polymeric matrix composites confirmed that the presence of fibres tends to directly influence the intensity of the damping factor in the vicinity of the main relaxation transition of the polymer matrix (Abdelmouleh et al. 2007; Idicula et al. 2005; Le Moigne et al. 2014; Mohanty et al. 2006; Pothan et al. 2003; Romanzini et al. 2013). A reason of the intensity reduction, is that there is less matrix by volume to dissipate the vibration energy, assuming that the damping factor of the matrix is higher than that of the fibres at the considered temperature. Moreover, fibres and favourable fibre/matrix interactions can reduce the mobility of polymer chains, leading to lower degrees of molecular motion and hence lower damping factors.

A possible quantification of the dissipation associated to the interface relies to the definition of an interfacial damping factor $\tan\delta_{in}$ calculated from the difference between the actual measured damping factor $\tan\delta$ of a composite and the theoretical damping factor $\tan\delta_c$ of the corresponding fibre-matrix system:

$$\tan\delta_{in} = \tan\delta - \tan\delta_c \tag{5.7}$$

There exist several models for estimating the theoretical damping factor $\tan\delta_c$ of the composite (Dong and Gauvin 1993). A simple model relies on the rule of mixture applied to the intrinsic damping ratios of the components:

$$\tan\delta_c = V_f \tan\delta_f + \left(1 - V_f\right) \tan\delta_m \tag{5.8}$$

where V_f, $V_m\left(= 1 - V_f\right)$ and $\tan\delta_f$, $\tan\delta_m$ are the volume fraction and the damping ratio of the fibre and the matrix, respectively.

When the damping factor of the matrix becomes much higher than the damping factor of the fibre, which usually occurs for a polymer in the vicinity of its main relaxation temperature, Eq. 5.8 simplifies in:

$$\tan\delta_c = \left(1 - V_f\right) \tan\delta_m \tag{5.9}$$

In order to account for the variable level of the interactions between polymer and fibres, Ziegel and Romanov (1973) proposed an interfacial adhesion factor B and a rewriting of Eq. 5.9 as follows:

$$\tan\delta_c = \left(1 - BV_f\right) \tan\delta_m \tag{5.10}$$

B is a correction parameter that can be related to the effective thickness of the fibre/matrix interphase around the fibres. The stronger the interfacial interactions, the thicker the immobilized layer of polymer chains and the higher the value of parameter B (Dong and Gauvin 1993).

In a study about the interface in flax/PLA composites, Le Moigne et al. (2014) evaluated the influence of organosilane treatments on the viscoelastic behavior of the biocomposites submitted to a temperature ramp. The authors focused their discussion on the damping factor measurements in the vicinity of the main relaxation temperature. Incorporating non-treated flax fibres in the matrix led to a strong decrease of the damping, which was amplified by the treatments. The authors completed their analysis of the interface by calculating from Eq. 5.10 the value of parameter B for the different biocomposites. Based on the results of parameter B and considering an elementary fibre of 20 µm in diameter, it was possible to calculate an equivalent thickness of interphase (Fig. 5.20). The resulting values of interphase thickness were in agreement with those reported in literature for other composites systems based on glass fibres. The corresponding improvements of the interfacial adhesion were also consistent with the increased stiffness and strength measured for the treated biocomposites.

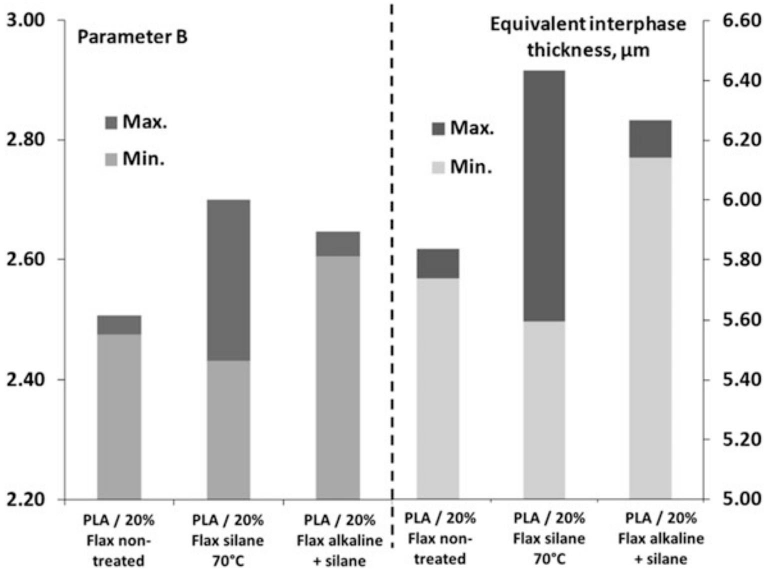


Fig. 5.20 Values of parameter B from Eq. (5.10) and equivalent interphase thickness for the different PLA/flax biocomposites. Reprinted from Le Moigne et al. (2014), with permission from Elsevier

