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Lina Fernanda Ballesteros

Michele Michelin

António Augusto Vicente

José António Teixeira

Miguel Ângelo Cerqueira

Lignocellulosic Materials and Their Use in Bio- based Packaging



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Lina Fernanda Ballesteros
Centre of Biological Engineering
University of Minho
Braga
Portugal

José António Teixeira
Centre of Biological Engineering
University of Minho
Braga
Portugal

Michele Michelin
Centre of Biological Engineering
University of Minho
Braga
Portugal

Miguel Ângelo Cerqueira
International Iberian Nanotechnology
Laboratory
Braga
Portugal

António Augusto Vicente
Centre of Biological Engineering
University of Minho
Braga
Portugal

ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISSN 2510-3407 ISSN 2510-3415 (electronic)
Biobased Polymers
ISBN 978-3-319-92939-2 ISBN 978-3-319-92940-8 (eBook)
<https://doi.org/10.1007/978-3-319-92940-8>

Library of Congress Control Number: 2018943246

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

Preface

The use of bio-based resources for the development of new materials and structures, such as packaging materials, is one of the bioeconomy's key points. Thus, the harnessing of natural materials with a biodegradable character can help to reduce CO₂ emissions and use efficiently natural resources and materials. The use of bio-based polymers for packaging provides several advantages over usual polymers, but also present in most cases a poor barrier to moisture and weak mechanical properties that limit their application in foods. If these drawbacks are overcome, it will be the beginning of a new era to the bio-based packaging materials. One of the strategies is the use of lignocellulosic materials that can be used as main materials or as additives in the production of bio-based packaging and thus contribute to reduce the use of petroleum-based materials. Therefore, before using lignocellulosic materials for packaging applications, it is important to understand their main constituents, extraction methodologies and their main physico-chemical properties. The way as they can be added to packaging materials and how the lignocellulosic materials influence the main properties of packaging should also be fully understood.

Therefore, this book will provide a comprehensive review on the use of lignocellulosic materials for the development of bio-based packaging for food applications. Aspects such as, sources and extraction methods of lignocellulosic materials; main constituents of lignocellulosic materials; functionality of lignocellulosic materials; the development of bio-based and biodegradable packaging; incorporation of lignocellulosic materials in bio-based packaging materials; and properties and functionality of bio-based packaging, will be discussed. Other bio-based polymers are also considered, including the polymers extracted from biomass, those synthesized by bio-derived monomers and those produced by microorganisms. In the end, examples of the use of packaging based on lignocellulosic materials for food applications will be given.

It is expected that this book will be considered as a reference for all aspects of the use of lignocellulosic materials in the development of bio-based packaging, providing important and new information regarding the development of bio-based packaging for food applications.

Braga, Portugal

Lina Fernanda Ballesteros
Michele Michelin
António Augusto Vicente
José António Teixeira
Miguel Ângelo Cerqueira

Acknowledgements

This study was supported by the FCT under the scope of the strategic funding of UID/BIO/04469/2013 unit and COMPETE 2020 (POCI-01-0145-FEDER-006684) and BioTecNorte operation (NORTE-01-0145-FEDER-000004) funded by the European Regional Development Fund under the scope of Norte2020—Programa Operacional Regional do Norte. Michele Michelin is a recipient of a Portuguese Foundation for Science and Technology (FCT) fellowship (SFRH/BPD/100786/2014).

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About the Authors



Lina Fernanda Ballesteros is graduated in Food Engineering from the University of Caldas, Colombia, where she received a meritorious mention and honours degree for the work developed in her Thesis in 2006. She finished her Ph.D. in Chemical and Biological Engineering at the University of Minho in Braga, Portugal, in 2016. Her research has been focused on the development of food packaging materials and the reutilization of agro-industrial wastes to extract compounds of interest for the food industry. Since October 2016, she is a postdoctoral researcher at the Centre of Biological Engineering of the University of Minho and until now, she has published ten papers in peer-reviewed journals, one chapter, ten extended abstracts in international conferences and six abstracts in international conferences.



Michele Michelin is graduated in Biology (2001) by the Centro Universitário Barão de Mauá and holds master's degree (2005) and doctoral degree (2009) in Sciences—Compared Biology, at the Faculdade de Filosofia Ciências e Letras de Ribeirão Preto (FFCLRP) from Universidade de São Paulo, Ribeirão Preto, Brazil. From 2010 to 2012, she worked as postdoctoral researcher in the Centre of Biological Engineering (CEB) at University of Minho. Between July and December 2012, she was postdoctoral researcher at Universidade Tiradentes (UNIT), Sergipe, Brazil. From January 2013 to June 2015, she was postdoctoral researcher in the Laboratory of Microbiology and Molecular Biology at FFCLRP from USP, and during

this period, she performed a short-term mission at Department of Agricultural and Biological Engineering from Purdue University, USA. Currently, she is a postdoctoral researcher at CEB from University of Minho. Until now she published 25 papers in peer-reviewed journals; 7 chapters; 4 extended abstracts and around 40 abstracts in national and international conferences.

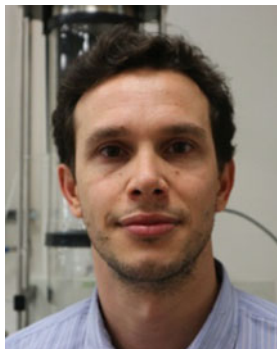


António Augusto Vicente is graduated in Food Engineering in 1994 from the Portuguese Catholic University in Porto, Portugal, and finished his Ph.D. in Chemical and Biological Engineering in 1998 at the University of Minho in Braga, Portugal. He has received his habilitation in chemical and biological engineering from the University of Minho in 2010. From an early stage of his career, he has kept close contact with the food industry and he is involved in several research projects, both national and international, together with industrial partners either as a participant or as a project leader. He has supervised 27 Ph.D. theses; he has also supervised several M.Sc. theses and 15 postdoctoral fellows. He has published over 200 research articles in international peer-reviewed journals, 4 patents and over 25 chapters in international books. He is presently an Associate Professor with Habilitation and Director of the Biological Engineering Department of the University of Minho in Braga, Portugal.



José António Teixeira is currently Professor at Biological Engineering Department, University of Minho (since 2000). He has a degree in Chemical Engineering from University of Porto (1980) and a Ph.D. in Chemical Engineering also from University of Porto (1988). He was responsible/co-responsible for the Supervision of 31 Ph.D. theses and 20 post-docs and has been the coordinator of 32 scientific research projects, 7 of which international. He was awarded the “Stimulus to Excellence”, 2006, from FCT, the “Seeds of Science” in “Engineering and Technology”, 2011, from “Ciência Hoje” and the “Scientific Merit Award”, Universidade do Minho, 2015. He is the co-editor of the books “Reactores Biológicos—Fundamentos e Aplicações” (in Portuguese), Engineering Aspects of Milk and Dairy

Products and Engineering Aspects of Food Biotechnology and the author/co-author of over 500 peer-reviewed papers.



Miguel Ângelo Cerqueira is graduated in Chemical and Biological Engineering (2005), at the University of Minho (UM) where he received two scholar merit awards and a scholarship merit award. He finished his Ph.D. in December 2010 and from the developed work, he received the award for the best Ph.D. Thesis 2011 by the School of Engineering of UM. From April 2011 to February 2016, he was postdoctoral researcher at UM focused on the development of bio-based nanostructures for food applications. In 2014, he was selected as one of the winners of the Young Scientist Award of the 17th IUFoST World Congress of Food Science and Technology. Since March 2016, he is researcher in the Food Processing Group at the International Iberian Nanotechnology Laboratory, and till now he published more than 75 papers in peer-reviewed journals; 2 patents; 5 papers in non-peer-reviewed journals; 2 books, 18 chapters; 15 extended abstracts in international conferences; 52 abstracts in international conferences; and 18 abstracts in national conferences.

Abbreviations

AFEX	Ammonia fibre/freeze explosion
AFM	Atomic force microscopy
BW	Beeswax
CA	Cellulose acetate
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystal
CO ₂ P	Carbon dioxide permeability
DCC	Dicarboxylic acid cellulose
DP	Polymerization degree
EB	Elongation at break
EVOH	Ethylene vinyl alcohol copolymer
FTIR	Fourier transform infrared
<i>G</i>	Guaiacyl
<i>G'</i>	Storage modulus
GRAS	Generally recognized as safe
GTA	Glycerol triacetate
<i>H</i>	<i>p</i> -hydroxyphenyl
HCl	Hydrochloric acid
HPC	Hydroxypropyl cellulose
HPL	Hydroxypropyl alkaline lignin
HPMC	Hydroxypropylmethyl cellulose
HSAC	Alpha-hydroxy sulphonic acid cellulose
IGE	Indian gooseberry extract
IL	Ionic liquids
LCA	Life cycle assessment
LCM	Lignocellulosic material
LDPE	Low-density polyethylene
LHW	Liquid hot water
LS	Lignosulphonate
MC	Methylcellulose

MCC	Microcrystalline cellulose
MFC	Microfibrillated cellulose
MW	Molecular weight
NC	Nanocellulose
NFC	Nanofibrillated cellulose
O ₂ P	Oxygen permeability
PBAT	Poly(butylene adipate-co-terephthalate)
PCL	Polycaprolactone
PE	Polyethylene
PEF	Pulsed-electric field
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PP	Polypropylene
PTT	Poly(trimethylene terephthalate)
PVDC	Polyvinylidene chloride
RH	Relative humidity
S	Syringyl
SEM	Scanning electron microscopy
SPI	Soya protein isolate
SS	Soya bean straw
TC	Taurine cellulose
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
T_g	Glass transition temperature
TS	Tensile strength
VC/VA	Vinyl chloride–vinyl acetate copolymer
WB	Wheat bran
WS	Wheat straw
WVP	Water vapour permeability

Chapter 1

Introduction



1.1 General Aspects and Outline

Lignocellulosic materials (LCMs) are the most available materials in the world. They are a source of biopolymers with outstanding features, which can be used as the main materials of packaging or as fillers and additives in bio-based packaging materials. This use can help to reduce CO₂ emissions and use efficiently natural resources and materials and thus follow one of the bioeconomy's key points, the use of bio-based materials for the development of new materials and structures. The use of LCMs for packaging can provide some advantages over usual polymers, such as biodegradability, edibility, and both compatibility with biopolymers and polymers according to the material used (i.e. hemicellulose is highly hydrophilic while lignin is hydrophobic). By another side, their use as fillers or additives can help improving the properties of bio-based packaging, that in most of the cases present poor barrier capacities and limited mechanical properties (e.g. cellulose structures have been used with this purpose in several types of packaging materials).

Before using lignocellulosic materials for bio-based packaging applications, it is important to understand their main constituents, extraction methodologies and their main physico-chemical properties. The way that can be used to produce packaging materials or how their addition to other materials will influence the main properties of packaging should also be totally understood.

This book provides a comprehensive review on the use of LCMs for the development of bio-based packaging for food applications. Despite being give a focus on the use of LCMs, other bio-based polymers are also presented, being considered in this group the polymers extracted from biomass (e.g. starch, proteins and lipids), the synthesized by bio-derived monomers [e.g. poly(lactic acid) (PLA) and bioethanol derivatives], and those produced by microorganisms [e.g. polyhydroxyalkanoates/polyhydroxybutyrate (PHA and PHB)], that are being already used in commercial packaging applications. Thus, this chapter provides a broad overview of the economic and environmental interest of using LCMs in

bio-based packaging and the recent numbers and developments on bio-based packaging materials. Chapter 2 primarily covers the definition of LCMs, their composition, and various sources where they can be found. It also presents the structure of lignocellulosic biomass; and a general description, advantages and disadvantages of the different pre-treatment methods. Chapter 3 summarizes the main functional properties of cellulose, hemicellulose, lignin, and their derivatives, including mechanical, chemical, thermal, rheological, and optical properties, as well as the antioxidant and antimicrobial activities. Chapter 4 presents the main processing conditions and methods to produce bio-based packaging using lignocellulosic materials. The most important properties and characterization methodologies are also presented, and in the end, the biodegradability and life cycle assessment of bio-based packaging materials are discussed. Chapter 5 presents an overview of the properties and use of lignocellulosic resources in bio-based packaging materials. It is based on the more recent studies in this field such as the development of bio-based packaging with the incorporation of cellulose and its derivatives, hemicellulose, and lignin, together with some works where mildly pre-treated lignocellulosic materials are used as filler. Furthermore, Chap. 6 presents examples of commercial applications and research studies on the application of lignocellulosic-based materials as packaging for foods. In the end, Chap. 7 presents the main conclusions and the future trends on the use of lignocellulosic materials on bio-based packaging.

1.2 Economic and Environmental Aspects of Bio-based Packaging

The use of bio-based materials for the development of new materials and structures is highly related to a bio-based economy where it is advocated that the use of materials with a biodegradable character can reduce CO₂ emissions and manage with efficiency natural resources and materials. Most of the bio-based packaging materials, but not all, are biodegradable (Fig. 1.1). Even those which are non-biodegradable generally have a smaller CO₂ footprint and are associated with efforts to create more sustainable and environmentally friendly products (Attaran et al. 2017).

Bio-based packaging materials are part of a group of materials called bioplastics. Bioplastics can be classified into three segments according to the materials used and their sources (bio-based) and the final behaviour after their functional life (biodegradability) (European-Bioplastics 2016). This classification is based on: (a) materials synthesized naturally from plants and animals, or entirely synthesized from renewable resources such as cellulose, lignin, starch, proteins, chitosan, poly (lactic) acid (PLA) and polyhydroxyalkanoates/polyhydroxybutyrate (PHA and PHB); moreover, technologies to synthesize polymers such as polyethylene, polypropylene, and nylon from biological resources were recently added to this group. (b) Polymers which are synthesized from petroleum sources but are

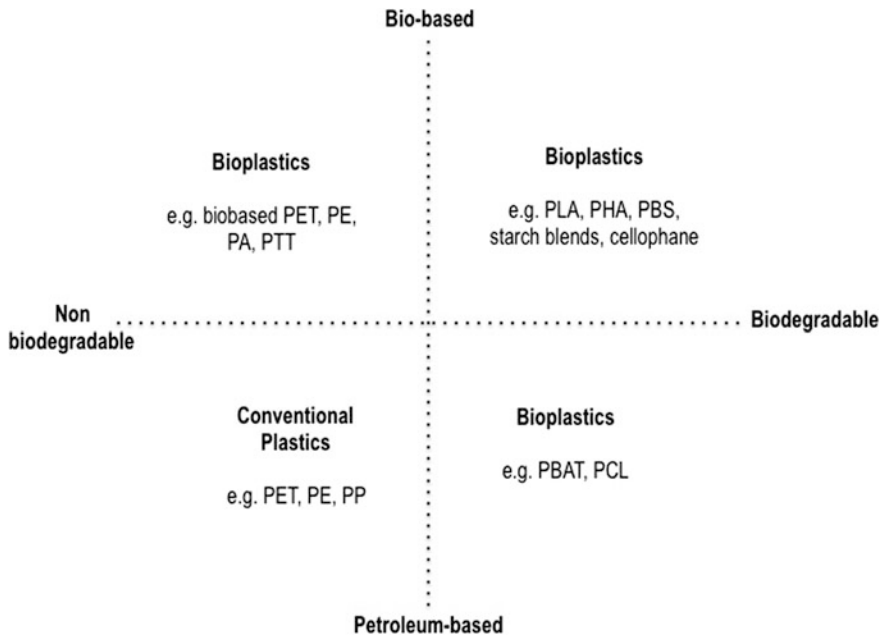


Fig. 1.1 Packaging materials based on their source and biodegradability (Adapted from European-Bioplastics, 2016)

biodegradable at the end of their functionality (e.g. polycaprolactone—PCL—and poly(butylene adipate-co-terephthalate)—PBAT); (c) mixtures of different sources with the combination of bio-based and petroleum-based monomers, such as polymers like poly(trimethylene terephthalate)—PTT, bio-thermosets and bio-based blends (Reddy et al. 2013).

At this point, one of the challenges for industries and researchers is the development of bio-based structures using natural macromolecules and their derivatives in order to achieve the economic and environmental goals proposed (European-Commission 2011). The use of bio-based materials will promote a sustainable processing of biomass into a spectrum of marketable products and energy, increasing the capacity of the industry. Additionally, the European Commission has set a long-term goal to develop a competitive, resource-efficient and low carbon economy by 2050 (Scarlat et al. 2015).

The production of petroleum-based polymers is one of the greatest markets worldwide. As a result, the annual world plastics production in 2015, mainly using petroleum-based polymers, reached the value of 322 million tons where packaging represents around 40% of the applications (Plastics-Facts 2016). Petroleum resources are extensively used in the production of these polymers that still highly depend on these sources, leading to concerns in terms of both economic and environmental sustainability. Petroleum-based polymers have been connected to some of the great problems in the World, such as waste accumulation in the oceans,

significant contributions to greenhouse emissions, non-renewability, and non-biodegradability. In fact, 34 million tons of plastic wastes are generated each year throughout the world and 93% of them are disposed of in landfills and oceans (Pathak et al. 2014). Thus, in order to create a sustainable ecosystem and prevent the possible disposal of plastic wastes in the environment, the use of renewable feedstocks gained a lot of attention in the last years.

LCMs have been presented as interesting materials for the development of value-added compounds for chemical (e.g. lignin as adhesive), pharmaceutical (e.g. microcrystalline cellulose as excipient) and food applications (e.g. carboxymethylcellulose as food thickener). Besides the use of lignocellulose-derived sugars and building blocks for the synthesis of other compounds, cellulose, hemicellulose, and lignin have also been seen as excellent macromolecules for the development of materials and composites. In this sense, their use in food packaging is one of the promising applications of these materials (Anwar et al. 2014; Isikgor and Becer 2015; Doherty et al. 2011). Cellulose has been used for years in paper (i.e. sheets and cartoon box) and regenerated cellulose (i.e. cellophane) production for packaging purposes. Due to their properties, the paper is mostly applied in tertiary packaging while regenerated cellulose has been competing with petroleum-based materials, such as polypropylene and polyethylene, in the primary packaging.

As mentioned previously, LCMs are the most abundant renewable resource in the world where cellulose (30–50%), hemicelluloses (15–35%), and lignin (10–25%) are intertwined resulting in a complex matrix that determines their physical and biological properties. These polymers are mainly present in the secondary cell wall of plants, like other constituents such as pectin, proteins and ash, which can also be found in smaller amounts. Among LCMs, cellulose is the most available material (approximately 75–100 billion tons of cellulose can be produced annually worldwide), and due to its biodegradability and renewability, the chemical industry has devoted great interest and importance to the modification of the cellulose structure and its properties aiming at expanding its potential applications. Lignin and hemicellulose have also shown to be of great interest due to their biodegradable and renewable characteristics, and several researchers have studied the possibility to use them as added-value materials (Laurichesse and Avérous 2014; Zhu et al. 2016).

In the early 20th century happened a great shift in the food industry due to the high consumption of industrialized foods, which fostered the use of petroleum-based packaging. This change led to the generation of large volumes of packaging materials being discarded and persisting in the environment beyond their functional life. This growth led to the interest of industry and governmental stakeholders in decreasing the use of petroleum-based packaging materials by bio-based ones. So, the use of bio-based materials for the development of packaging materials has increased in the last years and great efforts have been done to become feasible their technical and economical use in the industry. Currently, bioplastics represent about one per cent of the plastic produced annually, and the market is already growing by about 20 to 100 per cent per year and can reach to 6.1 million tonnes in 2021, due to the demand of more sophisticated materials, applications, and products (European-Bioplastics 2016).

1.3 Bio-Based Packaging Developments

Bio-based packaging is already a reality and several materials are commercially available (PLA, starch, and PCL). However, they still do not present prices and properties comparable to petroleum-based ones, being these two aspects presented as the main difficulties to world spread these materials. For example, PLA can present an average price, in 2017, of 5 €/kg while PE can go down to 1 €/kg. Cellulose-based packaging materials are available from Innovia Films with Cellophane™ and Natureflex™ brands. Companies such as Novamont with the Mater-Bi® products (starch-based materials) and NatureWorks with the PLA-based materials are the companies leading the commercialization of these materials. PHA and PHB have been commercialized by Metabolix and Biocycle. BIO-PE from Braskem, Dow, or Solvay and bio-polyurethane from Cargill, Dow or DuPont are also commercialized materials derived from renewable sources.