5.3 Thermal Analysis of the Interphase

Thermal analysis is defined by the IUPAC (International Union of Pure and Applied Chemistry) recommendations (Lever et al. 2014) and ICTA (International Confederation for Thermal Analysis) publications (Lombardi 1980) as including all techniques in which a sample property is measured versus temperature. It includes thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) that will be detailed below, but also dielectric thermal analysis (DEA), dynamic mechanical analysis (DMA detailed in the previous section), thermoluminescence (TL), thermomechanical analysis (TMA), thermodilatometry (TD) and so on.

Thermogravimetry analysis (TGA) is commonly used to determine selected characteristics of materials that exhibit mass loss due to decomposition, oxidation, or loss of volatiles such as moisture. Differential scanning calorimetry (DSC) measures differences in heat flow inputs into a sample and a reference when they are subjected to a controlled temperature program. Practically, all physical and chemical processes involve changes in enthalpy or specific heat. For example, as a solid sample melts, higher heat flow will be required to maintain the sample temperature at the temperature of the reference. Melting is thus an endothermic phase transition. Likewise, as the sample undergoes exothermic processes, such as crystallization, less heat is required to maintain sample temperature at the reference temperature. These phase transitions are first-order transitions. The glass transition characterized by a sudden increase of molecular mobility manifests itself in DSC by a second-order transition, i.e. an endothermic jump in the heating curve.

5.3.1 Thermogravimetry Analysis

The thermal stability of untreated natural fibres has been widely studied. A three-step process is commonly suggested. The first mass-loss occurring between 25 and 150 °C is generally associated to dehydration of chemically bound moisture (up to 10%). Hemicelluloses decomposition may also occur in this range up to 180 °C. Lignin begins to decompose at 160 °C and continues up to 400 °C. Cellulose decomposition is the third step that occurs between 200 and 300 °C with a rapid mass loss between 300 and 360 °C. As already exposed in Chap. 4 Sect. 4.5.1, the presence of grafted molecules onto natural fibres modifies their thermal stability. In the case of alkaline and acetylated treatments, hemicellulose and lignin extraction induces an improvement of the thermal stability of natural fibres in the temperature range 250–350 °C. Moreover TGA curves exhibited higher temperature peaks for alkali pre-treated acetylated fibres (Kabir et al. 2013). As concerns natural fibres treated by enzymes, George et al. (2014) concluded that enzymes can be used to address the limited thermal stability of natural fibres by selectively removing the least thermally stable pectic and hemicellulosic components. Physical treatments such as plasma treatments did not really influence the thermal stability of natural fibres as shown by Sinha (2009) and more recently by Scalici et al. (2016). Finally the effects of silane treatments were also investigated by Kabir et al. (2013). No change was observed as concerned hemicellulose decomposition in comparison to untreated fibres, indicating that silane treatments did not remove hemicellulose and that silane grafting protected the fibre from thermal decomposition at higher temperatures. In the case of alkali pre-treated silanised fibres, an enhancement of the thermal resistance at 250–300 °C was observed.