LCMs have also been seen as promising materials for the development of bio-based packaging materials as main material but also as a filler or additive that can improve the properties of bio-based packaging. This is witnessed by the exponential growth of the number of papers published these past few years when the keywords “packaging” and “cellulose” are searched. However, it is clear that the use of hemicellulose and lignin is still in its “infancy”, once the total number of papers is approximately 100 when the keywords “packaging” and “hemicellulose”, and “packaging” and “lignin” are searched (Fig. 1.2). These numbers are expected to increase based on the efforts of industrial and scientific communities in developing new alternatives for petroleum-based packaging materials.

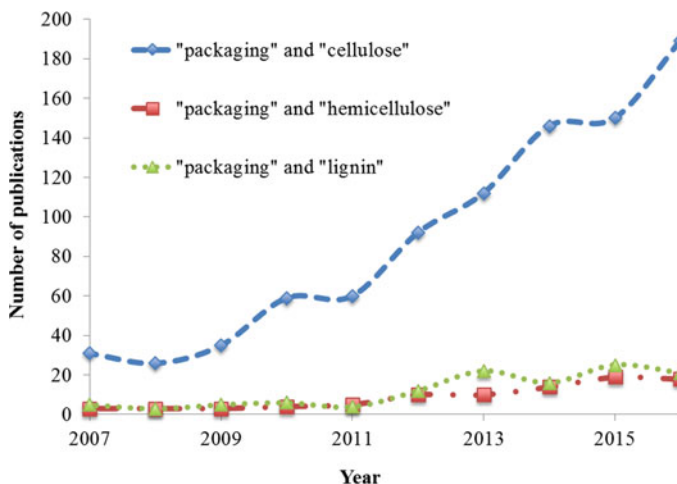


Fig. 1.2 Number of publications searching by keywords: “packaging” and “cellulose”; “packaging” and “hemicellulose”; and “packaging” and “lignin” in ISI Web of Science database (Institute for Scientific Information, 2017)

Table 1.1 Overview of international research and development projects carried out during the last decade within the bio-based food packaging topic

Project name	Duration	Materials	Description
BIOCOMPLACK—Eco-friendly food packaging with enhanced barrier properties (http://www.biocompack.com/about)	June 2016–November 2018	Cellulose, PLA	Biocompack project aims the development of bio-based, biodegradable and compostable food packaging with enhanced barrier properties. The three main points of innovation are the use of cellulose nanocrystals, the multilayer structure, and the PLA biopolymer reinforced with organoclay, which contain natural food preservatives
DIBBIOPACK—A new range of smart and multifunctional packages (http://www.dibbiopack.eu/)	March 2012–February 2016	PLA, PHA, cellulose	Dibbiopack aimed to develop new bio-based materials specially adapted for the performing of a wide range of packages while also improving their thermal, mechanical and barrier properties through nanotechnology and innovative coatings and integrating different intelligent technologies or smart devices to provide more information about the products and processes for the packaging value chain
EuroPHA (http://164.138.208.83/~europha/)	January 2013–December 2015	PHA	The Euro PHA project aimed to develop 100% natural and biodegradable bioplastic formulations for food packaging applications based on PHA. Bioplastics like PHA are long-term sustainable alternatives because they can show equal performance to conventional petrochemical plastics, originate from renewable non-food resources and are 100% biodegradable

(continued)

Table 1.1 (continued)

Project name	Duration	Materials	Description
PULPACKTION—Optimised moulded pulp for renewable packaging solutions (http://www.bbi-europe.eu/projects/pulpacktin)	October 2016–September 2020	Cellulose, thermoplastic starch, PLA	Pulpacktion project aims to develop cellulose-based tailored-to-purpose packaging solutions for specific food and electronic packaging applications which needs medium and high barrier requirements and that nowadays are packing in polymer fossil based solutions. The flexible packaging manufacturing system will be combined with 100% bio-based coatings and films on the cellulose-based substrate based on a fully bio-based approach where new bio-based polymer blends will be optimized. These new blends will be based on thermoplastic starch (TPS), PLA, other bio-additives, and reinforcements such as microfibrillated cellulose (MFC) that will be processed into multilayer films, composites, and coatings
SUCCIPACK—Development of active, intelligent and sustainable food packaging using polybutylenesuccinate (http://www.succipack.eu/)	January 2012–December 2014	Polybutylene succinate (PBS)	Succipack project demonstrated a process to produce PBS-based plastics suitable for food packaging. The innovations included a process to improve the resistance of PBS-based packaging to oxygen and water, resulting in increased shelf-life and food safety. During the project demonstration film wrapping and containers (trays) for packaging cheese, meat, fish and vegetarian food products were produced and tested
SUNPAP—Scale-up nanoparticles in modern papermaking (http://sunpap.vtt.fi)	July 2009–September 2012	Nanocellulose	SUNPAP project aimed to scale up efficient and innovative production routes to deliver nanofibrillated cellulose (NFC) as a functional additive for the development of new, renewable fibre-based packaging products using flexible, energy-efficient and environmentally friendly processes

(continued)

Table 1.1 (continued)

Project name	Duration	Materials	Description
SUSFOFLEX—Smart and sustainable food packaging utilizing flexible printed intelligence and materials technologies (http://www.susfoflex.com/)	January 2012–December 2014	PLA	Susfoflex resulted in prototypes of a PLA-based plastic, an innovative pack design, and two types of sensors to indicate whether the food inside is safe to eat. During the project also nanoclays and silver nanoparticles were used. As a demonstration, the project used the PLA-based plastic for food packaging applications, such as fruit, salads and similar products. The package had a reservoir to collect liquid exuded by the fruit, thus increasing shelf life and maintaining quality
ISA-PACK—A flexible sustainable active and intelligent packaging technology platform enabling enhanced shelf life, quality and safety of fresh food produce (http://www.isapack.eu/)	January 2012–December 2014	PHBV	ISA-Pack aimed the development of a flexible sustainable, active and intelligent technology platform for the packaging of fresh food products, targeting extended shelf life and quality, enhanced safety, and reduced food and packaging wastes. Whilst suitable for a wide range of foods, ISA-Pack validated the resulting materials and technologies for modified atmosphere and stretch wrap packaging of fresh meat
FLEXPAKRENEW—Design and development of an innovative coefficient low-substrate flexible paper packaging from renewable resources to replace petroleum based barrier films (http://www.flexpakrenew.eu)	September 2008–August 2011	Starches, functionalised starches, starch derivatives, modified hemicelluloses	FlexPakrenew aimed to develop innovative flexible functional packaging solutions, using renewable resources to replace petroleum-derived barrier films. The project focused on paper-based multilayer materials that are recyclable, biodegradable and environmentally friendly. The challenge of this project was to develop a flexible packaging paper, with barrier properties (grease, water, oxygen and water vapour barrier) competitive with those of untreated plastic films (medium barrier) or to treated plastic films (high barrier)

(continued)

Table 1.1 (continued)

Project name	Duration	Materials	Description
ECOBIOPACK (http://www.ecobiocap.eu/)	March 2011–February 2015	PHBV and wheat straw fibres	EcoBioCAP focused on the development of ecoefficient, biodegradable packaging solutions for foods. Packaging were developed using advanced composite structures based on constituents (biopolyesters, fibres, proteins, polyphenolic compounds, bioadhesives and high performance bio-additives) derived from food (oil, dairy, cereal and beer) industry by-products and by applying innovative processing strategies to enable customisation of the packaging's properties to fit the functional, cost, safety and environmental impact requirements of the targeted fresh perishable foods
SUSTAINPACK—Innovation and sustainable development in the fibre based packaging value chain	June 2004–September 2008	Cellulose	SustainPack aimed to ensure the future prominence and competitiveness of fibre based packaging using the exciting new opportunities in the field of nanotechnology, material coatings, and communication technologies. Other aims were to reduce supply chain costs and add value by enhancing the functionality of fibre based packaging
SUSTAINCOMP—Development of sustainable composite materials (http://www.sustaincomp.eu)	September 2008–August 2012	PLA, starch based, PHA, PHB, nanocellulose, wood-based fibre biocomposite	The vision of SustainComp was to introduce several families of new advanced wood-based bio-(nano) composites for a number of commercial sectors in the society. The project resulted in an array of new high-value wood-based materials using resource efficient, and therefore sustainable, production methods

The European Union has launched several calls for the development of sustainable packaging for foods and other applications, which has led to the development of several projects that reached interesting outputs and can be utilized to increase the use of bio-based packaging in food applications. Some of them are based on LCMs, not only using by-products from industry but also agro-industrial residues that are used either without or with slightly treated, as well as purified. Some of the international projects that have focused on the development of sustainable food packaging are presented in Table 1.1.

Therefore, LCMs are expected to be one of the driving forces for the development of bio-based packaging in the forthcoming years. The next chapters will provide a review on the use of LCMs for the development of bio-based packaging, being focused on the main sources, constituents and extraction methods of LCMs, as well as on their main functionalities. The incorporation of LCMs in bio-based packaging materials and their effect on the properties of these materials will also be discussed. It is expected in this book will provide its readers with an overview of the most relevant aspects of the use of LCMs in the development of bio-based packaging for food applications.

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Chapter 2

Lignocellulosic Materials: Sources and Processing Technologies



2.1 Current Perspective

Lignocellulosic biomass is a potential feedstock for the sustainable production of bioenergy and value-added products. However, the natural recalcitrance of this material is a major bottleneck for its exploitation. The current technologies require processing methods (i.e. pre-treatments) with severe conditions to disrupt the plant cell wall structure and remove their main components. So, pre-treatment is an important process in chemical and food engineering, enabling the recovery of valuable soluble components from raw materials. The processes should be energy-efficient, as simple as possible, cost-effective, environmentally friendly, applicable to a wide variety of feedstocks, and should ensure purity of the obtained products (Cybulska et al. 2013; Phitsuwan et al. 2013). Ongoing research is focusing on optimizing and improving these technologies in order to reduce the energy demands, the use of chemicals and the formation of by-products.

2.2 Lignocellulosic Materials: Definition, Composition and Sources

Lignocellulose refers to the materials constituting the essential part of the cell wall of plants, i.e. cellulose, hemicellulose, and lignin (Fig. 2.1). Celluloses and hemicelluloses (carbohydrates) are tightly linked to the lignin (aromatic polymer) through covalent and hydrogen bonds, making the structure highly complex and robust. Other components such as pectin, proteins, lipids, and ashes can also be found in these materials, but in less amount. The cellulose, hemicellulose, and lignin are mainly present in the secondary plant cell wall. In general, the plant cell wall is composed of distinct layers containing different components that vary considerably among them. The primary cell wall is normally very thin and the main

components are polysaccharides—cellulose microfibrils (low content), a high amount of substituted polysaccharides representing various hemicelluloses, and pectins (containing high water content: $\sim 60\text{--}70\%$ of the mass). The secondary cell wall comprises the major part of the cell wall and is usually thicker than the other parts. It also contains polysaccharides—the major portion of cellulose microfibrils and various hemicelluloses (about 70%)—but the water content is reduced ($\sim 5\%$) due to the presence of the hydrophobic polyphenolic lignin (Menon and Rao 2012; Michelin et al. 2014; Loqué et al. 2015).

Table 2.1 presents some examples of LCMs and their composition. It is important to highlight that the chemical composition of these materials depends strongly on their sources, such as hardwood, softwood, or grasses, but in general, they comprise 30–50% of cellulose, 15–35% of hemicellulose and 10–25% of lignin. Also, the chemical composition of a specific type of lignocellulosic material can vary due to the genetic variability among different sources, age, climatic and soil conditions. Nowadays, a considerable amount of waste materials is being generated through agricultural practices mainly from various agro-based industries (Anwar et al. 2014). These materials are generally categorized as **forest residues**, **agricultural or crop residues**, **herbaceous energy grasses**, and **municipal and industrial wastes**. **Forest residues** include mainly woody biomass, namely hardwoods and softwoods, followed by wood residues from logging and wood-processing such as saw-milling and manufacturing of plywood and particle board, pruning and bark thinning residues, while **agricultural or crop residues** are generated by different agricultural productions, such as rice, maize, wheat, cassava, groundnuts, soybeans, sugarcane, jute and cotton stalks. **Herbaceous energy grasses** include the perennials switchgrass and *Miscanthus giganteus*, and **municipal and industrial wastes** are also potential recyclable cellulosic materials that can originate either from residential or non-residential sources such as food wastes

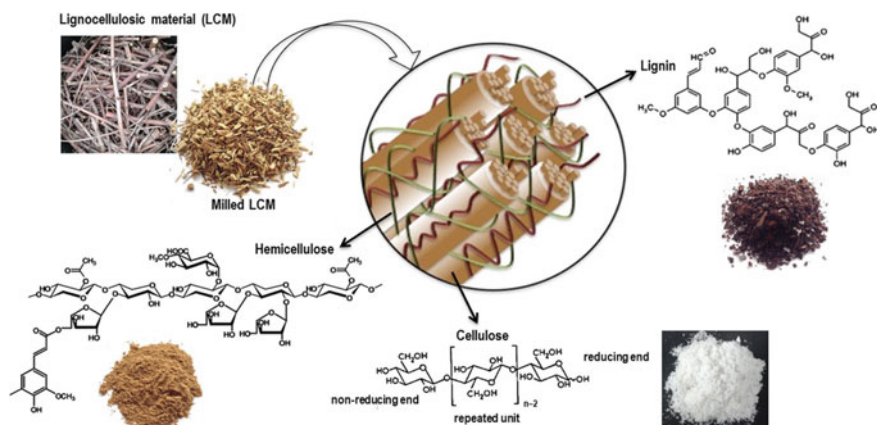


Fig. 2.1 Structure of the plant cell wall (Adapted from Michelin et al. 2014)

and paper mill sludge. A detailed revision about different sources of residues can be found elsewhere (Limayem and Ricke 2012; Hadar 2013).

2.3 Structure of Lignocellulosic Materials

2.3.1 Cellulose

Cellulose is considered the most abundant renewable polymer on Earth, being the major component of plant cell walls, responsible for mechanical strength. There are some living species such as bacteria (e.g. *Acetobacter*, *Acanthamoeba*, and *Achromobacter* spp.), algae (e.g. *Valonia*, *Micrasterias rotate*, *Chaetomorpha* spp.) and sea animals (e.g. tunicate) that can produce cellulose in large quantities (George and Sabapathi 2015; Klemm et al. 2005). However, the main source where this polymer is found is the plant's cell walls. It comprises a linear homopolymer of D-glucose units linked by β -1,4 glycosidic bonds forming chains that can contain over 10,000 glucose units. Cellulose chains are cross-linked by strong hydrogen bonds to form cellulose microfibrils. These microfibrils present crystalline regions, which are very recalcitrant to degradation. They also present less ordered regions (non-crystalline), known as amorphous regions, in which the crystalline structure has not formed during synthesis or has been disrupted, and therefore being easier to degrade (Sorek et al. 2014; Michelin et al. 2014). These microfibrils are often associated in the form of bundles or macrofibrils (Menon and Rao 2012; Brinchi et al. 2013).

Table 2.1 Composition of lignocellulosic materials

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Agricultural				
Sugarcane bagasse	37.5	30.6	25.3	Michelin et al. (2016)
Corn cob	35.8	30.7	18.5	Michelin and Teixeira (2016)
Wheat straw	34.0	23.2	20.2	Michelin and Teixeira (2016)
Rice husk	36.7	20.0	21.3	Garrote et al. (2007)
Grasses				
Switchgrass	37.0	34.7	22.7	Yan et al. (2010)
<i>Miscanthus</i>	45.0	25.4	26.5	El Hage et al. (2010)
Softwood				
Pine	41.8	22.3	30.1	Normark et al. (2014)
Spruce	43.8	20.8	28.8	Shafiei et al. (2010)
Hardwood				
Poplar	46.8	16.8	23.4	Zhou et al. (2015)
Maple	41.8	26.3	27.1	Zhang et al. (2013)
Oak	45.2	24.5	24.3	Shafiei et al. (2010)
<i>Eucalyptus</i>	44.7	20.1	27.7	Romaní et al. (2014)

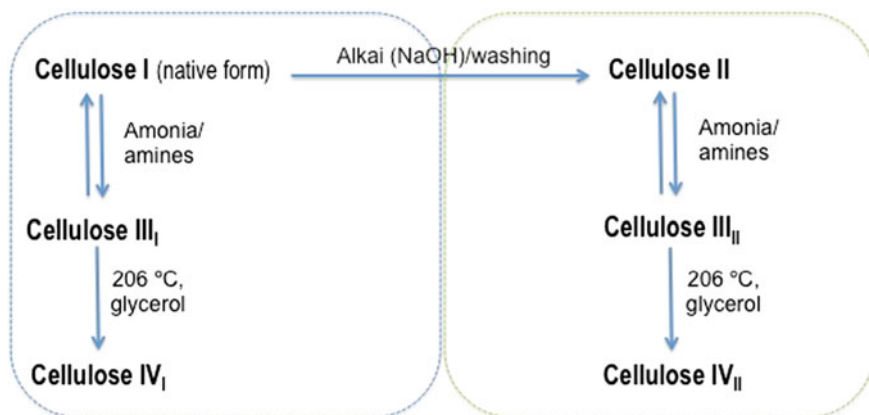


Fig. 2.2 Cellulose allomorphs and their interconversion steps (Adapted from Lavoine et al. 2012, and SriBala et al. 2016)

In nature, cellulose exists as cellulose I wherein all cellulose chains are arranged parallel to each other with respect to their reducing and non-reducing ends. The orientation of the microfibrils has a strong effect on the mechanical properties of the fibres of various plant types. Native cellulose (cellulose I) occurs in two different crystalline forms (suballomorphs) designated $I\alpha$ and $I\beta$, coexisting in variable portions depending on the origin of the cellulose. The other allomorphs of cellulose are cellulose II (alkalization of cellulose in water solution—mercerized cellulose or regenerated), cellulose III (the ammonia-treated cellulose) and cellulose IV (the cellulose modified by thermal treatment). The steps involved in the interconversion of different cellulose allomorphs are illustrated in Fig. 2.2. Among all the allomorphs, cellulose II is the most stable form due to an additional hydrogen bond per glucose unit (Zhang and Lynd 2004; SriBala et al. 2016; Lavoine et al. 2012; Abdul Khalil et al. 2012).

The interconversions between the allomorphic structures of cellulose can be performed by the action of chemical reagents or thermal treatments. So far, the polymorphism of cellulose is an aspect that intrigues the researchers due to the non-elucidated aspects. A more detailed description of cellulose crystallites is provided, among others, in the review papers from Moon et al. (2011) and Habibi et al. (2010).

2.3.2 Hemicellulose

Hemicellulose is a complex branched heteropolymer of lower molecular weight than cellulose that acts as a bonding agent between lignin and cellulose through a variety of covalent and noncovalent interactions, respectively. It consists of C6-sugars (glucose, mannose, and galactose) and C5-sugars (mainly arabinose and

xylose), besides some sugar acids (uronic acids) namely, D-glucuronic, D-galacturonic or D-4-*O*-methylgalacturonic acids, and acetyl groups, which can partially substitute the hydroxyl groups of sugars. Based on their primary structure, four main groups of hemicelluloses may be defined, i.e. xyloglycans (xylans), mannoglycans (mannans), β -glucans, and xyloglucans.

Xylans, one of the main hemicelluloses of the secondary cell wall, are composed of D-xylose residues linked by β -1,4-glycosidic bonds. However, most xylans occur as heteropolysaccharides, containing different substituent groups in the main chain, such as arabinosyl and glucuronosyl residues, being referred as arabinoxylans and glucuronoxylans, respectively (Hansen and Plackett 2008; Michelin et al. 2014; Girio et al. 2010). Xylans are mainly present in grasses such as switchgrass and *Miscanthus*, and angiosperm hardwoods, such as *Eucalyptus*, willow, and aspen (Sorek et al. 2014).

Hemicelluloses respond differently to biomass pre-treatments. The glycosidic linkages in hemicelluloses are relatively labile to acid hydrolysis, which allows complete depolymerisation by a relatively mild acid condition. However, the released sugars are particularly susceptible to dehydration under dilute acidic conditions at high temperatures and can form toxic by-products such as furfural and hydroxymethylfurfural (Sorek et al. 2014).

2.3.3 Lignin

Lignin is an amorphous polyphenolic macromolecule present in the cell wall of plants made of phenylpropanoids: guaiacyl (*G*), syringyl (*S*) and *p*-hydroxyphenyl (*H*) units, derived from the random polymerisation of the monolignols: *p*-coumaryl, coniferyl and sinapyl alcohols, respectively (Doherty et al. 2011). These units are mainly linked by labile bonds as well as by resistant interunit bonds, which result in a complex macromolecule with a great variety of functional groups and unique properties for each type of plant. In softwoods, the *G* structure is dominant, while hardwood lignins normally contain a mixture of *S* and *G* structures, being the *S* structure the majority part. The *H* structures are predominant in lignins found in grasses (Wang et al. 2009). These different proportions influence the physico-chemical properties of lignin.

Lignin binds covalently to hemicellulose and forms a protective barrier around the polysaccharides, which includes an effective physicochemical barrier against microbial attack and oxidative stress. It is responsible for much of the mechanical strength and hydrophobicity, being the most recalcitrant component of LCMs to degradation (Michelin et al. 2014).

The lignin content in cell wall varies from one plant to another, and it is a crucial parameter affecting the decomposition efficiency of the polysaccharides. In general, softwoods from gymnosperms such as pine contain more lignin (25–35% of the cell wall) than do hardwoods such as poplar (18–25%), grasses (10–30%) or agricultural residues (Sánchez 2009). One of the interesting findings is that lignin binds

and inactivates cellulolytic enzymes, and therefore, to promote the access of enzymes to the cellulose component, the lignin must be modified or removed by a pre-treatment (Sorek et al. 2014).

2.4 Processing Technologies

As described previously, the entangled ultrastructure of LCMs consists of inherent characteristics such as strong lignin layers, high cellulose crystallinity and low accessibility to chemicals, which inhibit the digestibility of the biomass and consequently, the extraction of their components. Therefore, processing of the biomass is required to extract their components (i.e. cellulose, hemicellulose and lignin) or modify their structure. This processing is known as pre-treatment. So, pre-treatment is a key step in the overall process to overcome biomass recalcitrance, wherein a wide variety of methodologies and technologies are used to expose and disrupt the lignocellulosic matrix, through the removal of lignin/hemicellulose and decrystallization of cellulose. They comprise physical, chemical, physicochemical, and biological pre-treatment or their combination, as described below. Each one of these methods has been reported to present distinct advantages and disadvantages (Table 2.2).

Physical pre-treatment technologies include mechanical comminution, pulsed-electric field and pyrolysis. The **mechanical comminution** involves the chipping, grinding and milling of the LCMs for the reduction of particle size and cellulose crystallinity. This is generally the initial step of the LCMs processing. After that, the biomass is ready for the next pre-treatment step. Another physical pre-treatment is the **pulsed-electric field (PEF)** that involves electric discharges in the form of pulses which are applied to a sample placed between two electrodes. When a high-intensity electric field is applied, structural changes are produced in the plant cell wall, resulting in an increase of mass permeability and mechanical rupture. PEF pre-treatment can create permanent pores in the cell walls that facilitate the entry of acids or enzymes used to break down the cellulose (Kumar et al. 2009). **Pyrolysis** has also been used to pre-treat LCMs. It uses temperatures greater than 300 °C, where cellulose is rapidly decomposed to gaseous products and residual char. At lower temperatures, the decomposition is much slower, and the products formed are less volatile (Kumar et al. 2009).

Regarding the physicochemical pre-treatments, the most employed is the hydrothermal pre-treatment **steam explosion** that treats the LCMs under pressurized steam at a high temperature in a short period of time in order to promote hemicellulose hydrolysis. It is then finished by a sudden decompression that destroys the fibrils' structure. In combination with partial hemicellulose hydrolysis and solubilisation, the lignin is redistributed and in some extent removed from the LCMs being the cellulose accessibility increased. Catalysed steam explosion can be performed by the addition of an acid, improving the hydrolysis and leading to the complete removal of the hemicellulosic fraction and thus decrease the formation of

inhibitory compounds if lower temperatures are used (Sun and Cheng 2002; Alvira et al. 2010). Similar to the steam explosion, **liquid hot water (LHW)** or **auto-hydrolysis** causes the solubilisation of hemicellulose in the liquid fraction. The process is catalysed by acetic acid from acetyl groups and other acid components released from hemicellulose, and also by hydronium ions generated in situ by water auto-ionization, which reduces the pH significantly. In this pre-treatment, the rapid decompression does not occur and during the process, lignin is re-located on the surface of LCMs, which normally makes cellulose more accessible (Michelin et al. 2014). The formation of degradation products can be avoided by controlling the pH between 4 and 7 (Mosier et al. 2005) and in this case, it is also considered a chemical pre-treatment.

Other physicochemical pre-treatments include ammonia fibre/freeze explosion (AFEX), wet oxidation and CO₂ explosion. During **AFEX** the biomass is exposed to liquid ammonia (anhydrous or concentrated more than 70%) under high temperature and pressure, and then the pressure is quickly released. Ammonia reacts primarily with lignin causing thus its depolymerisation and disrupting lignin-carbohydrate linkages, together with partial decrystallization of cellulose. Liquid ammonia causes cellulose swelling and a phase change in the crystal structure from *cellulose I* to *cellulose III*. AFEX produces only a pre-treated solid fraction (it does not produce a slurry). In a typical AFEX process, the dosage of liquid ammonia is 1–2 kg ammonia per kg of dry biomass, the temperature is 90 °C, and the residence time is 30 min (Balat 2011; Sun and Cheng 2002). **Wet oxidation** is an oxidative pre-treatment method that employs oxygen or air as a catalyst. It allows the reactor operating at relatively low temperatures and short times. The addition of oxygen at temperatures above 170 °C makes the process exothermic, reducing the total energy demand. Moreover, it has been shown that the addition of Na₂CO₃ decreases the formation of inhibitory compounds by maintaining the pH from neutral to alkaline range. The main reactions in wet oxidation are the formation of acids from hydrolytic processes and oxidative reactions. It has been proven to be an efficient method for solubilisation of hemicelluloses and lignin, as well as to increase digestibility of cellulose (Alvira et al. 2010). **CO₂ explosion** uses carbon dioxide that in contact with aqueous solutions forms carbonic acid, favouring polymers' hydrolysis. CO₂ molecules can penetrate the small pores of the LCMs, which is facilitated by the high pressure of the process. After the explosive decompression occurs the disruption of cellulose and hemicellulose and the increase of accessible surface area. The studies using carbon dioxide include trials with supercritical CO₂, referring to a fluid that is in a gaseous form but is compressed at temperatures above its critical point to a liquid-like density. Supercritical conditions can effectively remove the lignin, increasing the substrate digestibility. Moreover, delignification can be improved by the addition of co-solvents (e.g. ethanol) to the process (Cybulska et al. 2013).

The next two pre-treatments can be also considered physicochemical pre-treatments since both thermal and non-thermal effects are often involved. **Microwave** is an alternative heating source that consists of a rapid delivery of energy to the total volume, and subsequent a rapid heating of the lignocellulosic

structure, accelerating thus, the solubilisation of the compounds (Quitain et al. 2013). It has been used in association with other chemical pre-treatments (microwave-assisted pre-treatment), e.g. aqueous glycerol or alkaline glycerol (Diaz et al. 2015), and alkali pre-treatment (Zhu et al. 2006). On the other hand, **ultrasounds** generate pressure differences within a solution for the enhancement of physical (mechanoacoustic) and chemical (sonochemical) processes. The mechanoacoustic effect can change the surface structure of the biomass, and the sonochemical production of oxidizing radicals can lead to a chemical attack of the lignocellulosic components (Bussemaker and Zhang 2013). Furthermore, the combination of ultrasounds with conventional techniques has been used to enhance the pre-treatment performance (Yunus et al. 2010; Velmurugan and Muthukumar 2012).

The most common chemical process used in the pre-treatment of LCMs is dilute-acid hydrolysis. **Dilute-acid hydrolysis** uses less severe conditions than concentrated acid hydrolysis and solubilises hemicellulose, mainly achieving high xylan-to-xylose conversion yields. It can be performed at high temperature (e.g. 180 °C) during a short period of time; or at a lower temperature (e.g. 120 °C) for longer retention times (30–90 min) (Alvira et al. 2010). Normally, shorter reactor residence times and higher pre-treatment temperatures result in higher soluble xylose recovery yields and enzymatic cellulose digestibility (Balat 2011). **Alkali hydrolysis** is another chemical pre-treatment that uses alkaline solutions for LCMs treatment to remove lignin and part of the hemicellulose and to increase the accessibility of cellulose. It is a delignification process where a significant amount of hemicellulose is also solubilized. The mechanism proposed is the saponification of the intermolecular ester bonds that crosslink xylan hemicelluloses and other components, such as lignin and other hemicelluloses. Dilute NaOH is usually used for alkali pre-treatment of LCMs and is described to cause less sugar degradation than the acid pre-treatments (Sun and Cheng 2002; Peral 2016).

Other chemical pre-treatments include organosolv, ionic liquids, and ozonolysis. **Organosolv** is a delignification process, where an (aqueous) organic solvent acts as a lignin extractant (breaking the lignin structure and solubilizing it). The addition of acid catalysts results in hemicellulose depolymerisation (high xylose yield), however, satisfactory delignification can be achieved by increasing process temperatures (above 185 °C), avoiding acid addition. More recently, **ionic liquids (IL)** have been explored in the pre-treatment of LCMs. IL are salts generally formed by large organic cations and small inorganic anions, that exist as liquids at low temperatures (often at room temperature). They have been described as designer solvents since the adjustment of the anion and the alkyl constituents of the cation results in varied solvent properties. Recent studies have shown that cellulose and lignin can be dissolved in a variety of IL and easily regenerated from these solutions (Alvira et al. 2010). **Ozonolysis** includes the use of ozone gas, a powerful oxidant soluble in water and readily available, to break down the lignin and hemicellulose and increase the biodegradability of the cellulose. It is highly reactive towards conjugated double bonds and functional groups with high electron density, such as lignin. Therefore, ozone attacks lignin releasing soluble compounds of low molecular

weight, such as organic acids (e.g. formic and acetic), which can cause an abrupt decrease in pH (Balat 2011; Sun and Cheng 2002).

Other of the possibilities for the processing of LCMs is the **biological pre-treatment**. It involves the use of wood-degrading microorganisms, such as brown-, white- and soft-rot fungi, in order to degrade lignin and solubilize hemicellulose and very small quantities of cellulose. Lignin degradation by white-rot fungi (e.g. *Phanerochaete chrysosporium*), the most effective basidiomycetes for biological pre-treatment of LCMs, occurs through the action of lignin-degrading enzymes, such as peroxidases and laccases (Alvira et al. 2010). Due to some disadvantages of this pre-treatment (see Table 2.2) the direct use of enzymes has been considered, despite their high cost (Peral 2016).

2.4.1 Processing of Lignocellulosic Material Components

It is known that the extraction/purification of LCM components (i.e. cellulose, hemicellulose and lignin) for further biotechnological applications generally involves the use of integrated pre-treatment technologies. Therefore, this section provides some examples of pre-treatments utilised to extract or modify those lignocellulosic components and also shows their possible applications as packaging materials.

2.4.1.1 Cellulose Processing

The cellulose obtained from LCMs is not only targeted for liquid biofuels and chemicals production applications, but also for the synthesis of reactive intermediate materials (e.g. nanocellulose–NC) for further end-product processing. There is a wide diversity of cellulose particle types that depend on cellulose source and pre-treatment processes used. They have been studied for various commercial applications. One such example is microcrystalline cellulose (MCC) a commercially available cellulose (>1000 nm diameter) used in pharmaceutical and food applications and also used as starting material to prepare nanocellulose (Abdul Khalil et al. 2012).

In fact, micro- and nanocellulose have shown to be very suitable for the formulation of packaging materials, i.e. composites and nanocomposites. Nanocellulose presents extraordinary properties that are related to the nanoscale effect of their structure and several new and innovative bio-based materials are being presented in very different applications (Siró and Plackett 2010; Brinchi et al. 2013; Abdul Khalil et al. 2012). Several denominations have been given for the materials obtained from cellulose at nanoscale and in some cases, their main characteristics are somehow controversial. They can be categorized into **cellulose nanocrystal** (CNC, or cellulose nanowhiskers), that is formed by rigid rod-like particles with diameters and lengths of 2–70 nm and between 100–600 nm,

Table 2.2 Technologies, chemicals and conditions used in the pre-treatment of LCMs as well as the main advantages and limitations of their processing

Processing technologies	Chemicals	Conditions	Advantages	Limitations/ disadvantages
Mechanical comminution	–	–	<ul style="list-style-type: none"> – Reduces cellulose crystallinity – Increases the specific surface area – Increases the efficiency of downstream processing 	<ul style="list-style-type: none"> – Power consumption relatively high (depending on the final particle size and the LCM characteristics) – Process needs more research
Pulsed electric field	–	5–20 kV/cm, short pulse times (100 μ s). It can be performed at room conditions	<ul style="list-style-type: none"> – Disrupts plant cells – Simple equipment – Low energy requirement (short pulse times) 	– Process needs more research
Ultrasounds	Water or other solvents, acid or alkali solutions	Generally, it is used high-power and low-frequency treatment (below 100 kHz)	<ul style="list-style-type: none"> – Increases the pore size – Enhances the accessibility of surface area – Enhances the yield of subsequent processing – Increases the purity of the recovered material – Reduces the times of subsequent processing – Green technology 	<ul style="list-style-type: none"> – Degrades lignin components
Microwave (MW)	Water or other polar solvents	12.2 cm (2.45 GHz)–domestic MW; 33.3 cm (900 MHz)– industrial MW, 5–20 min	<ul style="list-style-type: none"> – Rapid and selective heating – Reduced energy requirements – Higher yields even at milder conditions – Green technology 	<ul style="list-style-type: none"> – Limited scale up – Safety consideration regarding industrial use – Non-homogeneous MW irradiation

(continued)

Table 2.2 (continued)

Processing technologies	Chemicals	Conditions	Advantages	Limitations/disadvantages
Liquid hot water (LHW) or Autohydrolysis	Water	160–240 °C, few minutes to 1 h	<ul style="list-style-type: none"> – Does not require the addition and recovery of any catalyst or chemicals – Low-cost reactor (limited corrosion problems) – Generation of low concentrations of inhibitors – Simple and economical operation – Green technology 	<ul style="list-style-type: none"> – High energy requirement – High water demand – Long residence time – A severe condition can generate some toxic compounds/inhibitors
Steam explosion	Water; catalysed steam explosion can be performed by the addition of dilute acid (e.g. 0.5–3.0% H ₂ SO ₄) or SO ₂	160–260 °C (corresponding pressure 0.69–4.83 MPa), few minutes	<ul style="list-style-type: none"> – Cost-effective – No recycling or environmental costs (unnecessary addition of acid catalyst, except for softwoods) – Considered the most cost-effective option for hardwood and agricultural residues 	<ul style="list-style-type: none"> – Generation of some toxic compounds/inhibitors – Use of acids (catalyst) brings problems related to equipment requirements – Less effective for softwood
Ammonia fibre/freeze explosion (AFEX)	Ammonia	Generally 60–100 °C, high pressure and variable period of time Pressures >12 atm are required at room temperature	<ul style="list-style-type: none"> – Increases accessible surface area (cellulose becomes more accessible) – Does not produce inhibitors – High effectiveness for herbaceous and low lignin content LCM 	<ul style="list-style-type: none"> – High cost of ammonia – Need to recycle – Less effective for LCM with high lignin content

(continued)

Table 2.2 (continued)

Processing technologies	Chemicals	Conditions	Advantages	Limitations/ disadvantages
CO ₂ explosion	CO ₂	56.2 bar	<ul style="list-style-type: none"> - Increases accessible surface area - Cost-effective - Non-toxic, non-flammable, and easy to recover - Does not form inhibitory compounds 	<ul style="list-style-type: none"> - Does not affect lignin or hemicellulose - Very high-pressure requirements
Dilute-acid hydrolysis	Dilute acids, such as sulphuric, nitric, hydrochloric between 0.2–2.5%, or organic acids (e.g. fumaric, maleic, tartaric and acetic)	High temperature (e.g. 180 °C) during a short time; or lower temperature (e.g. 120 °C) for longer retention time (30–90 min)	<ul style="list-style-type: none"> - High glucose yield - Solubilizes hemicellulose, mainly xylan to xylose - Increases accessible surface area and pore volume - Changes lignin structure 	<ul style="list-style-type: none"> - High cost of acids - Needs for recovery - High cost of corrosion resistant equipment - Formation of toxic/inhibitory compounds - pH neutralization requirement for downstream processes - Not efficient for biomass with high lignin content
Alkali hydrolysis	Dilute alkali solutions, such as sodium, potassium, calcium and ammonium hydroxides	<140 °C, few minutes; or room temperature, hours or days	<ul style="list-style-type: none"> - Efficient removal of lignin - Increases accessible surface area and porosity of LCM - Low inhibitor formation - Low energetic demand (no requirement of high reaction temperatures) - Less sugar degradation than other pre-treatments (e.g. acid hydrolysis) 	<ul style="list-style-type: none"> - Long residence time - High concentration of alkali solutions when performed at room temperature - High cost of alkali solutions - Some of the alkali solutions are converted

(continued)

Table 2.2 (continued)

Processing technologies	Chemicals	Conditions	Advantages	Limitations/ disadvantages
Organosolv	Aqueous organic solvents (e.g. ethanol, acetone, and ethylene glycol). Catalysed organosolv can be done by adding an inorganic acid (HCl or H ₂ SO ₄)	High temperatures (185–210 °C); or low temperature (below 180 °C) with addition of acid catalyst	<ul style="list-style-type: none"> – Many caustic salts can be recovered – Recovery lignin with high purity and low molecular weight (excellent properties) – Recovery very low or sulphur free lignin – May use solvents of low boiling point, toxicity and cost (e.g. ethanol) – Ease solvent recovery (simple distillation/ low energy requirement) 	<ul style="list-style-type: none"> – Need for removal of solvents from system (e.g. evaporation, condensation techniques) – Need for solvent recycling – High cost of some solvents
Ozonolysis	Ozone	Usually at room temperature	<ul style="list-style-type: none"> – Efficient removal of lignin – Does not produce toxic/inhibitory compounds 	<ul style="list-style-type: none"> – Requires large amount of ozone – Expensive
Wet oxidation	Oxygen	170–200 °C, 10–15 min, pressures from 10 to 12 bar O ₂	<ul style="list-style-type: none"> – Low formation of inhibitors – Efficient removal of lignin – Minimizes the energy demand (exothermic) 	<ul style="list-style-type: none"> – High cost of oxygen and catalyst
Ionic liquids (IL)	Ionic liquids, e.g. 1-Ethyl-3-methylimidazolium acetate ([Emim]Ac)	Mild processing conditions (low temperatures)	<ul style="list-style-type: none"> – Tunable physicochemical properties (e.g. viscosity, melting point, polarity, etc.) depending on the selection of the anion and cation) 	<ul style="list-style-type: none"> – High solvent costs – Need for solvent recovery and recycle

(continued)

Table 2.2 (continued)

Processing technologies	Chemicals	Conditions	Advantages	Limitations/ disadvantages
Pyrolysis	–	Higher than 300 °C	<ul style="list-style-type: none"> – Low vapour pressures (tendency to remain liquid in a wide range of temperature) – Good chemical and thermal stability – Non-flammability – Considered green solvents 	<ul style="list-style-type: none"> – High viscosity (a serious limit to mass and phase transfer) – Need more studies regarding to toxicity data – Still in initial stage, and it is needed further research – Need to improve the economics of the process
Biological	–	Mild temperature, long periods (days to weeks)	<ul style="list-style-type: none"> – Produces gas and liquid products – Low capital costs – Low energy requirements – No chemicals requirement – Mild operational conditions 	<ul style="list-style-type: none"> – High temperature – Ash production – Very slow pre-treatment – Low yields – Long-time process – Careful control of growth conditions – Most lignolytic microorganisms consume not only lignin but also hemicellulose and cellulose

respectively; and **nanofibrillated cellulose** (NFC), also known as microfibrillated cellulose (MFC), that is formed by long and flexible microfibrils of around 5–60 nm diameter and more than 1000 micrometres in length. They are chemically similar, but with different physical characteristics (Abdul Khalil et al. 2012; Brinchi et al. 2013; Ng et al. 2015).