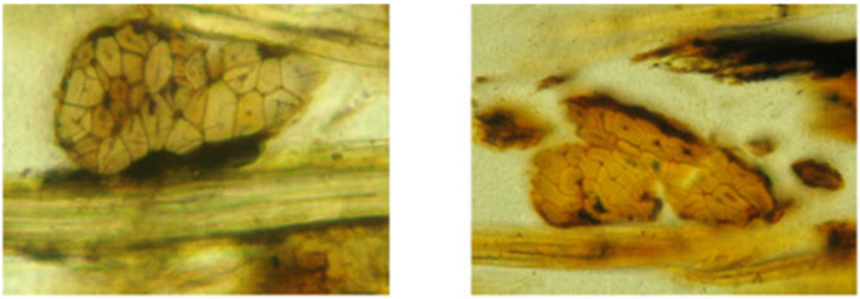
Only few papers studied the effect of natural fibres surface treatments on the thermal stability of biocomposites themselves. Pracella et al. (2010) showed a lower thermal stability of PP/hemp fibres biocomposites when a maleic anhydride modified PP is introduced or when maleic anhydride grafted hemp fibres are used. On the contrary, Sisti et al. (2016) give evidence of a greater thermal stability of PBS biocomposites containing retted hemp fibres compared to PBS/unretted hemp biocomposites, in agreement with TGA results carried on fibres alone. But major papers are generally focused on the development of specific flame retardants grafted onto natural fibres (Shumao et al. 2010; Chen et al. 2011; Suardana et al. 2011; Dorez et al. 2014a). Dorez et al. (2014a) showed a loss of thermal stability of polybutylene succinate (PBS)/flax fibres biocomposites when fibres are grafted with different phosphorus compounds. Phosphorylation of flax fibres that occurs at low temperatures seemed to favour their dehydration inducing both an enhancement of the residue formation and PBS degradation. An increase of the residue with the grafting rate was observed and the action was stronger with phosphorus-based molecules (such as dihydrogen ammonium phosphate DAP) compared to phosphonated polymers (poly-dimethyl(methacryloxy)methyl phosphonate homopolymer or corresponding copolymer with methylmethacrylate). It was assumed that only a part of phosphonic acid functions of each polymer chain was covalently bonded onto the fibre surface contrary to DAP. Moreover the advantage provided by the grafting strategy of phosphonated molecules onto the natural fibres and their localization at the interface was pointed out compared to additive strategy of the same molecules in PBS (Dorez et al. 2014b). Recently Fan and Naughton (2016) suggested a mechanism describing the decomposition steps close to the fibre/matrix interface in the case of hemp fibre reinforced polyester composites. These authors observed that an increase in temperature leads successively (i) to primary cell wall decomposition and interfacial separation due to fibre shrinkage, (ii) then to secondary cell wall decomposition (which are lignin poor) within the char region, and (iii) finally to lignin rich primary cell walls decomposition leading to a deeply blackened but still intact region. When ignition occurred, fibres are completely decomposed leaving a residue of charred material and voids (Fig. 5.21).

Concluding, TGA is considered to highlight the improvement of the thermal stability of natural fibres after surface modification. But up to only few studies were focused on the understanding of the thermal degradation mechanisms within biocomposites in relation to the fibre/matrix interface and its modification.

5.3.2 Differential Scanning Calorimetry

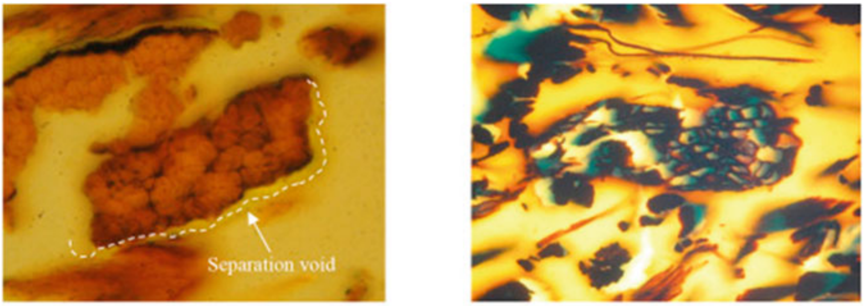
Differential scanning calorimetry (DSC) can be used to study the effect of fibres surface treatments on the crystallization of polymer matrices. Surface and resulting interface modifications can influence two main factors as regard to the polymer crystallization in composites: (i) the nucleating effect of fibres that influences the crystallization kinetics, and (ii) the steric hindrance induced by fibre/matrix interactions that alters the growth of the polymeric crystals and could inhibit crystallization.

Generally, an increase in the crystallinity ratio is obtained and is associated to the appearance of a transcrystalline region at the fibre/matrix interface. This increase can reach up to 9% as shown by Joseph et al. (2003) studying the influence of hemp fibres surface modifications (isocyanate-based treatment, oxidative treatment by KMnO4) and by Pracella et al. (2010) analysing the effect of the addition of maleic anhydride modified PP, both in the case of PP/hemp biocomposites. Similar tendencies were also observed for poly(hydroxybutyrate-co-valerate) (PHBV) reinforced by torrefied wheat straw fibres (Berthet et al. 2016) and for poly (lactic acid) (PLA) reinforced by acetylated cellulose fibres (Spiridon et al. 2016). Wang et al. (2011) found that alkali or aminosilanes (APS) had little or no influence on the nucleation ability of sisal fibres in sisal/PLA biocomposites. In contrast, Sisti et al. (2016) give evidence of a decreased PBS crystallinity when retted hemp fibres are used compared to unretted ones, probably due to propounced steric hindrance thanks to stronger chemical interactions between the matrix and the fibres. Similar conclusions were proposed by Le Moigne et al. (2014) for silanised or alkali pre-treated silanised flax fibres incorporated in PLA and by Bourmaud and Baley (2007) with addition of maleic anhydride grafted PP in PP/hemp biocomposites. The authors attributed the decreased nucleating effect of the treated fibres to enhanced interactions between the matrix and the fibres that immobilize polymer chains at the fibres surface.