The isolation of these nanocelluloses from LCMs generally occurs in two stages. The first one is a pre-treatment of the LCMs that involves the complete or partial removal of matrix materials, mainly hemicelluloses and lignin, and then, the isolation of the cellulosic fibres occurs. In the second stage, CNC can be obtained from purified cellulose fibres after the dissolution of the amorphous regions by a chemical pre-treatment (generally strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time). Unlike CNCs, NFCs exhibit both amorphous and crystalline parts and present a web-like structure (Lavoine et al. 2012) and are mainly produced by a mechanical treatment (e.g. homogenizer, microfluidizer, and grinder) (Brinchi et al. 2013).

The development of disintegration methods that are less energy-consuming has become a priority in the industrialization of cellulose-based structures. Thus, some combinations of pre-treatments and mechanical treatments have been suggested, such as enzymatic pre-treatment, and TEMPO-mediated oxidation.

Actually, NFC and CNC have been extensively introduced in polymer composites as reinforcing elements (Ng et al. 2015; Lavoine et al. 2012). One of the most used methods for the production of CNC from cellulose is still based on controlled sulphuric acid hydrolysis, owing to the stability of the resulting suspensions (Brinchi et al. 2013). For example, Johar et al. (2012) extracted cellulose fibres and cellulose nanocrystals from grounded rice husk by using an alkali solution (4% NaOH for lignin and hemicellulose degradation) and bleaching pre-treatments for the fibres extraction; subsequently, CNC were obtained from these fibres using acid hydrolysis pre-treatment (10 mol/L H₂SO₄) at 50 °C for 40 min under continuous stirring. The CNC was recovered after washing and dialysis against water until pH 5–6, with an additional step of sonication to disperse the CNC. On the other hand, Deepa et al. (2011) used steam explosion process for the extraction of cellulose from banana fibres and obtained NFC after acid hydrolysis.

2.4.1.2 Hemicellulose Processing

Several methods have been used to obtain hemicelluloses from plant sources including alkali pre-treatment, organic solvent extraction, as well as the steam explosion or microwave pre-treatment. The composition of the extracted hemicellulose can be highly dependent on the isolation process and deacetylation, degradation, or possible contamination with lignin during the pre-treatment can happen.

Höije et al. (2005) used different methods to extract hemicellulose from barley husks aiming at finding a suitable method for the isolation of arabinoxylans of high molecular weight that could be later used for the preparation of high oxygen

barrier films or coatings. Four different types of pre-treatments were used before alkaline extraction: enzyme pre-treatment, acidic (HCl) pre-treatment, or acidic (HCl) pre-treatment combined with chlorite delignification, or acid (HCl) pre-treatment plus NH_4OH combined with organosolv (ethanol) delignification. The purpose of the pre-hydrolysis step (to remove proteins and delignification) showed to be essential to achieve the objective since the type of treatment had a great impact on the yield of arabinoxylans as well as on their molecular weight. Gabriellii et al. (2000) extracted hemicellulose from aspen (*Populus tremula*) by an alkali extraction method. The extraction was then followed by hydrogen peroxide treatment, ultrafiltration and spray drying. Resultant hemicellulose was studied by nuclear magnetic resonance spectroscopy and size-exclusion chromatography and showed a glucuronoxylan of relatively high molar mass that was evaluated regarding their film- and hydrogel-forming properties.

Purified hemicelluloses still have few commercial applications than cellulose and lignin, but the interest in the production of value-added products has increased in the last years (Mikkonen et al. 2010; Höije et al. 2008; Fonseca Silva et al. 2011).

2.4.1.3 Lignin Processing

The chemical and physical properties of lignin are totally different from those of cellulose and hemicellulose. The extraction of lignin from LCMs is conducted under conditions where lignin is progressively broken into lower molecular weight fragments, resulting in changes to its main properties. The typical molecular weight (MW) of isolated lignin is in the range 500–400,000 g/mol, but the degree of polymerisation in Nature is difficult to measure due to lignin fragmentation during the extraction. In addition to the source of the lignin, the method of extraction used may also influence the final composition and properties of lignin (Doherty et al. 2011).

Most processes of lignin extraction occur by acid or base-catalysed mechanisms. Based on that, there are several types of lignin that can be classified into two categories: sulphur-containing lignin and sulphur-free lignin (Espinoza-Acosta et al. 2014). Sulphur-containing lignins are obtained by the **sulphite pulping process**, which uses a metal sulphite and sulphur dioxide; the **Kraft process**, which utilises sodium hydroxide and sodium sulphite under strongly alkaline conditions to cleave the ether bonds in lignin; or the **soda process**, that uses a typical alkaline hydrolysis with sodium hydroxide.

Sulphite lignins (also known as lignosulphonates or lignin sulphonates) are products of sulphite pulping from pulp and paper mills. The process is usually conducted between 140 and 160 °C and the pH of the acid sulphite process is from 1.5 to 2.0, while the bisulphite process is from pH 4.0 to 5.0 (Smook 2002). The lignosulphonate is often highly crosslinked, and its MW varies widely, depending on the source of the lignin and the exact processing conditions (Johansson et al. 2012),

with approximately 5% sulphur content. Unlike natural lignin, lignosulphonates are water-soluble due to the presence of sulphonate groups. The sulphur content is one of the major factors restricting its use in value-added applications, and hence, most of this type of lignin is currently used for energy generation (Doherty et al. 2011). However, the presence of both hydrophilic and hydrophobic domains in lignosulphonates enables them to be mixed with different kinds of polymers that often results in enhanced thermochemical and mechanical characteristics (Ten and Vermerris 2013).

Kraft lignins, also called sulphate lignins, are obtained from the Kraft pulping process in pulp and paper mills. Currently, it is the main traditional method for pulping, producing the largest volume of lignin (Smook 2002) which is present as a low-MW fraction in the “black liquor” (alkaline liquid remaining after pulp extraction). The delignification process happens in three stages. The first phase occurs around 150 °C and is controlled by diffusion; the second stage (where 90% of delignification currently happens) takes place between 150 and 170 °C, and the final stage arises at even higher temperatures. Lignin may be recovered from the black liquor by lowering the pH to 5–7.5 with acid addition. Kraft lignin is hydrophobic and needs to be modified to improve reactivity. The high sulphur content (1–2%) of kraft lignin is also one of the major reasons for its application in energy generation in pulp mills (Doherty et al. 2011).

The soda process was the first chemical pulping method that led to the development of the Kraft pulping (current dominant technology). The soda process is now becoming the predominant method for chemical pulping of non-wood material such as bagasse, wheat straw, and sisal due to the viable chemical recovery methods and effluent treatment technology. The pulping process involves heating the biomass in a pressurized reactor to 140–170 °C in the presence of 13–16% alkali (typically sodium hydroxide). Soda lignin has good potential for use in high value-added products production since it does not contain sulphur or considerable remains of hemicellulose, or oxidized defect structures (Doherty et al. 2011).

On the other hand, sulphur-free lignin, which is obtained from LCMs conversion processes such as organosolv are produced in small amounts, but may evolve into industrial-scale products. Organosolv lignins are extracted by organic solvents (e.g., ethanol, formic acid, acetic acid, methanol), and the main advantages over sulphonated and Kraft lignins include greater ability to be derivatized, lower ash content, higher purity (due to lesser carbohydrate content), generally lower molecular weight and higher hydrophobicity, moreover, they are sulphur-free (Lora and Glasser 2002). This delignification process is not used widely because of the cellulose pulp produced present lower quality than those obtained from soda or Kraft processes (Doherty et al. 2011). However, various works have focused on organosolv pre-treatment to recovery lignin and enzymatically digestible cellulose (Wildschut et al. 2013; Romani et al. 2011; Amiri and Karimi 2016).

Kraft lignin, lignosulphonates and soda lignin are produced in large amounts. In spite of their abundance, only a minimal part of them is commercialized. To

increase industrial use of lignins it is necessary not only to improve lignin extraction processes, but also to determine the chemical composition and structure of lignins, characterize their chemical reactivity and functional properties, and the same time that new applications are developed (Ugartondo et al. 2008; Boeriu et al. 2004).

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Chapter 3

Functional Properties of Lignocellulosic Materials



3.1 General Aspects

Cellulose, hemicellulose, and lignin exhibit very interesting functional properties, including mechanical, thermal and rheological properties, and their antioxidant and antimicrobial activities. Some functional properties of cellulose, hemicellulose and lignin are summarized in Fig. 3.1. The functionality can vary from fraction to fraction, being the fractions' properties affected by the source and the pre-treatment used during processing. Briefly, the main functional properties of each lignocellulosic fraction (i.e. cellulose, hemicellulose and lignin) and the lignocellulosic materials as a whole are presented below.

3.1.1 Cellulose Properties

Cellulose is low-cost, biodegradable, and non-toxic, and at the same time exhibits interesting functional properties related to its molecular structure. Due to these interesting chemical, physical and biological properties, cellulose has been widely used in the paper, food, pharmaceutical and cosmetic industries (Peng et al. 2011; Santana-Méridas et al. 2012). However, cellulose presents some limitations due to its high polarity and hydrophobicity, becoming poorly compatible with other matrices (Belgacem and Gandini 2005). As a result, cellulose is usually submitted to specific degradation and/or modification processes (as explained in Chap. 2), in order to enhance its functionalities and expand the use of this biopolymer and its derivatives in different areas including the food packaging industry. For instance, alkali cellulose (mercerization process) may have a crystalline form of hydrated cellulose being more stable than that of natural cellulose, which would increase its absorbability and make it easy to react with a great variety of substances (Chen 2014).

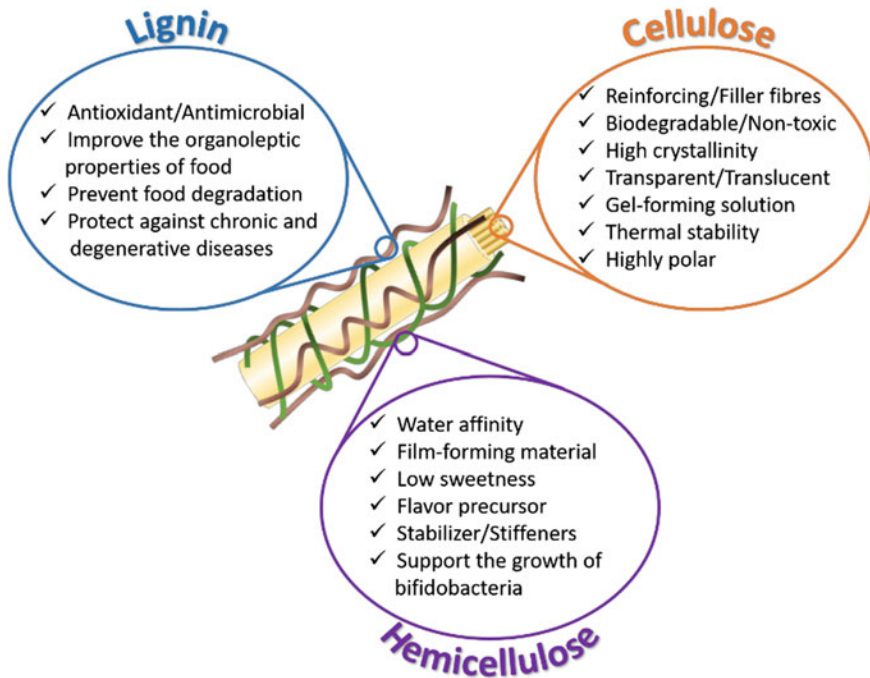


Fig. 3.1 Functional properties of lignocellulosic materials

Nowadays, cellulose at the micro- and nanoscale levels has gained great attention because of its mechanical, chemical, optical and rheological characteristics. Cellulose structures at nanoscale possesses several advantages, such as high specific strength and modulus, high surface area and unique optical properties (Peng et al. 2011). Additionally, considering the safety and efficacy of this cellulose, it has attracted increasing attention in biomedical applications since toxicity tests conducted so far indicate that it is non-toxic to cells (Brinchi et al. 2013).

Morphology of cellulose and cellulose derivatives, including the type or size of crystalline particles (as already discussed in Chap. 2), directly affects the main properties and the corresponding applications of cellulose derivatives (Brinchi et al. 2013; Moon et al. 2011; George and Sabapathi 2015). Examples are the degree of crystallinity and polymerisation degree (DP) that influence the physical properties of nanofibrillated cellulose (NFC) matrix since high DP of cellulose leads to films with higher tensile strength (Brinchi et al. 2013; Lavoine et al. 2012). On the other hand, cellulose derivatives obtained from bulk cellulose or cellulose fibres, result in materials with different degrees of crystallinity depending on the treatment used or the suitable combination of them in order to extract high cellulose crystalline regions. Table 3.1 presents the crystallinity degree and particle dimensions of some cellulosic derivatives.

Table 3.1 Degree of crystallinity and particles sizes of cellulose and cellulosic derivatives

Particle type	Crystallinity* (%)	Particle size		References
		Width	Length	
Softwood (black spruce) Hardwood (<i>Eucalyptus</i>)	– –	~ 35 μm ~ 20 μm	>3000 μm >500 μm	Beck-Candanedo et al. (2005)
Wood fibre Plant fibre	43–65	15–50 μm	>1300 μm	Beck-Candanedo et al. (2005), Neagu et al. (2006)
MCC	80–85	>1000 nm	>1000 nm	Abdul Khalil et al. (2012), Levis and Deasy (2001)
MFC/NFC	51–69	5–60 nm	>1000 nm	Abdul Khalil et al. (2012), Brinchi et al. 2013, Ng et al. (2015)
CNC	65–95	2–70 nm	100–600 nm	Abdul Khalil et al. (2012), Brinchi et al. (2013), Ng et al. (2015)

*Degree of crystallinity relative to cellulose

MCC Microcrystalline cellulose; *MFC* Microfibrillated cellulose; *NFC* Nanofibrillated cellulose; *CNC* Cellulose nanocrystals

Mechanical properties of cellulose and its derivatives have been widely studied. Compared to pure cellulose, which exhibits both crystalline and amorphous regions, NFC and cellulose nanocrystal (CNC) (which present high crystalline values) possess a higher axial elastic modulus than the synthetic fibre Kevlar, and mechanical properties that are within the range of materials used as reinforcement such as boron nanowhiskers, clay nanoplatelets, carbon fibre and steel wire. These characteristics are attributed to their crystalline regions, presenting for a bundle of stretched cellulose chain elastic modulus values in axial and transverse directions ranging between 110–220 and 10–50 GPa, respectively, a tensile strength up to 7700 MPa and a density of 1.6 g/cm³ (Brinchi et al. 2013; Moon et al. 2011). Additionally, factors such as crystallinity degree, crystal structure ($I\alpha$, $I\beta$, II), nanoparticle defects, dimension, and anisotropic nature within crystalline cellulose (non-symmetric structure of the cellulose chain and its arrangement), may influence the measurement of mechanical properties. These properties mean that cellulose-based materials rank near the top of high-performance natural materials and can be employed as reinforcement and fillers to make environmentally friendly products. Table 3.2 presents the mechanical properties of cellulose-based materials extracted from natural sources and compared to conventional reinforcing fibres.

Chemical properties, on the other hand, are given by cellulose structure. The high reactive surface of –OH side groups, their hydrophilicity, and chirality allow the incorporation of other chemical species in order to promote the functionalization of the surface, occurring thus a chemical modification. This modification is the basis for wide hydrogen bond networks, providing cellulose with a multitude of partially crystalline fibre structures and different morphologies (Klemm et al. 2005).

Table 3.2 Mechanical properties of cellulose-based materials compared to conventional reinforcing fibres

	Material	Young's modulus (GPa)	Elongation at break (%)	Tensile strength (MPa)	References
Natural cellulose fibres	Cotton	5.5–26.5	7–8	287–800	Kalia et al. (2009)
	Ramie	61.4–128	1.2–3.8	400–938	Bledzki et al. (1996)
	Hemp	–	1.6	690	Bledzki and Gassan (1999)
	Flax	27.6–100	2.4–3.2	45–1100	Bledzki et al. (1996)
	Sisal	9.4–22	3–7	468–640	Kalia et al. (2009)
	Coir	4–6	30	175	Kalia et al. (2009)
	MCC	21–29*	–	–	Moon et al. (2011)
	CNC	105*	–	–	Moon et al. (2011)
Conventional reinforcing fibres	Carbon (standard)	230–240	1.4 – 1.8	4000	Kalia et al. (2009)
	Kevlar-49	124–130*	–	3500	Callister and Rethwisch (2012)
	Boron nanowhiskers	250–360*	–	2000–8000	Ding et al. (2006)
	Clay Nanoplatelets	170*	–	–	Hussain et al. (2006)
	E-glass	70	2.5	2000–3500	Kalia et al. (2009)

*Reported as elastic modulus in axial direction

MCC Microcrystalline cellulose; CNC Cellulose nanocrystals

Carboxymethylation, sulfation, acetylation, tritylation as well as oxidation, derivatization, and grafting have shown to be suitable processes in the modification and chemical functionalization of cellulose in obtaining different cellulosic derivatives (Varshney and Naithani 2011). These methodologies enable an effective synthesis of cellulose since the hydroxyl groups provide convenient sites for substitution reactions in order to obtain by-products with specific desired characteristics, increasing the applications of the obtained cellulose products and highlighting the relationship between structure and functional properties (e.g. solubility, film formation, stability). Additionally, the chemical modification of the surface can help in a more controlled dispersion of some cellulose structures within an extensive range of polymeric matrices as well as a better control of both the interaction between particle-to-particle and particle-to-matrix bond strength (Moon et al. 2011).

Thermal properties of cellulose and its derivatives are usually related to the chemical degradation of the materials when subjected to high temperatures. Some studies have indicated the onset of thermochemical degradation of cellulose structures occurring between 200 and 400 °C (Fukuzumi et al. 2008; Michelin and Teixeira 2016). It has been also shown that the particle size and the pre-treatment used to obtain the cellulosic material affect the thermal properties. As a result, CNC starts to decompose at a lower temperature than MCC due to the increasing number of free chain ends at the surface, which are liable to an earlier decomposition. The thermal resistance of CNC can be increased by neutralizing the sulphate groups, which are a residue of the sulfuric acid used in its extraction process (Johansson et al. 2012). However, Petersson et al. (2007) evaluated the thermal stability of different neutralized cellulose derivatives including MCC, CNC (obtained by sulphuric acid hydrolysis of the same crystalline cellulose) and chemically modified CNC suspensions using *tert*-butanol (B-CNC) and a surfactant (S-CNC). The study revealed that CNC and B-CNC began an earlier degradation close to 260 °C, compared to MCC and S-CNC, which presented a thermal degradation around 300 °C. As previously mentioned, the thermal resistance of CNC results to be lower than that presented by MCC, due to the acid hydrolysis pre-treatment to which the particles are subjected. Whereas, S-CNC achieve thermal degradation values similar with MCC which are related to the high content of surfactant used to modify the CNC. Recent works have shown that post-treatments such as hydrophobization can strongly improve this thermal stability, a development that opens the door to new possible applications (Lavoine et al. 2012). Cellulose-based nanostructures thermally degrade at higher temperatures than poly(lactic acid) (PLA) or polyhydroxyalkanoates (PHAs). However, they can contain considerable amounts of tightly bound water, which would bring about accelerated polymer degradation when using nanocellulose as filler in PLA or PHAs. For this reason, there has been much attention paid to processes for drying the cellulose-based nanostructures while maintaining its nano-scale characteristics, a challenge that is inherently difficult with cellulose because of the agglomeration phenomena associated with capillary effects during drying (Johansson et al. 2012).

The influence of cellulose structures on **optical properties** of composites is related to different characteristics such as size, shape, ordering, charge, and dispersity of the cellulose into the matrix (Snyder et al. 2013). Additionally, cellulose concentration in the composite and its thickness can affect the transmittance and clarity of the final material.