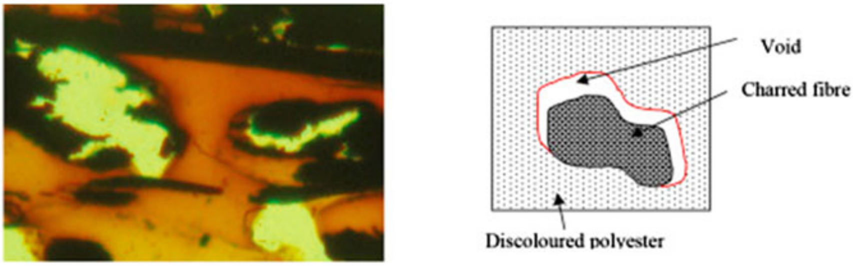
A=Virgin hemp fibre bundles

B=Discoloured fibre bundle (onset of thermal damage: mid degradation region)



C=Deeply discoloured with interfacial separation (just below char front)

D=Deeply blackened with decomposition of secondary cell wall (mid char region)



E=Completely decomposed (pyrolysis front)

F=Illustration of degradation of interfacial bond

Fig. 5.21 (from A to E) Progressive steps of the decomposition of a hemp fibres reinforced polyester biocomposite located at the fibre/matrix interface; (F) Illustration of degradation of interfacial bond. Reproduced from Fan and Naughton (2013) with permission from Elsevier

Furthermore, variations in the glass transition temperature *Tg* related to changes in molecular mobility in the interphase zone can also be detected. As an example, Le Moigne et al. (2014) measured a positive shift of the glass transition temperature *Tg* of about 2 °C in silane treated flax fibres/PLA composites which was attributed to reduced molecular mobility of PLA chains in the interphase zone due to enhanced fibre/matrix interactions. In this regard, Lipatov (1977) and later Théocaris (1987) proposed relations allowing to evaluate the interphase thickness in filled polymer systems based on the measurement of the variation of thermal capacity of the composite at the glass transition temperature Tg. For fibre reinforced composites, Eq. 5.11 was proposed:

$$\left(\frac{\Delta r_i + r_f}{r_f}\right)^2 - 1 = \frac{\lambda v_f}{1 - v_f} \tag{5.11}$$

with r_f the radius of the fibres, Δri the interphase thickness, vf the fibre volume fraction, λ an interaction parameter related to the fraction of macromolecular chains whose mobility is reduced in the interphase zone and $\lambda = 1 - \Delta C_p^c/\Delta C_p^m$, with ΔC_p^c the variation of thermal capacity of the composite at Tg, and ΔC_p^m the variation of thermal capacity of the matrix at Tg. Correlation between the interphase thickness evaluated by Eq. 5.11 and the tensile strength of sized glass fibre composites/PP has been found (Karian 1996). Nevertheless, this model has not been applied yet to natural fibre reinforced composites.

Concluding, changes in the polymer crystallization and glass transition in biocomposites related to surface treatments and fibre/matrix interactions are considered as relevant phenomena when studying the interfacial properties in natural fibre based composites. Opposite trends are observed depending on the nature of surface modifications of natural fibres. New developments on high performing microscopic techniques, such as atomic force microscopy AFM, coupled with thermal analysis should allow to progress in the understanding of macromolecular organization and interactions at the interphase in natural fibre reinforced composites.

5.4 Concluding Remarks

Although numerous studies investigated the development of natural fibres treatments intended to improve the interfacial adhesion with polymer matrices, no standardized methods for quantifying the quality of the interphase within natural fibre reinforced composites emerge, and various approaches are currently developed. They benefit from the recent development of new means of observation and characterization techniques as Atomic Force Microscopy (AFM) or X-ray computed tomography which make it possible to study the interphase region at the nanometric scale. It should be pointed out that the study of the interphase in such material cannot be based on a single "universal" technique and generally requires a set of experimental techniques and eventually modelling approaches which each provides information on the interphase. When evaluating the efficiency of a specific natural fibre treatment and its effect on the interfacial properties of a composite material, a multi-technique approach should thus be conducted:

- **Microscopic observations** (optical, SEM, X-ray tomography…) would provide (i) qualitative information on the microstructure of the matrix/reinforcement interphase zone (cohesion, trancrystallinity) and the interfacial breakage mechanisms (failure surface by SEM), and (ii) quantitative informations can be obtained by image analysing with measurements of microstructural parameters such as distribution and orientation of reinforcements, or (iii) local mechanical measurements in the interphase region (AFM, nano-indentation…);
- **Physico-chemical characterizations** of natural fibres and their composites are likely to provide information in terms of (i) chemistry: elemental composition, chemical structure of the functionalizing molecules and nature of the chemical bonds with matrix or the fibres (AES, ToF-SIMS, XPS, EDX, NMR, IR, Raman, GPC…), (ii) physico-chemistry and topography: surface energy, polarity (contact angle, IGC) and roughness (AFM) of the fibres (iii) physics: crystallisation and relaxation phenomena related to the mobility of macromolecular chains of the polymer matrix and/or coupling agent in the interphase zone (DSC);
- **Micromechanical analyzes** (pull-out, fragmentation, in situ tensile test by SEM) allow to assess (i) the mechanical behaviour and failure mechanisms at the interface and (ii) the interfacial shear strength (IFSS) between the reinforcement and the matrix for a single fibre model composite, being far from a real composite material;
- **Dynamic mechanical analysis** (DMA/DMTA) gives specific information on (i) the viscoelastic behaviour of the composites and (ii) relaxation phenomena related to the mobility of macromolecular chains of the polymer matrix and/or coupling agent in the interphase zone and can be coupled with DSC analysis;
- **Static mechanical analysis** (tensile, shear) would provide information on (i) the macroscopic mechanical behaviour of the composites at small strain (stiffness, visco-elasticity), (ii) their mechanisms of damage at large strain (ductility, ultimate strength, ILSS), thus indirectly characterizing the consequences of the quality of the interfacial adhesion.

References

Abdelmouleh M, Boufi S, Belgacem M, Dufresne A (2007) Short natural–fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. Compos Sci Technol 67:1627–1639

Ahimou F, Semmens MJ, Novak P, Haugstad G (2007) Biofilm cohesive measurement using a novel atomic force microscopy methodology. Appl Environ Microbiol 73(9):2897–2904

Alemdar A, Zhang H, Sain M, Cescutti G, Müssig J (2008) Determination of fiber size distributions of injection moulded polypropylene/natural fibers using x-ray microtomography. Adv Eng Mater 10:126–130

Assarar M, Scida D, El Mahi A, Poilâne C, Ayad R (2011) Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: flax–fibres and glass–fibres. Mater Des 32:788–795

Agarwal BD, Broutman LJ, Chandrashekhara K (2006) Analysis and performance of fiber composites. Wiley

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

Beckermann GW, Pickering KL (2009) Engineering and evaluation of hemp fibre reinforced polypropylene composites: micro–mechanics and strength prediction modelling. Compos Part A Appl Sci Manuf 40:210–217

Bergeret A, Krawczak P (2012) Liaison renfort/ matrice– Définition et caractérisation. Techniques de l'Ingénieur 33:1–25

Berthet MA, Angellier-Coussy H, Machado D, Hilliou L, Staebler A, Vicente A, Gontard N (2015) Exploring the potentialities of using lignocellulosic fibres derived from three food by–products as constituents of biocomposites for food packaging. Ind Crops Prod 69:110–122

Berthet MA, Commander JM, Rouau X, Gontard N, Angellier Coussy H (2016) Torrefaction treatment of lignocellulosic fibres for improving fibre/matrix adhesion in a biocomposite. Mater Des 952:223–232

Bledzki AK, Jaszkiewicz A (2010) Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres—A comparative study to PP. Compos Sci Technol 70 (12):1687–1696

Bourmaud A, Baley C (2007) Investigations on the recycling of hemp and sisal fibre reinforced polypropylene composites. Polym Degrad Stab 92:1034–1045

Bourmaud A, Ausias G, Lebrun G, Tachon ML, Baley C (2013) Observation of the structure of a composite polypropylene/flax and damage mechanisms under stress. Ind Crops Prod 43:225–236

Cech V, Palesch E, Lukes J (2013) The glass Fiber–polymer matrix Interface/interphase characterized by nanoscale imaging techniques. Compos Sci Technol 83:22–26

Chen D, Li J, Ren J (2011) Combustion properties and transference behaviour of ultrafine microencapsulated ammonium polyphosphate in ramie fabric–reinforecd poly(L–lactic acid) biocomposites. Polym Int 60(4):599–606