As a final point, some cellulose-based structures present interesting **rheological properties** that can be described in terms of pseudoplasticity and shear-thinning behaviour. Pääkkö et al. (2007) studied the rheological behaviour of enzymatically pre-treated NFC and the relation between this behaviour and the mechanical properties of these materials. The study showed that from concentrations of 0.125 to 5.9% the NFC suspensions displayed a gel-like behaviour. In addition, the values of the storage modulus were rather high. For a 3% NFC suspension, the storage modulus (G') was about 10^4 Pa, as compared to the storage modulus of a 3% suspension of nanoscale cellulose crystallites, which was $G' \approx 10^2$ Pa. The authors

attribute this high elastic modulus to the long fibrils, which form an inherently entangled network structure. Furthermore, cellulose sulphates [e.g. carboxymethyl cellulose (CMC) and hydroxypropyl cellulose (HPC)] among other cellulose derivatives have been extensively used since their water-soluble sodium salts offer excellent rheological properties. Each polymer chain in a dilute solution of CMC is hydrated and extended, and exhibits a stable viscosity. In aqueous solution, it represents a complex rheological system since it forms aggregates and associations, and then higher-level structures (Varshney and Naithani 2011). Hence, the gel-forming capacities of these materials make them very interesting for application as anionic polyelectrolytes, film-forming materials, and biologically active polymers (Klemm et al. 2005).

3.1.2 Hemicellulose Properties

Hemicellulose is another important constituent of plant fibre materials. As shown in Table 2.1, the content and chemical structure of hemicellulose can change according to the raw material used. Various studies have been focused on the chemical structure of different hemicelluloses and the composition of their main and branched chains. Mannose, for example, is the most important hemicellulose monomer in softwood, followed by xylose, glucose, galactose, and arabinose, in contrast to hardwood hemicellulose, where the most representative sugar is xylose, followed by mannose, glucose, and galactose with a small amount of arabinose and rhamnose. It has been proved that these chemical structural differences significantly influence the functional properties of each material.

On the other hand, hemicellulose can be easily hydrolysed by using diluted acid or sodium hydroxide (alkaline) pre-treatments. This is possible due to its high branching, low polymerisation degree, and low crystallinity. In this way, oligomers and monomers from hemicellulose with important functional groups can be obtained.

Physicochemical properties, as already mentioned, can be affected by the chemical structure and the polymerisation degree of hemicellulose. **Rheological behaviour** of this polymer is associated with its relative affinity with water, which once added to it, induces to a viscous state or turn it into a gelling agent (Chen 2014). As the concentration of hemicellulose in the aqueous solution rises, the viscosity of the solution also increases. When the concentration of hemicellulose reaches to 4%, the solution is to be regarded as a gel (Chen 2014). However, this behaviour is strictly related to the presence of arabinose and xylose in the hemicellulose structure, since C5-sugars are responsible for fixing water masses into different hemicelluloses. Therefore, if the percentage of these monomers in the hemicellulose is too low, the spatial organization keeps xylose and arabinose away from water, resulting in low affinity of hemicellulose to water (He et al. 2008).

Recently, **bioactive properties** of hemicellulose derivatives such as galacto-oligosaccharides and xylo-oligosaccharides, have been highlighted. These

compounds can be obtained by different methods including extraction from raw materials, hydrolysis of polysaccharides, and enzymatic and chemical synthesis from disaccharide substrates (Santana-Méridas et al. 2012). Most of them are not degraded by human digestive enzymes, thus oligosaccharides reach the colon and potentially serve as substrates for the colonic microbiota supporting the growth of bifidobacteria and other lactic acid bacteria that are considered beneficial for human health (Gniechwitz et al. 2007; Bielecka et al. 2002). These types of hemicellulose known as non-digestible oligosaccharides present other interesting benefits for the human health, including decrease of cholesterol levels in the blood (Delaney et al. 2003), control of blood glucose and insulin response, (Jenkins et al. 1976), action against infectious and tumour diseases, and immunostimulatory capacity (Simões et al. 2010). Unlike starch and simple sugars, non-digestible oligosaccharides are not used by mouth microflora, meaning that the production of acid and polyglucans (cariogenic compounds) does not occur, protecting thus the teeth (Crittenden and Playne 1996). As a result, the non-digestible oligosaccharides have been employed as a low cariogenic sugar substitute in the production of confectionery, chewing gums, yoghurt and different drinks. They have also been suitable for the elaboration of low-caloric diet products and for the production of special diabetic foods, among other applications (Crittenden and Playne 1996; Van Loo et al. 1999).

3.1.3 Lignin Properties

Lignin contains several functional chemical groups, including hydroxyl (phenolic or alcoholic), carbonyl, carboxyl, and methoxyl in different amounts. These groups present a strong influence on lignin properties and depend on the source and the process used during extraction (Boeriu et al. 2004). Hydroxyls and many polar groups result in strong intramolecular and intermolecular hydrogen bonds, which makes the intrinsic lignin difficult to solubilize, while the presence of phenolic hydroxyl and carbonyl allow lignin to be dissolved in alkaline solutions (Chen 2014).

The condensation or degradation processes makes the isolated lignin able to be separated into soluble and insoluble lignin. The depolymerisation of lignin can be made through physical, chemical or enzymatic pre-treatments, in which is obtained a degraded or solubilized material with irregular morphology, specific chemical characteristics (including molecular weight and functional groups), and unique functional properties. When lignin is depolymerised, it can be used for the synthesis of valuable chemicals as well as bioactive compounds. In fact, one of the major difficulties is to determine its polymerisation degree because during the extraction process, lignin is invariably degraded into low molecular weight fragments. The **molecular weight** (MW) of lignin generally varies between 500–400,000 g/mol (Thakur and Thakur 2015), being the lignosulphonate typically ranged between 5000–400,000 g/mol, Kraft lignin ranged between 1000–5000 g/mol and the lignin obtained using organosolv represented by values between 500 and 3000 g/mol.

Although Kraft lignin represents the greatest production of technical lignins, the lignosulphonates are the most exploited and commercialized source of lignin, mainly due to their solubility in water at a wider pH range, and the generally higher molecular weight. On the other hand, organosolv lignin presents high homogeneity than the others lignins, low and relatively narrow MW distribution, high chemical purity, high solubility in organic solvents and hydrophobicity, and also present a great number of applications (Norgren and Edlund 2014).

Lignin applications have been developed through its isolation, and subsequent chemical functionalization in order to understand better the structure and thus, increase the lignin application in different fields. Due to its structural characteristics, lignin presents a great potential for chemical modifications, which can result in improved reactivity and thus to value-added materials with specific properties. Commonly, chemical modification is performed through the formation of new active sites or the functionalization of hydroxyl groups (e.g. etherification, esterification, reaction with isocyanates, silylation, phenolation, and oxidation/reduction). Considering the reaction parameters and reagent used, the esterification is the easiest type of lignin modification to be performed (Laurichesse and Avérous 2014; Gordobil et al. 2016).

Lignin exhibits relevant bioactive properties such as **antioxidant** and **antimicrobial activities**. These properties are imparted by the numerous bioactive compounds related with the aromatic structure of lignin and the occurrence of phenolic residues. Table 3.3 shows some of the main bioactive compounds derived from lignin obtained from LCMs and their respective application.

Phenolic compounds, derived from lignin, are of great interest for chemical, pharmaceutical and food industries, since they present enormous benefits for human health. Previous research efforts have shown that their potential is related to their antioxidant activity (Ballesteros et al. 2014, 2017). Lignin antioxidant properties are resulting from their radical scavenging capacity that is negatively influenced by increasing heterogeneity, dispersity, molecular weight average, and carbohydrate mixtures (Domenek et al. 2013). These phenolic compounds (Table 3.3) can act against chronic-degenerative diseases such as cancer (Kasai et al. 2000), cardiovascular diseases, neurodegenerative diseases and diabetes mellitus (Martins et al. 2011; Mussatto 2015; Prasad et al. 2011). Antioxidant effects of phenolic compounds can also act against the ageing processes, which is associated with oxidative stress due to reactive oxygen species. Nonetheless, their properties are not limited to the antioxidant activity. Phenolic compounds present antimicrobial (Ballesteros et al. 2015), anti-inflammatory (Shin et al. 2015), anti-obesity (Cho et al. 2010), anti-diabetic (Karthikesan et al. 2010) and anti-carcinogenic properties (Kasai et al. 2000). The antimicrobial potential of phenolic compounds has been proved against different pathogenic fungi that affect post-harvesting of fruits (e.g. *Alternaria sp.*, *Cladosporium cladosporioides*, *Phoma violacea*, *Penicillium italicum* and *Penicillium expansum*), revealing a significant percentage of inhibition against the growth of these microorganisms (Ballesteros et al. 2015). It has also shown a potential inhibiting effect against the Influenza virus (Mussatto 2015) and against microorganisms commonly associated with toxic-food infections such as

Table 3.3 Bioactive compounds derived from lignin of different lignocellulosic materials (LCMs)

LCM	Bioactive compounds	Application	References
Pine bark	Phenolic compounds	Antioxidant Anti-inflammatory	Vuorela et al. (2005)
Rice straw	Phenolic compounds, ferulic, <i>p</i> -coumaric and vanillin acids, flavonoids	Antioxidant	Moniz et al. (2015)
Flaxseeds	Phenolic compounds, <i>p</i> -coumaric, ferulic, and glucoside acids	Antioxidant Antihypertensive Anti-cancerous	Alu'datt et al. (2013), Beejmohum et al. (2007)
Sugarcane bagasse	Phenolic compounds	Antioxidant	Brenelli et al. (2016)
Wheat straw	Phenolic compounds, hydroxycinnamic acids	Antioxidant	(Azadfar et al. (2015)
Pomegranate husk	Polyphenols	Antifungal	Osorio et al. (2010)
Grape stalks	Phenolic compounds	Antioxidant	Amendola et al. (2012)
<i>Eucalyptus</i> wood chips	Gallic and vanillic acids, quercetin	Antioxidant	Conde et al. (2011)
Corncoobs	4-hydroxybenzoic vanillic, <i>p</i> -coumaric and ferulic acids, quercetin	Antioxidant	Conde et al. (2011)
Barley germplasm	Homogentisic, benzoic, protocatechuic, syringic, chlorogenic, and vanillic acids, anthocyanins, catechin, myricetin	Antioxidant	Kim et al. (2007)

Staphylococcus aureus, *Listeria monocytogenes*, *Salmonella enteritidis*, and *Escherichia coli* (Prado-Martin et al. 2012).

Lignin can be applied for stabilization of food and feed, and lignin derivatives may also be used as pesticides, dispersants, emulsifiers or sequestrants. These applications are related to the antioxidant and antifungal properties present by such lignin derivatives (Boeriu et al. 2004). On the other hand, lignin derivatives such as phenolic compounds improve the organoleptic properties of foods from vegetable origin, and can also be used as raw material in the development of functional foods or as natural preservatives against food degradation (Ballesteros et al. 2014; Rodríguez-Meizoso et al. 2010).

Concerning other specific properties, lignin behaves as a **thermoplastic material**, exhibiting a glass transition temperature (T_g) that varies widely depending on the extraction method used, water content, polysaccharides, molecular weight, chemical modification, and thermal history. The T_g of isolated lignin samples is often difficult to determine due to the broad heterogeneity of the lignin structure and molecular weight. While T_g generally rises with increasing molecular weight, high water contents lead to lower T_g values, indicating that water acts as a plasticizer in

lignin (Brinchi et al. 2013; Laurichesse and Avérous 2014; Thakur and Thakur 2015; Doherty et al. 2011).

The thermal decomposition of lignin is a complex process and occurs over a broad temperature range. This process occurs, for instance, because the various oxygen-based functional groups have different thermal stability with scissions occurring at different temperatures. The decomposition of the lignin structure starts at relatively low temperatures, i.e., 150–275 °C. It is thought that the first decomposition step is due to the dehydration of the hydroxyl groups located in the benzyl group. The cleavage of α - and β -aryl-alkyl-ether linkages takes place between 150 and 300 °C. Around 300 °C, aliphatic side chains start splitting off from the aromatic ring while the carbon-carbon cleavage between lignin structural units occurs at 370–400 °C. The complete rearrangement of the backbone at higher temperatures (500–700 °C) leads to 30–50% char and to the release of volatile products (CO, CO₂, CH₄, H₂) (Laurichesse and Avérous 2014).

Nowadays, lignin has been tested as polymer reinforcement due to its **mechanical properties**. In general, it has been added as additive/filler in polymeric materials (lignin-polymer blends) and composites to improve mainly thermal and mechanical properties. For instance, Gordobil et al. (2016) studied the potential of organosolv, Kraft *Eucalyptus* and spruce lignins as feedstock for polymeric materials. They performed a chemical modification (esterification) to enhance the reactivity. Thermal parameters showed a correlation with some structural and compositional characteristics (ash and sugars content, molecular weight and degree of condensation).

Lignin can also act as compatibilizers, plasticizers, hydrophobizing agents, flame retardants or optical modifiers or stabilizers (Domenek et al. 2013).

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Chapter 4

Processing, Production Methods and Characterization of Bio-Based Packaging Materials



4.1 Production of Bio-based Packaging

The final properties of the bio-based packaging are highly influenced by the raw materials used, however, the processing conditions are also one of the factors that change the final behaviour of the packaging material. Packaging materials can be produced by “wet process” and “dry process” methods. During the “wet process” method, the polymers are solubilized or dispersed in a solvent, forming a homogeneous mixture that after solvent evaporation, results in the packaging material (i.e. film). The “dry process” method is based on the thermoplastic properties of the materials; in this case, the polymer is melted during processing, forming thus, the packaging material. According to the type of “dry process” used it can result in a film (e.g. blowing), a tray (moulding) or a bottle (injection). Other methodologies such as in situ polymerisation and bi-layer technologies (electrospinning and lamination) can also be used to develop packaging materials with unique properties (Agarwal et al. 2014; Urbanczyk et al. 2009; Jang et al. 2008; Fabra et al. 2013).

The production of bio-based packaging materials with the incorporation of lignocellulosic materials is influenced by the purity and chemical characteristics of the materials used. The way that lignocellulosic materials are used, i.e. as the main material of the packaging or as a filler/additive to form a biocomposite, will influence the way by which the package will be produced as well as its final properties. One of the parameters influencing the use of lignocellulosic materials in packaging is their compatibility with other bio-based materials. This compatibility influences the final properties of the mixture and is related with how the different phases (lignocellulosic material and bio-based polymer) interact and will be organized in the matrix. The compatibility of the materials is driven by their interfacial tension; this property tends to zero when the materials are miscible. Oppositely, large interfacial tensions lead to phase separation, and the processing and production of packaging materials will be more difficult. One of the solutions to circumvent this problem is the addition of interfacial agents with a hydrophilic and

hydrophobic region that reduce the interfacial tension and thus act as compatibilizers (Jyotishkumar et al. 2014).

In the next sections, the methodologies based on the “wet process” and “dry process” will be presented and discussed. Table 4.1 presents some examples of the methodologies used for the production of bio-based packaging materials using lignocellulosic materials.

4.1.1 *Wet Process*

As commented previously, the “wet process” method is based on the evaporation of the solvent used in the solubilisation of the materials (i.e. film forming solution) and is commonly named “casting”. This methodology is very common when bio-based packaging is being developed and when the development is still at laboratory scale. The low thermostability of polymers and the lack of knowledge of some lignocellulosic materials are the main reasons for the use of the “wet process” as the choice method for the production of bio-based packaging materials. This methodology is also used when the bio-based packaging is applied as a coating; in this case, the film-forming solution is directly applied on a surface (packaging material or food surfaces) creating a coating that dries on the surface and then forms a thin film layer. During the hydration process, the main solvents used are water and ethanol, but other solvents can be used according to the materials that will be cast [e.g. for poly(lactic acid) (PLA) chloroform is normally used as solvent]. The production of films by casting is a step-by-step process where: (a) the polymer is dissolved and mixed with the solvent and other additives such as plasticizers; (b) the film-forming solution is heated or the pH is adjusted (this will depend on the material used) until the total dissolution of the polymer is achieved; and (c) the film-forming solution is poured on a solid surface such as Petri dishes (Cerqueira et al. 2012) or teflon-coated glass plates (Sothornvit et al. 2009), and then, left to dry. During the drying stage, it is possible to control the temperature and relative humidity in order to decrease the time needed for solvent evaporation. Also, the chambers used, with or without forced air convection, will influence the drying process (Rossman 2009). Nowadays, it is already possible to buy equipment able to control all the parameters, and batch and continuous systems have been presented for the production of films by casting at the pilot and industrial scales (Mathis 2017; Explore 2016). In some cases, the mixture of the materials should be performed at different steps, being the main material normally dissolved firstly and only then, the additives or fillers are added. Besides, a degassing process can be required (normally a vacuum system is used) for the elimination of air bubbles formed during the processing (Martins et al. 2012).

In other situations, if micro- or nanostructures (e.g. nanoclays, cellulose nanocrystals, silver nanoparticles) are added to the film-forming solutions, their dispersion is critical and aggregation phenomena should be avoided. In these cases, ultrasounds can be used to guarantee the good dispersibility of the materials (Martins et al. 2013; Abdollahi et al. 2013).

Table 4.1 Examples of the production conditions of bio-based packaging materials using lignocellulosic materials

Material	Packaging type	Methodology	Pre-extrusion	Homogenization conditions	References
Starch/Kraft lignin	Film	Moulded with hot press 140 °C 250 bar, 10 min	Twin-screw extruder		Baumberger et al. (1997)
Starch/lignin/CNC	Film	Casting, 40 °C, 24 h	n.a.	Water and stirring at 80 °C	Baumberger et al. (1997)
PLA/CNC	Film	Casting	n.a.	Chloroform using Ultra-turrax, sonication, stirring at 40 °C	Sanchez-Garcia and Lagaron (2010)
Soy protein/Hydroxypropyl lignin	Film	Moulded with hot press 140 °C, 20 MPa, 10 min	Single-screw extruder	n.a.	Chen et al. (2006)
PHBV/lignin	Film	Moulded with hot press 170 °C, 10 MPa, 6 min	Twin-screw extruder	n.a.	Kovalcik et al. (2015)
PLA/MFC	Film	Moulded with hot press, 190 °C, 0–2.5 MPa, 0.5–3.5 min	Twin-screw extruder (using liquid feeding)	Water and acetone, stirring and ultrasonication	Herrera et al. (2015)

CNC Cellulose nanocrystal; PLA Poly(lactic acid); PHBV Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); MFC microfibrillated cellulose
n.a. Not available

One specific material for the use of the “wet process” is cellulose. Vacuum filtration and dynamic sheet former are the methods of choice for the production of films or membranes from cellulose, allowing the production of homogeneous films. Also, the methodologies of casting and spraying processes have been presented for the production of films (Sehaqui et al. 2010; Wågberg et al. 2008).

4.1.2 Dry Process

The “dry process” method involves the mixture and melting of the polymers and additives during processing, that will be subsequently blown or extruded to form a film (e.g. bags or sheets) or injected into a mould (e.g. trays and bottles). These processes allow obtaining packaging materials at low cost, and at the same time avoid the use of solvents, being thus considered, a more environmentally friendly process.

The process consists in the melting of the materials at a specific temperature aiming at obtaining a product with low viscosity and strong enough to guarantee that extension is the major form of deformation and flow. This is used to shape the molten material that flows through a shaping die that is later blown to form a pouch, or laminated to obtain a film. In the case that the molten materials are injected into a mould, it is possible to produce trays and bottles. The processing conditions used in the extrusion barrel and die such as temperature and pressure, and the speed of the screw will depend on the thermal and rheological behaviour of the materials used. According to the type of materials (amorphous or crystalline), the processing temperatures should be higher than the glass transition or the melting point, respectively (Vicente et al. 2011).

These processing methodologies are generally used for the production of packaging materials based on synthetic materials, and currently, are being adapted to use with bio-based packaging materials. Some examples are the use of PLA and polyhydroxybutyrate (PHB), which have been processed and produced at industrial scale using the “dry-process” method (Taghleef-Industries 2016; Amcor 2016). On the other hand, proteins and polysaccharides present a small range of processability, due to their higher thermal instability, which limits the use of the “dry process” method for the production of packaging using these materials. Despite these limitations, several authors have studied the “dry process” method to produce packaging using proteins and polysaccharides (Fakhouri et al. 2013; Garrido et al. 2016; Pelissari et al. 2011), showing the possibility of using these cost-effective processes to produce bio-based packaging materials from these polymers. These achievements have been possible through a rigorous control of the parameters that influence the processing as well as their optimization. The materials used, extrusion temperature, residence time in the barrel and die, pressure and flow rate, are some of the most important parameters that should be controlled (Lafleur and Vergnes 2014).

4.1.3 Other Processing Technologies

Besides the classical wet and dry processing technologies used in the development and production of packaging materials, other technologies have been used aiming at enhancing the properties of packaging materials. One of the examples is in situ polymerisation for the production of bio-nanocomposites, where the nanostructures are mixed with a solution of monomers and after polymerisation activation, the nanostructures are maintained in the polymers structure forming a composite (Ojijo and Ray 2013). In addition, the formation of a layer or multilayer through the deposition of a material can be used for the functionalization of packaging materials. The use of a coating, for example, can improve the properties of the packaging materials adding different active compounds to impart e.g. antimicrobial or antioxidant properties. The coating can be added by lamination and by electrohydrodynamic processing. The main advantages of using these techniques are the possible deposition of thermolabile compounds (that cannot be added through the “dry process”) and active compounds that should act on the surface of the packaging material (e.g. to be in contact with the food product) (Fabra et al. 2016; Cerqueira et al. 2016).

4.2 Properties and Characterization Techniques

Both raw and final packaging materials need to be characterized in order to guarantee their correct application. In the first case, the thermal behaviour and solubility are important parameters that should be evaluated for a successful processing of the materials, and finally, after the production of bio-based packaging transport and mechanical properties will dictate the suitability of the packaging for food products. Nevertheless, the packaging final properties are highly influenced by the chemical characteristics of polymers used during production, being the most important the chemical structure, crystallinity, polarity and molecular weight (Park and Chinnan 1995; Miller and Krochta 1997). The fillers/additives added and the methodology used for production will also have a great influence on the packaging final properties. In the next section, the most used techniques for the characterization of raw materials used in packaging production and in the characterization of the final packaging material are presented.

4.2.1 Thermal and Mechanical Properties

The evaluation of the thermal properties of raw materials is crucial for the development and production of packaging materials. While for the “wet processes” to know the melting point or glass transition temperature (for crystalline or amorphous materials, respectively) of the materials is not crucial, in the “dry processes” the determination of glass transition temperature (T_g) and/or melting point temperature

(T_m) is very important. The glass transition is exhibited by amorphous polymers or by the amorphous regions of partially crystalline polymers when a hard, brittle, glass-like state is transformed into a viscous or rubbery fluid with the increase of temperature. On the other hand, the melting is a characteristic of crystalline polymers and corresponds to the transition from a solid to liquid state at a given pressure (usually the atmospheric pressure) (Sperling 2006).

These parameters can be determined by differential scanning calorimetry or dynamic mechanical analysis. Afterwards, and when bio-based packaging are produced, T_g and T_m can be determined in order to evaluate the effect of the processing conditions in the materials properties. Another important property that should be determined is the thermal stability through thermogravimetric analysis where the thermal stability is related to the composites degradation that is followed by weight loss of the materials with the increase of the temperature. The thermal properties of the finished packaging materials are very important mainly if the materials will be thermos-sealed. During heat-sealing, the polymer layers are placed between two heated plates to provoke the melting of the polymer. During this process, the application of moderate pressure on the surface of the melted polymer leads to interfacial interactions between the two surfaces, joining them together.

Along with the thermal characteristics, the mechanical properties are also very important in the evaluation of the packaging performance. In fact, bio-based packaging materials with satisfactory mechanical properties are potential alternatives for substituting petroleum-based packaging in food applications. Some of the standardized tests (normally using a Universal Testing Machine) to evaluate mechanical properties of packaging materials provide information regarding the tensile strength (TS), elongation-at-break (EB), elastic modulus, compression and puncture strength. Normally, bio-based packaging presents lower TS than common petroleum-based packaging films, while EB values vary according to the materials, being in some cases possible to obtain similar values between bio- and petroleum-based packaging materials to this specific property. One of the main issues of bio-based packaging materials is their sensitivity to water (high hydrophobicity) that makes storage conditions (i.e. relative humidity - RH) one of the factors that most affect their mechanical properties. In these cases, water will act as a plasticizer, being the hydrophilic hydroxyl groups attached to active sites of the polymer, decreasing the intermolecular forces between polymers chains and consequently, decreasing the physical strength of the materials. Thermal and mechanical properties of different bio-based packaging with the incorporation of lignocellulosic materials at different values of RHs and temperature of storage have been studied. Some results are presented in Table 4.2.

4.2.2 Barrier Properties

Barrier properties, such as permeability to oxygen and carbon dioxide, are one of the main features of packaging materials for foods. The packaging capacity to provide a barrier to gases and other volatile compounds between the food products

Table 4.2 Comparison of the mechanical properties of bio-based packaging materials under different test conditions

Materials	Test conditions	TS (MPa)	EB (%)	References
Alginate	25 °C, 55% RH	0.413		Aadil et al. (2016)
Alginate/lignin/PEG	25 °C, 55% RH	0.625		Aadil et al. (2016)
Starch	25 °C, 58% RH	13.3	0.93	Baumberger et al. (1997)
Starch/Kraft lignin	25 °C, 58% RH	≈17	≈1.4	Baumberger et al. (1997)
Starch/Kraft lignin	25 °C, 71% RH	≈5.1	≈0.6	Baumberger et al. (1997)
Starch	25 °C, 60% RH	1.717	47.278	Miranda et al. (2015)
Starch/lignin	25 °C, 60% RH	3.198	28.967	Miranda et al. (2015)
Starch/lignin/CNC	25 °C, 60% RH	6.201	27.114	Miranda et al. (2015)
PLA	n.a.	58.22	6.03	(Sanchez-Garcia and Lagaron 2010)
PLA/CNC	n.a.	36.48	12.57	Sanchez-Garcia and Lagaron (2010)
PHBHV	25 °C, 0% RH	23.1	24	Kovalcik et al. (2015)
PHBHV/lignin	25 °C, 0% RH	23.1	10	Kovalcik et al. (2015)
Chitosan	25 °C, 33% RH	84.1	7.1	Crouvisier-Urien et al. (2016)
Chitosan/lignin	25 °C, 33% RH	29.8	1.7	Crouvisier-Urien et al. (2016)
Chitosan/lignin	25 °C, 75% RH	12.0	32.7	Crouvisier-Urien et al. (2016)

TS Tensile strength; EB Elongation at break

PEG Polyethylene glycol; CNC Cellulose nanocrystals; PLA Poly(lactic acid); PHBHV Polyhydroxybutyratevalerate

n.a. Not available

and the external environment allows protecting foods against moisture and aroma losses, and, oxygen and carbon dioxide permeation increasing thus, the shelf-life and quality of the foods.

There are two main factors that influence the transport of molecules through a film: i) diffusion, that represents the rate at which a molecule permeates through the packaging material; ii) sorption, that is affected by the partition coefficient between the surface and the outer fluid, and also by the solubility of the molecules in the matrix (George and Thomas 2001; Krochta 2002). Permeability considers these two

factors together, being related to the difference of permeate concentration between the two sides of the film. The most studied transport properties in packaging materials are the permeabilities to water vapour (WVP), oxygen (O_2P) and carbon dioxide (CO_2P).

The WVP is a very important parameter in food packaging materials due to the relevance of controlling the moisture loss in foods. WVP can be measured using a cheap and simple equipment (cups sealed with the films in controlled conditions of RH and temperature, being the water loss weighted during the time) that allows evaluating the mass transfer mechanisms through packaging in different conditions (different values of temperature and RH can be obtained very easily). Due to that, WVP is one of the most studied parameters in packaging materials. One of the main drawbacks of bio-based packaging is their hydrophilic nature, presenting high WVP values when compared with petroleum-based packaging. Several strategies have been presented to control the WVP of those bio-based materials, such as the addition of plasticizers, surfactants, lipids and waxes and the use of fillers such as fibres and particles.

Most of the materials need a plasticizer to increase flexibility and processability of the materials, leading in most of the cases to an increase of the permeability values. However, in materials where the presence of micro-cracks and pores can be an issue, they can help to reduce the WVP values (Garcia et al. 2000). In order to decrease WVP of packaging materials, hydrophobic or partially hydrophobic compounds are frequently added to the matrix during the formulation or by forming a layer in the film by the application of a coating. Lipids and waxes and some surfactants present the capacity to decrease WVP. Some examples include the use of oils in the film's matrix in order to decrease the WVP values of the films; corn starch and methylcellulose with soybean oil (Bravin et al. 2006) and hydrogenated palm oil mixed with arabinoxylan extracted from maize bran (Péroval et al. 2002) were evaluated and their use have led to a decrease of the WVP values of the films.

Bio-based packaging materials are generally a good barrier to oxygen and carbon dioxide. According to the application foreseen to the packaging, the degree of oxygen and carbon dioxide permeability should be adjusted; i.e. for fresh and fresh-cut fruits and vegetables, moderate barriers should be considered. As for WVP, a great number of factors can also influence the barrier capacity of packaging materials for O_2 and CO_2 , being the most significant in this type of materials the RH. Besides, according to the application, the presence of volatile organic compounds in foods can be an important factor, and therefore the permeability to aroma and flavour is also very important and should be determined in those cases. However, the permeability of aroma and flavour compounds through packaging materials has not been thoroughly investigated because of the complex behaviour of these compounds in foods and possible interaction with packaging materials. The determination of the aroma and flavour permeability follows the same permeation principles of water vapour, and oxygen and carbon dioxide, nonetheless, that permeability is more difficult to determine due to the solubility and diffusion coefficients of these organic compounds which are pressure-dependent and concentration-dependent, respectively (e.g. the organic compound may interact

with the polymer, changing the permeation rate). So, a sensitive analytical equipment is needed, and the presence of co-permeate organic compounds can greatly influence permeability values compared to those values obtained for pure compounds (Robertson 2013).

Recently, new and alternative methods have been used to enhance the performance of packaging materials. The development of bi-layer and laminate films showed to decrease WVP values of chitosan and starch-based films (Pereda et al. 2011; Slavutsky and Bertuzzi 2015). Moreover, the incorporation of nanostructures, such as cellulose-based nanostructures, were successfully applied to decrease the WVP of packaging materials (Miranda et al. 2015; Sanchez-Garcia and Lagaron 2010), due to the increase of the effective path length of diffusion of the water molecules (Azeredo 2009).

4.2.3 *Optical Properties*

Some of the most important optical properties of the packaging materials are opacity, transparency, colour and gloss, but also haze, refractive index, and clarity are normally considered (Robertson 2013). They are related to the polymer structure (e.g. degree of crystallinity and purity) and by the possible addition of additives to the matrix.

The opacity and transparency of a material provide an indication of how much light passes through the film: i.e. the higher the opacity, the lower the amount of light that pass through the material; this can be easily measured using a colorimeter or a spectrophotometric equipment. On the other hand, clarity is an important factor that evaluates the degree of distortion of an object when viewed through the film of a packaging. When lignocellulosic materials with low purity are added to the film matrix, the colour of the films can change due to the presence of coloured compounds (e.g. lignin contains highly coloured compounds).

Film colour is an important factor in terms of the type of application of the packaging and consumer acceptance. One of the most used colour systems is the CIEL*a*b* colour system, where L* represents the lightness, and a* and b* are colour coordinates, where +a* is in the red direction, -a* is in the green direction; +b* is in the yellow direction, -b* is in the blue direction, low L* is black, and high L* is white.

The refractive index can also be used to evaluate the optical properties of packaging materials and measures the ability of a material to refract or bend light as it passes through the material (Rovira 2008). It will be highly influenced by the crystalline and amorphous character of the packaging material. While amorphous materials are transparent unless additives/fillers are present, impurities or chemical groups that absorb light radiation, the crystalline polymers will be influenced by the presence of crystal structures. If the crystal structures are smaller than the wavelength of light the packaging will be transparent, however, if during the processing

the crystalline structures grow greater in diameter than the wavelength of the light, the film will be opaque.

4.2.4 Solubility

Bio-based packaging materials, mainly those produced using polysaccharides and proteins, present moderate resistance to water and their integrity in aqueous environments should be evaluated. Solubility indicates the degree of integrity of a film when immersed in an aqueous solution and is one of the important characteristics of bio-based packaging. In most of the cases, a non-soluble or low-soluble packaging is needed if the stored foods should be protected from water or if the aim is to avoid the dehydration. However, a high solubility is required for films and coatings applied in coated food products or in packaging systems where the solubility is needed (e.g. sachets meant to be dissolved in water during use). In these cases, several approaches have been tested to reduce and control the solubility of the bio-based packaging materials. Besides the addition of hydrophobic compounds, cross-linkers can be also used to decrease the solubility of bio-based packaging materials.

4.2.5 Chemical Structure and Morphology

The chemical structure of the materials can provide important information regarding the final properties of the packaging materials. Techniques such as Fourier transform infrared (FTIR) spectroscopy (which provides information regarding the chemical structure of the materials) and X-ray diffraction (which provides information about the crystallinity), when evaluated together with the thermal properties, can be very useful for the understanding the effect of addition of fillers/additives in the packaging materials. More specifically, FTIR provides information regarding the frequencies of vibrations between atomic bonds in the material and can be used to determine the components in a mixture, as well as the possible formation of new bonds between materials during their mixture and processing. X-ray diffraction gives valuable information about the crystallinity degree of the materials. It can be used for the identification of the crystal structure and size and verify the effect of adding fillers/additives on the crystallization degree of the produced packaging material.

The morphology of the packaging material can be accessed by microscopy. Optical microscopy can be used as a direct imaging technique in transparent films. In crystalline materials, polarized microscopy can be used to observe the way in which crystals are dispersed. However, in the case of packaging materials the most powerful microscopy techniques are scanning electron microscopy (SEM) and atomic force microscopy (AFM). They provide high-resolution images of the sample's surface and its three-dimensional appearance, which can be very useful when information about the packaging surface is needed.

4.2.6 Wettability of Bio-Based Coatings

The use of bio-based materials as food coatings has been extensively studied and is one of the applications of lignocellulose-based materials. The materials should be food grade and approved to be used as coatings, and in this case, they are called edible coatings. In fact, one of the most used materials as coatings in commercial products are cellulose derivatives such as CMC (e.g. fruits) and HPMC (e.g. fried products). The coating solutions must wet and spread on the surface of the food product and upon drying form a film on the food surface with the adequate properties and durability. The way that edible coatings will act on the food surface will be dependent on the wettability of the coating and on the surface properties of the food (e.g. surface tension).

Surface tension involves the measurement of the contact angles between several standard liquids and the materials' surface. Then it is possible to correlate the surface tension of the liquids with the contact angle values obtained and determine the so-called critical surface tension of the surface. Wettability can be determined by the balance between adhesive and cohesive forces, and is determined using the contact angle between the coating solution and the surface of the material and the liquid-vapour tension of the coating solutions. The adhesive forces lead the coatings to spread over the solid surface while cohesive forces cause their shrink. Wettability is one of the most important properties when evaluating the capacity of a solution to coat a food surface. In practical terms, the closer the wettability values are to zero, the better a surface will be coated. Several works studied the wettability of bio-based coatings on food surfaces and showed the possibility of choosing the coating formulation according to the best wettability value (Choi et al. 2002; Ribeiro et al. 2007; Lima et al. 2010).

4.3 Biodegradability and Life Cycle Assessment

One of the main claims of bio-based packaging materials is their environmental sustainability. This claim is based on the fact that they are obtained/produced from renewable sources and are biodegradable and/or compostable, thus reducing their environmental impact after use. Nowadays, this characteristic is one of the ways through which companies promote their materials and packed products, being several materials presented as “green”, “degradable”, “biodegradable” and “compostable”.

It is also important to mention that there are several bio-based materials that despite being obtained from a renewable source are not biodegradable (see Fig. 1.1, Chap. 1) (Soroudi and Jakubowicz 2013; Gómez and Michel Jr 2013). Due to this, it is important to evaluate the biodegradability of the final packaging material in order to ensure that produced packaging materials are biodegradable according to

international standards (e.g. ISO14855). For instance, Emadian et al. (2017) evaluated, the biodegradability values of several packaging materials, both bio-based and petroleum-based, and showed that according to the material and degradation conditions (soil, compost, and marine) used during testing, the biodegradability of PLA, PHB, polyhydroxyalkanoate (PHA), cellulose and starch-based plastics can vary from 10 to 100%. The structure and composition of the polymer or composite used in the production of the packaging play a key role in the biodegradation process. However, the environmental conditions (i.e. medium pH, moisture, oxygen concentration and temperature) are important in the biodegradation process. It was clear that instead of disposing bio-based packaging into landfills, composting should be considered, once the disposal of bio-based packaging in landfills contributes more to waste management problems than offers a really sustainable solution.

Gómez and Michel Jr (2013) also studied the biodegradability of different petroleum-based and bio-based packaging materials by evaluating their biodegradation during soil incubation, composting and anaerobic digestion based on ASTM D5988-03. They showed that only PHA presents a biodegradability in soil incubation near to cellulose paper (used as control), and that for biodegradation during composting and anaerobic digestion, the plastarch (blend of polypropylene with corn starch) and co-polyester + corn based plastic (blend of an aliphatic aromatic co-polyester with a corn starch-derived polymer) present the best results. In fact, the use of bio-based with petroleum-based materials for the development of composites has been presented as a solution to increase the biodegradability of the packaging materials (Abdel Ghaffar and Ali 2016).

Even if the biodegradability of the packaging materials is guaranteed, their sustainability can only be claimed after the assessment of its life cycle. For this, a tool called Life Cycle Assessment (LCA) is normally used. LCA evaluates the potential environmental impacts of a product, material, process, or activity. It is a comprehensive method for assessing a range of environmental impacts across the full life cycle of a product, from materials acquisition to manufacturing, use, and final disposition (EPA 2017). It allows the identification of hotspots in a product life cycle, the fair comparison of products and processes, and the definition of strategies to improve a product environmental performance. LCA is determined according to international standards (e.g. ISO14040) and should be focused on the final packaging system (packaging needed to pack food products) considering the different steps during the packaging production (i.e. source and production of biomaterials, packaging production, and disposal).

Álvarez-Chávez et al. (2012) studied the sustainability of several bio-based packaging materials and found that none of the bio-based plastics currently in commercial use or under development can be considered fully sustainable. This fact is explained by the use of genetically modified organisms for feedstock production, the use of toxic chemicals in the production process or their generation as by-products. Based on these results it is clear that some bio-based packaging materials are preferable from a health and safety perspective and others from an

environmental perspective; and therefore starch, PLA, and PHA are preferred over other bio-based polymers such as cellulose and lignin-based materials.

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Chapter 5

Use of Lignocellulosic Materials in Bio-based Packaging



5.1 Bio-Based Packaging

Bio-based materials have been often used to produce coatings, multilayers, and films by casting. However, technological advances have allowed processing some of these types of materials in a similar way to the petroleum-based plastics including film extrusion, spinning, injection moulding, thermoforming and sheets (Lim et al. 2008; Mahalik and Nambiar 2010; Song et al. 2011). Additionally, the origin and chemical structure of the materials used for the production of bio-based packaging play an important role in the final properties of the packaging. These materials can be modified depending on the techniques employed during the process of extraction. Thus, the type of molecular linkage and shape, the molecular weight, and the degree of polymerisation of the compounds can widely influence the physicochemical properties of the final matrix and affect the interaction between different materials (Martins et al. 2012; Mikkonen et al. 2007). The attributes that each component provides to overall packaging properties are also diverse, and in some cases, can determine the final use of packaging (Sothornvit and Krochta 2001). Plasticizers are often added to film-forming solutions aiming at improving packaging properties. These additives are usually molecules of low molecular weight and high boiling point, which are highly compatible with the polymers. Common plasticizers such as sorbitol, glycerol, and polyethylene glycol, are used to decrease brittleness and increase the flexibility of bio-based materials, which are important attributes in packaging applications (Pavlath and Orts 2009; Guilbert and Gontard 1995).

A great advantage of bio-based packaging materials is their biodegradability and possible edibility. They can also be used as vehicles for additives, antioxidant and antimicrobial agents, nutrients and flavours, improving packaging quality and increasing its functionality (Cerqueira et al. 2009). Therefore, bio-based packaging materials result in promising systems being used in different fields without endangering products that are in direct contact with the packaging.