Chichti E, George M, Delenne JY, Radjai F, Lullien-Pellerin V (2013) Nano–mechanical properties of starch and gluten biopolymers from atomic force microscopy. Eur Polym J 49 (12):3788–3795

De Rosa IM, Santulli C, Sarasini F (2009) Acoustic emission for monitoring the mechanical behaviour of natural fibre composites: a literature review. Compos Part A Appl Sci Manuf 40:1456–1469

Di Giuseppe E, Castellani R, Dobosz S, Malvestio J, Berzin F, Beaugrand J, Delisée C, Vergnes B, Budtova T (2016) Reliability evaluation of automated analysis, 2D scanner, and micro-tomography methods for measuring fiber dimensions in polymer-lignocellulosic fiber composites. Compos Part A Appl Sci Manuf 90:320–329

Dong S, Gauvin R (1993) Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials. Polym Compos 14:414–420

Dorez G, Otazaghine B, Taguet A, Ferry L, Lopez Cuesta JM (2014a) Improvement of the fire behaver of poly(1,4–butanediol succinate)/flax biocomposites by fiber surface modification with hosphorus compounds: molecular versus macromolecuar strategy. Polym Int 63(9):1665–1673

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

Downing TD, Kumar R, Cross WM, Kjerengtroen L, Kellar JJ (2000) Determining the interphase thickness and properties in polymer matrix composites using phase imaging atomic force microscopy and nanoindentation. J Adhes Sci Technol 14(14):1801–1812

Effah B, Van Reenen A, Meincken M (2015) Characterization of the interfacial adhesion of the different components in wood–plastic composites with AFM. Springer Sci Reviews 3:97–111

Fan M, Naughton A (2016) Mechanisms of thermal decomposition of natural fibre composites. Compos B 88:1–10

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

Fuentes CA, Ting KW, Dupont-Gillain C, Steensma M, Talma AG, Zuijderduin R, Van Vuure AW (2016) Effect of humidity during manufacturing on the interfacial strength of non–pre–dried flax fibre/unsaturated polyester composites. Compos Part A Appl Sci Manuf 84:209–215

Gao SL, Mäder E (2002) Characterization of interphase nanoscale property variations in glass fiber reinforced poypropylene and epoxy resin composites. Compos Part A Appl S 33:559–576

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

George M, Mussone PG, Bressler DC (2014) Surface and thermal characterization of natural fibres treated with enzymes. Ind Crops Prod 53:365–373

Graupner N, Fischer H, Ziegmann G, Müssig J (2014a) Improvement and analysis of fi–bre/matrix adhesion of regenerated cellulose fibre reinforced PP–, MAPP– and PLA–composites by the use of Eucalyptus globulus lignin. Compos Part B Eng 66:117–125

Graupner N, Rößler J, Ziegmann G, Müssig J (2014b) Fibre/matrix adhesion of cellulose fibres in PLA, PP and MAPP: A critical review of pull–out test, microbond test and single fibre fragmentation test results. Compos Part A Appl Sci Manuf 63:133–148

Gu Y, Li M, Wang J, Zhang Z (2010) Characterization of the interphase in carbon fiber/polymer composites using a nanoscale dynamic mechanical imaging technique. Carbon 48(11):3229–3235

Guillebaud-Bonnafous C, Vasconcellos D, Touchard F, Chocinski-Arnault L (2012) Experimental and numerical investigation of the interface between epoxy matrix and hemp yarn. Compos Part A Appl Sci Manuf 43:2046–2058

Herrera-Franco PJ, Drzal LT (1992) Comparison of methods for the measurement of fibre/matrix adhesion in composites. Composites 23:2–27

Herrera-Franco P, Valadez-González A (2004) Mechanical properties of continuous natural fibre–reinforced polymer composites. Compos Part A Appl Sci Manuf 35:339–345

Hodzic A, Stachurski ZH, Kim JK (2000a) Nano–indentation of polymer–glass interfaces. Part I. Experimental and mechanical analysis. Polymer 41:6895–6905

Hodzic A, Kim JK, Stachurski ZH (2000b) The nano–scratch technique as a novel method for measurement of an interphase width. J Mater Sci Lett 19:1665–1667

Idicula M, Malhotra SK, Joseph K, Thomas S (2005) Dynamic mechanical analysis of randomly oriented intimately mixed short banana/sisal hybrid fibre reinforced polyester composites. Compos Sci Technol 65:1077–1087