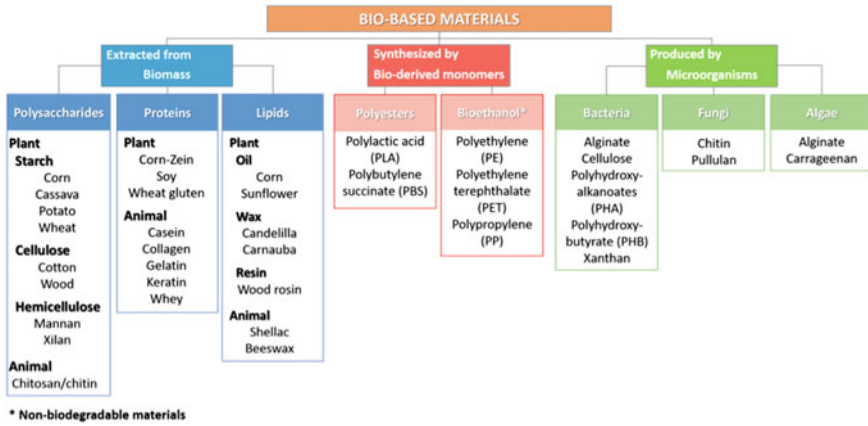


Fig. 5.1 Bio-based materials used in the bio-based packaging production (Adapted from Berezina and Martelli 2014 and Weber et al. 2002)

The materials used for the production of bio-based packaging can be divided into three main groups (Fig. 5.1). One of these groups are the ones extracted from renewable resources. Examples of these polymers include the lignocellulosic materials (i.e. cellulose, hemicellulose, and lignin) as well as polysaccharides (e.g. starch), proteins, lipids or waxes. The others groups are those synthesized through chemical or biotechnological routes such as poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs), among others, in which several times lignocellulosic derivatives are used as raw materials for their production.

5.2 Lignocellulosic Materials as Packaging Materials

Lignocellulosic materials (LCMs) can be used as main raw materials or as additives in food packaging industry. When they are used as additives the aim is to improve physicochemical properties and increase compost ability and biodegradability of the final packaging material. This has shown to be interesting not only with the application of purified materials from LCMs such as cellulose and cellulose derivatives, hemicellulose and lignin, but also the use of the raw LCMs with a very mild pre-treatment. In the following sections will be presented the main examples of the LCMs used to produce packaging materials as well as their use as additives for the production of bio-based packaging.

5.2.1 Cellulose and Cellulose Derivatives as Packaging Materials

Cellulose was one of the first materials used for the production of packaging. The first cellulose-based packaging was reported in China 200 BC, but only in the 19th

century, the paper and paperboard were industrialized. Nowadays, according to Kirwan (2007), up to 40% of all worldwide packaging is based on paper and paperboard, giving them the largest share of packaging materials used, by weight. Most of the paper and paperboard used for packaging are obtained from unbleached Kraft softwood pulps, while the bleached pulp is generally used for writing paper, book and cover papers (Robertson 2013). These pulps are based on cellulose fibres that self-bond forming a compact and overlapped network in a continuous sheet/film. The obtained packaging materials are printable and, according to the application, they can be flexible, semi-rigid and rigid. The type of paper and paperboard and their characteristics such as appearance, thickness and strength are affected by the fibre used (i.e. type of processing and fibre) and by paper and paperboard manufacture (i.e. the amount of fibre used). As explained in Chap. 2, the highly crystalline structure of cellulose, its hydrophilic nature, and low solubility makes it difficult to be used as packaging material before being subjected to any pre-treatment. Regarding cellulose-based materials, it has been shown that the alternating hydroxyl side chains along the cellulose backbone are responsible for the high moisture permeability of the packaging. On the other hand, cellulose with high crystallinity degree can result in a brittle material with flexibility and tensile strength reduced.

In the food industry, the paper coated with wax and polyethylene has been employed as a primary packaging, nevertheless, the majority of paper and paperboard are usually employed as a secondary or tertiary packaging.

In many other applications, cellulose is traditionally dissolved or derivatized to a more soluble form. During the process, the use of harsh reaction conditions, organic solvents, and hazardous chemicals are needed to obtain soluble cellulose derivatives able to be processed. One of the most known cellulose-based packaging materials is cellophane, developed in 1908 by Jacques E. Brandenberger, and improved in 1927 by William H. Charch from DuPont company (which acquired the US patent rights of cellophane) allowing to obtain a transparent and waterproof cellophane (Robertson 2013; Morris 2017). The most commonly used process for the production of cellophane films consists of the treatment of cellulose with sodium hydroxide and carbon disulphide where the cellulose is converted to cellulose xanthate (called the 'viscose process'). Then, the cellulose xanthate solution is extruded to form a cellophane film. Cellophane possesses good mechanical properties, nonetheless, it is a very hydrophilic material and consequently, highly sensitive to moisture. Cellophane is not considered a thermoplastic owing to the fact that theoretically, its melting temperature is above the degradation temperature. Cellophane films are usually available in different forms being uncoated or coated with nitrocellulose wax, polyvinylidene chloride (PVDC) and vinyl chloride-vinyl acetate copolymer (VC/VA) in order to improve their barrier capabilities and functionally. Additionally, cellophane-based packaging materials offer a range of unique attributes, that the plastic packaging is unable to equal and can be supplied in a wide range of brilliant colours. Cellophane-based materials have been used industrially as breathable packaging for baked goods, processed meats,

twist-wrapped confectionery packaging, cheeses and yeasts as well as in the fabrication of ovenable and microwaveable packaging among other applications.

Cellulose ethers, a group of cellulose derivatives, are biopolymers obtained by partial substitution of hydroxyl groups in cellulose by ether groups (Gennadios et al. 1997; Lin and Zhao 2007). Usually, these cellulose derivatives have excellent film-forming properties. Thus, they can be dissolved in aqueous solutions or in water-ethanol solutions in order to produce bio-based packaging materials with interesting oxygen and carbon dioxide barriers. However, water vapour permeability of most of the cellulose ether-based packaging materials is still relatively high when compared with another bio- and petroleum-based polymers. The most common and commercial cellulose-ether derivatives employed in the developing of bio-based packaging materials are carboxymethylcellulose (CMC), hydroxypropylcellulose (HPC), methylcellulose (MC), hydroxypropylmethyl cellulose (HPMC) and cellulose acetate (CA).

CMC, for example, is one of the most important cellulose derivatives in packaging applications. It presents excellent film-forming properties due to its biocompatibility with substances such as water-soluble polysaccharides, proteins, salts, surfactants and plasticizers (Nisperos-Carriedo et al. 1991). CMC-based films are generally odourless and tasteless, flexible, and transparent. They are water-soluble, resistant to oil and fats, and present a moderate strength, moisture, and oxygen permeability (Gennadios et al. 1997; Bourtoom 2008). CMC has been tested as a coating on apples, peaches, lettuce and carrots among others, showing its capacity to retain the original flavour and crispness and reduce the gas exchange rate (Lin and Zhao 2007).

On the other hand, MC-based films have shown to be the most resistant to water, due to it is the lowest hydrophilic derivatives when compared to the others cellulosic ethers (Kester and Fennema 1986). Additionally, MC and HPMC presented the ability to form thermally induced gelatinous films. They have been used to retard oil absorption in deep frying food products (Albert and Mittal 2002; García et al. 2002) acting in confectionery products as a barrier to the migration of lipid (Bourtoom 2008). These bio-based materials can also be used on fruits and vegetables, improving oxygen and oil barriers and decreasing moisture transfer (Olivas and Barbosa-Cánovas 2009). As a final point, CA is also extensively used in food packaging to wrap baked goods and fresh products. Although this material necessarily requires the addition of plasticizers to achieve a good film-forming solution, the resulting films show gloss and clarity, good printability, rigidity and dimensional stability. A negative point of CA-based materials is their relatively low gas and moisture barrier capacity (Puls et al. 2011).

Nowadays, also plastic materials are using cellulose-based fibres to obtain composites for packaging applications. The main objective is to obtain cellulose-based packaging films with different properties using environmentally friendly technologies (Sirvio et al. 2013; Liimatainen et al. 2015; Yang et al. 2011). One of these examples has been reported by Sirvio et al. (2013) where cellulose fibres modified by periodate oxidation were derivatized, resulting in dicarboxylic acid cellulose (DCC), alpha-hydroxy sulfonic acid cellulose (HSAC) or taurine

cellulose (TC) that were used on films production. These films exhibited tensile strengths and moduli comparable with those of synthetic polymers and presented higher water vapour barrier properties than cellophane and at the same time a good transparency and flexibility (Fig. 5.2). Another possibility for the production of cellulose-based films is to dissolve cellulose in environmentally friendly solvents. Yang et al. (2011) tested different cellulose sources (cotton linters, microcrystalline cellulose, and softwood bleached Kraft pulp) for different dissolution and regeneration conditions using aqueous alkali (NaOH or LiOH)/urea solutions. Produced films exhibited high oxygen barrier properties, being superior to conventional cellophane, poly(vinylidene chloride), and poly(vinyl alcohol).

Besides using cellulose as main material, it is also possible to add cellulose (after mechanical processing and chemical modification) to other bio-based materials, aiming at obtaining reinforced materials with enhanced properties. Thus, nanofibrillated cellulose (NFC) and cellulose nanocrystal (CNC) (see Chap. 2 and 3 for the main differences between these materials) have been employed to produce films and coatings, and reinforce bio-based polymers such as poly(lactic) acid (PLA) and starch, obtaining packaging materials with multifunctional capabilities (Wang et al. 2010; Cheng et al. 2007; Ganster and Fink 2006; Cabane et al. 2016).

The advantages of using NFC (also called microfibrillated cellulose - MFC) as packaging material have been extensively reviewed in the last years (Lavoine et al. 2012, 2014; Nair et al. 2014; Li et al. 2015; Ferrer et al. 2017), pointing the possibility of using it to produce packaging materials with low oxygen permeability values and high mechanical performance. Bedane et al. (2015) compared the properties of films using different cellulose-based materials and including NFC as one of those materials. TEMPO-oxidation was used for cellulose modification,

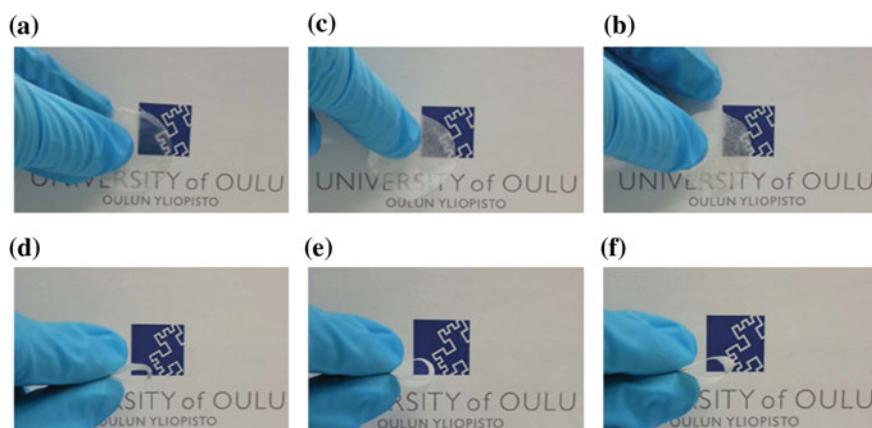


Fig. 5.2 Wood cellulose films demonstrating the transparency **a** dicarboxylic acid cellulose film (DCCF), **b** alpha-hydroxy sulfonic acid cellulose film (HSACF) and **c** taurine cellulose films (TCF); and flexibility of **d** DCCF, **e** HSACF and **f** TCF. Reproduced from Sirvio et al. (2013) with permission of The Royal Society of Chemistry

which was then used for films production. Results showed a decrease in the water sensitivity of the cellulose-based films when NFC and regenerated cellulose were used in comparison with unmodified paper (i.e. bleached Kraft pulp). Saarikoski et al. (2015) studied the possibility of mixing enzymatically treated cellulose with NFC in order to improve the properties of regenerated cellulose films. They showed an improvement in the mechanical properties of the films when NFC is added at concentrations lower than 5.5% (concentrations until 7% of NFC were tested).

One of the methods to produce hydrophobic cellulose-based films made from modified NFC is the simultaneous exfoliation and acylation of NFC. This method takes advantage of the synergistic effect of mechanical and chemical actions generated from ball milling in the presence of hexanoyl chloride. Results showed that it is possible to enhance the tensile strength and elongation at break of the films from 4.98 to 140 MPa and from 4.4 to 21.3%, respectively. Moreover, water resistance, water vapour permeability and optical properties are improved in the modified materials when compared to original NFC-based films (Deng et al. 2016).

As mentioned before, cellulose derivatives such as CMC, HPMC and MC, have also been explored as packaging materials and used as raw materials for the production of edible films and coatings. Nevertheless, their high hydrophilic behaviour led researchers to try to change their water sensitivity through the development of composites with other materials (blend between materials), or also by the incorporation of cellulose-based nanostructures (Tong et al. 2008; Arik Kibar and Us 2013; Quilaqueo Gutiérrez et al. 2012). One example was presented by Bilbao-Sainz et al. (2011), where they showed the effect of different cellulose nanostructures (NFC, NFC oxidized using TEMPO, and CNC) at different concentrations on the properties of HPMC-based films. Results showed that only CNC improved the overall properties, thus leading to an increase in the tensile strength and Young's modulus while enhancing the barrier to water vapour.

Other interesting work was presented by Oinonen et al. (2016), where films based on NFC and galactoglucomannan–lignin (GGM) networks were produced. Different formulations of NFC, GGM and glycerol were tested to produce films by casting. Results showed that it is possible to produce freestanding films with different formulations (Fig. 5.3) and thus, depending on the application, the amounts of reinforcing agent and plasticizer in the film formulation can be adjusted. Other works proposed the incorporation of CNC and NFC in order to improve the properties of chitosan (Abdul Khalil et al. 2016; Corsello et al. 2017) and calcium alginate-based films (Ma et al. 2017).

The incorporation of cellulose-based micro- and nanostructures in packaging materials results in composites with enhanced mechanical properties (tensile modulus, stiffness and strength), thermal stability, water vapour permeability, chemical resistance, surface appearance, and optical properties (as shown in Chap. 3). According to the structure used, i.e. CNC or NFC, the incorporation methodology in bio-based materials can change and different methodologies should be considered (see Chap. 4), e.g. NFC presents tendency to form more viscous suspensions than CNC and on the other hand, CNC showed a tendency to aggregate when mixed with other polymers. Due to these distinct behaviours, several

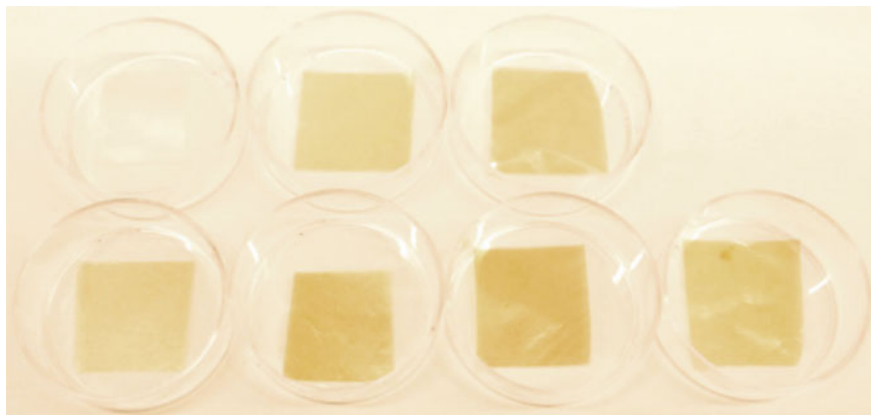


Fig. 5.3 Free-standing films with different formulations of microfibrillated cellulose (MFC), galactoglucomannan–lignin (GGM) and glycerol (G). Samples from left to right, top row: MFC, GGM50/MFC25/G25 and GGM50/MFC50/G0. Samples from left to right, bottom row: GGM50/MFC35/G15, GGM70/MFC15/G15, GGM70/MFC30/G0 and GGM70/MFC5/G25. Reprinted from Oinonen et al. (2016), Copyright (2017), with permission from Elsevier

packaging materials have been tested and evaluated after incorporation of these structures; in the last years, special attention has been given to their incorporation into different bio-based packaging materials.

From the biopolymers obtained from biomass, starch is perhaps the most used. The most known example of the group of bio-based polymers produced by classical chemical synthesis using renewable bio-based monomers is poly(lactic acid) (PLA), a polyester polymerised from lactic acid monomers; and from the ones produced by microorganisms or genetically modified bacteria the most known examples are polyhydroxyalkanoate (PHA) and polyhydroxybutyrate (PHB). In the next section are presented some examples of the use of cellulose and cellulose derivatives in these three biopolymers aiming the development of packaging.

5.2.1.1 Cellulose and Cellulose Derivatives in Poly(Lactic Acid)

Poly(lactic acid) (PLA) is a biodegradable, thermoplastic, and aliphatic (non-aromatic and non-cyclic) polyester, derived from renewable resources including corn starch, wheat, sugar cane, cassava roots or chips (Okano et al. 2010), and other various agricultural wastes (e.g. molasses, whey and green juice) (Garde et al. 2000). PLA is synthesized from lactic acid, obtained by anaerobic fermentation of all these carbohydrate feedstocks. It can be easily produced in a high-molecular-weight form through ring-opening polymerisation of lactide using a catalyst (Mahalik and Nambiar 2010). The properties of PLA are highly correlated to the ratio between the two mesoforms (D or L) of the lactic acid monomer (Farah et al. 2016). When using for example 100% L-PLA, a bio-based material with much high melting point and high crystallinity is obtained. On the other hand, for improving

thermo-mechanical properties (specifically the heat resistance) of the PLA materials, a combination of D- and L-PLA is needed. Other important mixture between copolymers (90/10, % D/L) provides a bio-based material that can be polymerised in the melt, oriented above its T_g , being processed easily, and showing a very high potential of melting, which is required for the packaging production (Farah et al. 2016) during the rigours of blow-forming processes and injection moulding.

Nowadays, PLA is one of the most commonly used bio-based polymers, with a great potential for packaging applications, being at this moment one of the highest consumed bioplastics in the world. The main industrial PLA production companies are Nature Works, invested by Cargill and PTT Global Chemicals, with the announced production of 140 000 metric tons of PLA per year (Berezina and Martelli 2014). Currently, PLA is employed in the production of food packaging, loose-fill packaging, and disposable foodservice tableware items. PLA packaging materials have a high water transmission rate, which makes them at the moment suitable to pack warm bread coming out of the oven and fresh products such as vegetables and fruits.

Recently, films of PLA with glycerol triacetate (GTA) and NFC have been prepared, showing that the incorporation of GTA and NFC resulted in higher values of elongation at break (from 2 to 31%) and toughness (from 1 to 8 MJ/m³). Nevertheless, it was also observed an increase in the degree of crystallinity and a decrease of the optical transparency (Herrera et al. 2015). On the other hand, Meriçer et al. (2016) studied the development of a packaging based on PLA and NFC. They applied thin layers of NFC on different PLA substrates (PLA film surface was activated by atmospheric plasma treatment) producing transparent multilayer composite films with a continuous, dense and defect-free structure. Moreover, the multilayer films presented higher mechanical and barrier properties than neat PLA films, showing the possibility of using this approach in high barrier packaging applications.

5.2.1.2 Cellulose and Cellulose Derivatives in PHA/PHB

Polyhydroxyalkanoates (PHA), of which polyhydroxybutyrate (PHB) is probably the most studied, are linear polyesters produced via fermentation by a large number of bacteria (*Bacillus mesentericus vulgaris*, *Cupriavidus*, and *E. coli* as well as others), which accumulate these compounds as energy and carbon reserves. The microbial growth on agro-industrial by-products and wastes and the consequent accumulation of PHA and PHB in the microbial cells have already been studied in order to enhance the economic efficiency and sustainability of the process (Da Cruz Pradella et al. 2012; Bhattacharyya et al. 2012; Cavalheiro et al. 2012; Koutinas et al. 2014). Although the obtained yields with these residues cannot be compared yet to the PHA and PHB production values when using pure carbon sources, these by-products increasingly gain more interest as they present a wide diversity of carbon sources including glucose, fructose, sucrose, xylose, lactose, glycerol, fatty

acids, amino acids as well as others, which can be used for PHA/PHB production by wild-type, adapted or genetically engineered microorganisms (Koutinas et al. 2014). There are more than 100 different PHA monomers, which can be combined in different ways among themselves in order to produce materials with diverse thermo-mechanical properties. Therefore, the properties of PHA are dependent on their monomer composition, the microorganism used in fermentation, as well as the nature of the carbon source used during the fermentation process (Cutter 2006; Khanna and Srivastava 2005).