Jakes JE, Hermanson JC, Stone DS (2007) Nanoindentation of the interphase region of a wood–reinforced polypropylene composite. In: 9th International conference on wood & biofiber plastic compsites. Wisconsin (USA)

Joseph PV, Joseph K, Thomas S, Pillai CKS, Prasad VS, Groeninckx G, Sarkissova M (2003) The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Compos Part A Appl Sci Manuf 34:253–266

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

Karian HG (1996) Designing interphases for mega-coupled polypropylene composites. Plast Eng 52(1):33–35

Kastner J, Plank B, Reh A, Salaberger D, Heinzl C (2012) Advanced x–ray tomographic methods for quantitative characterisation of carbon fibre reinforced polymers. In: 4th International symposium on NDT in aerospace. We.3.A.1

Kelly A, Tyson WR (1965) Tensile properties of fibre–reinforced metals: copper/tungsten and copper/molybdenum. J Mech Phys Solids 13:329–350

Kim JK, Sham ML, Wu J (2001) Nanoscale characterisation of interphase in silane treated glass fibre composites. Compos Part A Appl S 32:607–618

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 Duigou A, Davies P, Baley C (2013) Exploring durability of interfaces in flax fibre/epoxy micro–composites. Compos Part A Appl Sci Manuf 48:121–128

Le Duigou A, Merotte J, Bourmaud A, Davies P, Belhouli K, Baley C (2017) Hygroscopic expansion: A key point to describe natural fibre/polymer matrix interface bond strength. Compos Sci Technol 151:228–233

Le Moigne N, Longerey M, Taulemesse JM, Bénézet 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 SH, Wang S, Lee S-H (2007) Evaluation of interphase properties in a cellulose fiber–reinforced polypropylene composite by nanoindentation and finite element analysis. Compos Part A Appl S 38(6):1517–1524

Lever T, Haines P, Rouquerol J, Charsley EL, Van Eckeren P, Burlett DJ (2014) ICTAC nomenclature of thermal analysis (IUPAC Recommandations 2014). Pure Appl Chem 86(4):545–553

Li Y, Pickering KL, Farrell RL (2009) Determination of interfacial shear strength of white rot fungi treated hemp fibre reinforced polypropylene. Compos Sci Technol 69:1165–1171

Lipatov YS (1977) Physical chemistry of filled polymers. In: Moseley RJ (ed) International polymer science and technology monograph, vol 2, Moscou

Théocaris PS (1987) The mesophase concept in composites. Springer, Verlag Berlin

Lombardi G (1980) For better thermal analysis, 2nd edn. ICTA, Rome

Ludueña L, Vázquez A, Alvarez V (2012) Effect of lignocellulosic filler type and content on the behavior of polycaprolactone based eco–composites for packaging applications. Carbohydr Polym 87:411–421

Mai K, Mäder E, Mühle M (1998) Interphase characterization in composites with new non–destructive methods. Compos Part A Appl S 29:1111–1119

Marrot L, Bourmaud A, Bono P, Baley C (2014) Multi–scale study of the adhesion between flax fibers and biobased thermoset matrices. Mater Des 62:47–56

Martin N, Mouret N, Davies P, Baley C (2013) Influence of the degree of retting of flax fibers on the tensile properties of single fibers and short fiber/polypropylene composites. Ind Crops Prod 49:755–767

Miller B, Muri P, Rebenfeld L (1987) A microbond method for determination of the shear strength of a fiber/ resin interface. Compos Sci Technol 28:17–32

Miller B, Gaur U, Hirt DE (1991) Measurement and mechanical aspects of the microbond pull–out technique for obtaining fiber/resin interfacial shear strength. Compos Sci Technol 42:207–219

Mohanty S, Verma SK, Nayak SK (2006) Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites. Compos Sci Technol 66:538–547

Nikishkov Y, Airoldi L, Makeev A (2013) Measurement of voids in composites by X–ray Computed Tomography. Compos Sci Technol 89:89–97

Park JM, Quang ST, Hwang BS, De Vries KL (2006) Interfacial evaluation of modified Jute and Hemp fibers/polypropylene (PP)–maleic anhydride polypropylene copolymers (PP–MAPP) composites using micromechanical technique and nondestructive acoustic emission. Compos Sci Technol 66:2686–2699

Park JM, Kim PG, Jang JH, Wang Z, Hwang BS, DeVries KL (2008) Interfacial evaluation and durability of modified Jute fibers/polypropylene (PP) composites using micromechanical test and acoustic emission. Compos Part B Eng 39:1042–1061

Pothan LA, Oommen Z, Thomas S (2003) Dynamic mechanical analysis of banana fiber reinforced polyester composites. Compos Sci Technol 63:283–293

Pracella M, Haque MMU, Alvarez V (2010) Functionalization, compatibilization and properties of polyolefin composites with natural fibers. Polymers 2:554–574

Rials TG, Wolcott MP, Nassar JM (2001) Interfacial contributions in lignocellulosic fiber–reinforced polyurethane composites. J Appl Polym Sci 80(4):546–555

Romanzini D, Lavoratti A, Ornaghi HL, Amico SC, Zattera AJ (2013) Influence of fiber content on the mechanical and dynamic mechanical properties of glass/ramie polymer composites. Mater Des 47:9–15

Romhány G, Karger-Kocsis J, Czigány T (2003) Tensile fracture and failure behavior of thermoplastic starch with unidirectional and cross–ply flax fiber reinforcements. Macromol Mater Eng 288:699–707

Saba N, Jawaid M, Alothman OY, Paridah MTT (2016) A review on dynamic mechanical properties of natural fibre reinforced polymer composites. Constr Build Mater 106:149–159

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 composies; A preliminary study. Composites Part B Eng 94:167–175

Sever K, Sarikanat M, Seki Y, Erkan G, Erdoğan ÜH, Erden S (2012) Surface treatments of jute fabric: the influence of surface characteristics on jute fabrics and mechanical properties of jute/polyester composites. Ind Crops Prod 35:22–30

Shumao L, Jie R, Hua Y, Tao Y, Weizhong Y (2010) Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber–reinforced poly(lactic acid) biocomposites. Polym Int 59(2):242–248

Singh AP, Anderson R, Park BD, Nuryawan A (2013) A novel approach for FE–SEM imaging of wood–matrix polymer interface in a biocomposite. Micron 54–55:87–90

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

Sisti L, Totaro G, Vannini M, Fabbri P, Kalia S, Zatta A, Celli A (2016) Evaluation of retting process as a pre–treatment of vegetable fibers for the preparation of high–performance polymer biocomposites. Ind Crops Prod 81:56–65

Spiridon I, Darie RN, Kangas H (2016) Inlfuence of fiber modifications on PLA/fiber composites. Behavior to accelerated weathering. Composites Part B Eng 92:19–27

Suardana NPG, Ku MS, Lim JK (2011) Effects of diammonium phosphate on the flammability and mechanical properties of biocomposites. Mater Des 32:1990–1999

Tillman MS, Hayes BS, Seferis JC (2000) Analysis of polymeric composite interphase regions with thermal atomic force microscopy. J Appl Polym Sci 80:1643–1649

Torres FG, Cubillas ML (2005) Study of the interfacial properties of natural fibre reinforced polyethylene. Polym Test 24:694–698

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

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 S 42:66–74

Wright JR, Mathias LJ (1993) Physical characterization of wood and wood–polymer composites: an update. J Appl Polym Sci 48(12):2225–2239

Wurm A, Ismail M, Kretzschmar B, Pospiech D, Schick C (2010) Retarded crystallization in polyamide/layered silicates nanocomposites caused by an immobilized interphase. Macromolecules 43:1480–1487

Yang L, Thomason JL (2010) Interface strength in glass fibre–polypropylene measured using the fibre pull–out and microbond methods. Compos Part A Appl S 41:1077–1083

Yang L, Thomason JL (2012) Development and application of micromechanical techniques for characterising interfacial shear strength in fibre–thermoplastic composites. Polym Test 31:895–903

Yang P, Elhajjar R (2014) Porosity content evaluation in carbon fibre/epoxy composites using X–ray computed tomography. Polymer-Plastics Technol Eng 53:217–222

Young TJ, Crocker LE, Broughton WR (2013) Observations on interphase characterisation in polymer composites by nano–scale indentation using AFM and FEA. Compos Part A Appl S 50:39–43

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. Compos Part A Appl Sci Manuf 41:499–505

Zhandarov S, Mäder E (2005) Characterization of fiber/matrix interface strength: applicability of different tests, approaches and parameters. Compos Sci Technol 65:149–160

Zhang D, Milanovic NR, Zhang Y, Su F, Miao M (2014) Effects of humidity conditions at fabrication on the interfacial shear strength of flax/unsaturated polyester composites. Compos Part B Eng 60:186–192

Ziegel KD, Romanov A (1973) Modulus reinforcement in elastomer composites. II polymeric fillers. J Appl Polym Sci 17:1133–1142

Index

N. Le Moigne et al., *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*,
Biobased Polymers, https://doi.org/10.1007/978-3-319-71410-3