Medium-chain length PHA are thermoplastic elastomers with low melting points and tensile strengths and with high elongation to break (400-700%), and a relatively lower crystalline degree when compared to PHB, which is a highly crystalline thermoplastic, brittle and stiff, with high melting points, closed to 160–180 °C (Akaraonye et al. 2010; Khanna and Srivastava 2005). Additionally, PHA and PHB are biodegradable and biocompatible, resulting very suitable for the packaging industry. A very interesting property of PHA is their low water vapour permeability, being close to that of low-density polyethylene (LDPE), which is a petroleum-derived widely used in the packaging industry. PHB has properties closer to those of polypropylene (PP) in relation to melting temperature and mechanical behaviour, but it is stiffer and more brittle than PP (Bucci et al. 2005). Therefore, packaging made from PHB homopolymer offers poor impact resistance, limiting its use in specific packaging applications that require for example a high elongation at break values. In order to improve these characteristics, PHB can suffer morphologic changes or be blend with other bio-based materials (Philip et al. 2007). In this regard, CNC have been combined with polyhydroxyalkanoates (PHAs) and their derivatives, such as polyhydroxybutyrate (PHB), aiming the improvement of their final properties. One of the examples was presented by Malmir et al. (2017) who showed the possibility of improving the barrier properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) adding CNC into their matrix. The films produced by the casting method (up to 4% of concentrations) presented well-dispersed CNC (as showed by transmission electron microscopy), resulting in significant reduction of the matrix porosity and better barrier properties to water vapour and oxygen, with values up to approximately four times lower than neat PHBV. A similar behaviour was reported by other authors, but in this case when 5% of CNC was added to PHBV (Ten et al. 2010).

As explained before (Chap. 2) CNC can be obtained by different hydrolysis methods (e.g. using sulphuric and hydrochloric acids). With the objective of evaluating the influence of two types of CNCs in PHBV properties, CNC obtained by sulphuric acid hydrolysis (CNC-S) and hydrochloric acid hydrolysis under hydrothermal conditions (CNC-H) were used to reinforce PHBV-based films. The higher aspect ratio, crystallinity, and especially the absence of residual acid groups make of CNC-H a more interesting type of CNC to be added to PHBV films. Moreover, with CNC-H a better dispersion was achieved, with larger loading content, when compared with the CNC-S and therefore the films presented better mechanical properties. When compared to neat PHBV, the tensile strength and Young's modulus of the films with 12% of CNC-H were enhanced by 175% and

300%, respectively (Yu et al. 2013). CNC influenced the nucleation process of PHBV-based materials and thus the final crystallization pattern of the packaging material. In fact, it has been proved that CNC has the capacity to accelerate the crystallization process of PHBV and increase the crystallization temperature (Malmir et al. 2017).

Blends of PHB, PLA and CNC were also tested. In this case, modified CNC (using a surfactant) not only showed to increase the crystallinity, but also improved the processability of the polymers, the thermal stability and the interaction between both polymers, showing as well good optical properties (Arrieta et al. 2014a). The same materials were tested regarding their mechanical and barrier properties and showed that the blends of PLA-PHB with modified CNC presented high values of tensile strength and elongation-at-break (Arrieta et al. 2014b).

Nowadays, the limiting factor to using PHB in the packaging production is its high production costs when compared with plastics produced from petrochemicals. However, market expectations remain high for the development of PHB-based materials that have good potential for replacing petroleum-based materials in bottles, bags, textile fibres, and film applications, since it offers extra benefits as its biodegradability and biocompatibility (Puls et al. 2011), being expected that the incorporation of lignocellulosic could decrease price and improve properties.

5.2.1.3 Cellulose and Cellulose Derivatives in Starch

Starch is a polysaccharide widely available in different natural sources such as cereals, legumes, and tubers. This biopolymer is considered a suitable raw material for the production of bio-based packaging because of its enormous functionalities, biodegradability, low cost, and renewability (Rodríguez et al. 2006). As a packaging material, starch is economically competitive with materials derived from petroleum, being used in several commercial compostable plastics (López et al. 2015) and currently dominates the market of bio-based compostable packaging materials. Thermoplastic starch has been used to produce containers, bowls, plates, cups, egg trays and films food wrapping. However, starch-based polymers do not present good mechanical properties due to the brittle nature of starch. Therefore, this biopolymer is often blended with other hydrophilic materials including plasticizers in order to improve the mechanical properties as well as other important characteristics of packaging materials (Xu et al. 2005; Kibar and Us 2013; Ghanbarzadeh et al. 2011). Starch-based packaging materials are usually transparent and translucent (Myllärinen et al. 2002), odourless, tasteless, colourless (Lin and Zhao 2007; Rodríguez et al. 2006). They have low permeability to oxygen at low to intermediate relative humidity (RH) values when compared for example, with the commercial synthetic oxygen barrier material ethylene vinyl alcohol copolymer (EVOH) (Lin and Zhao 2007). However, oxygen permeability may be affected by the hygroscopic nature of other components (e.g. plasticizers) that make part of the matrix (Gaudin et al. 2000; Forssell et al. 2002), indicating if it can be used for liquid and high moisture products.

Usually, starch-based materials are subjected to an extrusion process in order to obtain thermoplastic starch materials. This characteristic is provided by the typical thermal and mechanical energies of the extrusion process, allowing physical and chemical modifications to the material. In the production of thermoplastic starches, plasticizers are expected to reduce the intermolecular hydrogen bonds and provide a better stability to the bio-based packaging material, improving thus their water and oxygen barrier properties. On the other hand, the blending of starch with other more hydrophobic polymers produce formulations that are suitable for injection moulding and blowing films. Nevertheless, compatibility is an issue when these types of blends and laminates are produced, needing the use of compatibilizers and other additives as processing aids (López et al. 2015). As a result, Miranda et al. (2015a) showed both the potential of using CNC and lignin in corn starch-based films. They showed that the presence of lignin and 1% of CNC increased the maximum stress and elastic modulus, as well as decreased the water vapour permeability of the films when compared with the film without lignin and CNC.

5.2.2 Hemicelluloses as Packaging Materials

Hemicelluloses are another relevant source of biopolymers for the development of bio-based packaging. The main hemicelluloses used to produce bio-based packaging are xylans and mannans linked to side chains of other hemicellulose sugars (e.g. galactose, arabinose, and glucose), being recovered in large quantities from agriculture and forestry industries. Xylans and mannans are very attractive due to their film-forming capacity, obtaining films with low permeability to oxygen, and aroma (Dang et al. 2008), and some cases, relatively high tensile strength (Mikkonen and Tenkanen 2012). Additionally, they may act as vehicles for additives, antioxidants and antimicrobials agents, nutrients and flavours.

Hemicellulose bio-based packaging are biodegradable, edible, and suitable materials for contact with food. The mechanical properties, particularly the tensile strength of some xylan- and mannan-based films can be comparable with those reported for other commercial materials currently used as food packaging. However, their elongation at break is much lower and needs to be improved (Mikkonen and Tenkanen 2012).

Although the production of hemicellulose-based packaging obtained from LCMs is still few studied, the development of xylan- and mannan-based packaging have occupied the interest of the industry, revealed by some patents related to this topic (Hansen and Plackett 2008). Xylophane, a Swedish company, proposed a method for the production of flexible films or coatings for packaging based on hemicelluloses combined with a crosslinking or hydrophobized agent (Gatenholm et al. 2008). Later on, the same company presented the possibility of using hemicelluloses and a nanocomposite (phyllosilicate) for the development of a packaging with improved moisture resistance (Gröndahl et al. 2013), which is the major disadvantage of these materials. On the other hand, Höjje et al. (2005) used hemicelluloses with different

MWs extracted from barley husks for the preparation of high oxygen barrier films or coatings. Glucuronoxylan extracted from aspen wood was used for the production of films and the effect of the addition of xylitol and sorbitol on the film-forming capacity of glucuronoxylan, as well as in their mechanical and barrier properties were evaluated. Results showed that films from glucuronoxylan with sorbitol present low oxygen permeability than commercial films from ethylene vinyl alcohol and low-density polyethylene (Gröndahl et al. 2004).

Besides patents, there are other scientific studies on hemicelluloses-based packaging where xylans or mannans can be used as main raw materials for bio-based packaging production or as an additive for the production of a composite. Saxena et al. (2011), for example, studied the barrier properties of films based on xylan reinforced with CNC, acacia bleached Kraft pulp fibres and softwood Kraft fibres. The results showed that xylan films reinforced with 10% of CNC (obtained through sulphuric acid treatment) presented the lower water permeability values among all the composite films studied. In the same way, packaging materials produced from xylan isolated from bleached birch Kraft pulp in combination with reinforcing nanoclays showed to be a promising system to improve the barrier properties related to water vapour and aromatic compounds (Talja and Poppius-Levlin 2011).

Xylans and mannans can also be used in blends with other compounds (e.g. other biopolymers, crosslinking agents, plasticizers, and surfactants) in order to enhance the moisture-barrier properties, strength, stiffness, and flexibility (Mikkonen et al. 2007). As a result, hemicelluloses obtained from wheat straw (WS) and wheat bran (WB) were proposed as bio-based materials for film production through a blend of galactomannan and k-carragennan, and chitosan, respectively (Costa et al. 2015; Ruiz et al. 2013). Using a blend of galactomannan and k-carragennan, results showed that the incorporation of WS hemicellulose extracted by autohydrolysis process can help in decreasing the water vapour permeability and increase the tensile strength values of polysaccharide-based films (Ruiz et al. 2013).

Hemicellulose-based packaging can be employed as edible inner packaging on food that contains low moisture or as inner layers making part of a multilayer film protected from moisture by hydrophobic outer layers. Additionally, they could be used as wrappers, plastic bags, or trays, if they are mixed with other materials (Mikkonen and Tenkanen 2012) but for evaluating the full potential of xylan- and mannan-based packaging films, it is necessary to know their behaviour under other industrial processing technologies, including extrusion and dispersion coating.

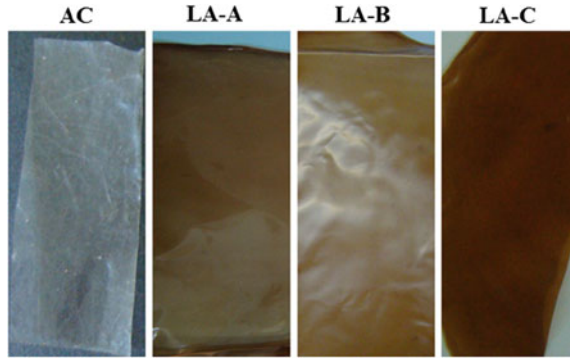
5.2.3 Lignin as Packaging Material

The use of lignins as main materials for packaging production is a hard task due to their unique structure; however, the possibility of using lignin as an additive in packaging materials has been explored since decades (Yoshida et al. 1987; Pouteau

et al. 2004; Wang et al. 1992). The use of lignin in bio-based materials is new, and only in the last 20 years, the effect of lignin on the properties of bio-based packaging materials has been studied in detail. One of the first studies was presented by Baumberger et al. (1997). They produced films by thermal moulding and casting using wheat starch and crude commercial lignosulphonates. Results showed that the incorporation of 10% lignosulphonates decreased the tensile strength and increased the elongation at break of the starch-based films independently of the composition of the lignosulphonates. More recently, the capacity of lignin to be added on starch-based films and the improvement of their mechanical properties have been evaluated. Bhat et al. (2013) produced starch-based films with the incorporation of 3–5% of lignin (obtained from oil palm black liquor waste). Results showed that films produced by casting containing lignin presented better thermo-mechanical and barrier properties than starch-based films without lignin. Films with 5% of lignin presented the best barrier to water vapour and the lowest solubility, presenting higher tensile strength and seal strength. Films with 3% of lignin presented better tensile strength and elongation at break values than films with higher lignin content. Furthermore using starch, Miranda et al. (2015b) evaluated the chemical, mechanical and morphological properties of cassava and corn starch-based films with the incorporation of lignin obtained from Piassava fibre. Films with the incorporation of 4% of lignin showed improved tensile strength and elastic modulus, however with a low elongation at break values. Other polysaccharides with great potential for the production of films aiming packaging applications are alginate and chitosan. Aadil et al. (2016) developed alginate-based films with the incorporation of lignin obtained from *Acacia* (Fig. 5.4). Results showed a good potential of lignin to be mixed with alginate-based films aiming the improvement of alginate-based films properties. Alginate films incorporated with lignin had significantly lower moisture content and water solubility and showed activity against gram-positive bacteria *Staphylococcus aureus*. Crouvisier-Urien et al. (2016) studied the incorporation of lignin in chitosan-based films. They showed that the incorporation of lignin increased the surface hydrophobicity of one side of the films and provided scavenging activity to the films.

The incorporation of lignin was also studied in protein-based films. Protein from vegetal sources such as wheat gluten, soy protein and corn-zein are some examples of the most studied proteins for the production of packaging, being used for the production of thermoplastic polymers (Hernandez-Izquierdo and Krochta 2008). Protein-based materials present excellent barrier properties to oxygen, carbon dioxide, and lipids, particularly at low RH (Gontard and Guilbert 1994). However, like starch- and other polysaccharide-based materials, barrier properties of packaging materials made from proteins are affected by their high water sensibility (Kester and Fennema 1986; Krochta 2002). This can be attributed to the inherent hydrophilicity of proteins and the hydrophilic plasticizers incorporated into the film matrix in order to impart flexibility, extensibility, and viscoelasticity (Sothornvit and Krochta 2001). Thus, covalent cross-linking agents and the incorporation of other materials are strategies often used to improve water resistance, cohesiveness,

Fig. 5.4 Alginate-based films containing different concentrations of lignin (0:100 AC, 10:90 LA-A, 20:80 LA-B, 30:70 LA-C). AC alginate, LA lignin/alginate. Reprinted from Aadil et al. (2016), Copyright (2017), with permission from Elsevier



rigidity, mechanical strength and barrier properties of protein-based packaging (Ustunol 2009).

Using fish gelatin, Núñez-Flores et al. (2012) studied the capacity of ligno-sulphonate (LS) from *Eucalyptus* wood to improve the extremely low water resistance of gelatin-based films. Results showed that gelatin films incorporated with LS, with a mixture ratio of 80:20 (gelatin:LS) or higher, reduced water solubility as well as the elongation-at-break of fish gelatin films and increased the tensile strength of the films. The films with LS showed radical scavenging capacity (DPPH assay) and antimicrobial capacity against the yeast *Debaryomyces hansenii*. In addition, soy protein films were produced and a modified lignin was added aiming improved films properties. Soy protein isolate (SPI) and hydroxypropyl alkaline lignin (HPL) composites have been prepared in an aqueous solution containing glutaraldehyde as the compatibilizer. Then the mixture was subjected to compression-molded to obtain the films. When 6% of HPL was added on SPI films the value of T_g increased from 62.5 to 70.4 °C, and the tensile strength of the SPI/HPL films with 6% HPL and 3.3% glutaraldehyde was enhanced from 8.4 to 23.1 MPa when compared with films without lignin (Chen et al. 2006).

Besides the incorporation of lignin in the polysaccharides- and protein-based films, bio-based polymers such as PLA and PHBV were also tested. Gordobil et al. (2015) showed that it is possible to use lignin as a filler of PLA in order to change their thermal properties. Kraft lignin and acetylated Kraft lignin were used for the production of composites with (PLA) in different concentrations (0.5, 1, 5, 10 and 20%) by extrusion. The addition of both types of lignin increased the thermal stability of PLA and leads to higher values of the surface contact angle of the composites and thus higher hydrophobicity. Regarding mechanical properties, the maximum strength and the elongation-at-break increased with the addition of low contents of Kraft lignin and acetylated Kraft lignin, respectively. Spiridon et al. (2015) also tested two types of lignin (from softwood and hardwood) in the production of PLA-based composites. The addition of lignin to the PLA matrix led to an increase in the impact strength and thermal stability of PLA. The authors applied accelerated weathering (artificial light of a mercury lamp at a temperature of 30 °C and 60% relative humidity during 600 h), and results showed that tensile and

impact strength decreased for all samples, but only slightly for PLA/lignin composites. Domenek et al. (2013) mixed PLA with lignin from gramineous plants and produced films by twin-screw extrusion followed by thermo-compression. A good dispersion of lignin in the matrix was observed as well as an improvement of O₂ permeability. Despite the decrease of mechanical properties of the films, the PLA films with lignin presented antioxidant activity due to the phenolic monomers released from lignin.

Lignin was also tested in the development of PHB-based composites. They retarded crystallization and reduced secondary nucleation, influencing the main properties of PHB (Ghosh et al. 1999). Using PHB as main material and acetylated lignin (lignin obtained from rice husk), Bertini et al. (2012) developed biocomposites by casting using chloroform as a solvent. The presence of acetylated lignin decreased the crystallization rate of PHB and increased the thermal stability of the composites, showing a similar behaviour of that of unmodified lignin. One of the few studies using lignin and PHB for the production of packaging materials was presented by Kovalcik et al. (2015). They produced thermoformed composite films using PHBV and Kraft lignin with increased opacity for higher lignin concentrations (Fig. 5.5). Results showed that the applied Kraft lignin is highly compatible with PHBV, however, gas permeability decreased with the presence of lignin (Kovalcik et al. 2015). One of the key points of using lignin in bio-based packaging materials is their compatibility, highly influenced by lignin source and extraction technology. Nevertheless, the works suggested that the use of lignin and modified lignin with good compatibility can be used as filler in bio-based materials for packaging applications.

5.2.4 Raw or Mildly Pre-treated LCMs as Packaging Material

While for some applications the extraction and purification with mechanical and chemical pre-treatments allow obtaining the lignocellulosic fractions with high purity, other applications include the use of raw lignocellulosic materials or with mild pre-processing. Overall, the incorporation of raw or mildly pre-treated lignocellulosic materials is not advantageous to improve the properties (increase the permeability and decrease the mechanical properties) of bio-based packaging. However, they can be used to decrease the density of final materials (e.g. for lightweight packaging materials). One of the works where the influence of the pre-treatment in the functionality of the lignocellulosic materials was studied was presented by Martelli-Tosi et al. (2017). They pre-treated/bleached soybean straw (SS) with alkali (NaOH 5 and 17.5%) and with hydrogen peroxide (H₂O₂) or sodium hypochlorite (NaOCl) and applied these materials as reinforcing filler in SPI-based films. Films filled with pre-treated SS presented higher mechanical resistance, lower elongation-at-break, and lower solubility in water, while the

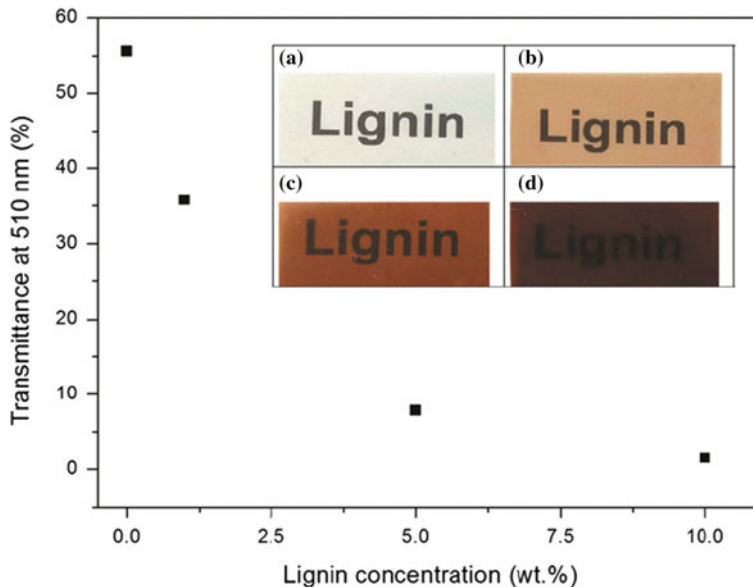


Fig. 5.5 Transmittance and photographs of PHBV films with increasing concentrations of lignin: **a** PHBV, **b** PHBV + 1% lignin, **c** PHBV + 5% lignin, and **d** PHBV + 10% lignin. Reprinted from Kovalcik et al. (2015), Copyright (2017), with permission from Elsevier

addition of non-treated SS did not affect the properties of the soy protein isolate-based films.

Berthet et al. (2015) studied three different agro-residues as fillers in PHBV. Wheat straw, brewing spent grains and olive mills were dry ground and compared regarding their use as fillers in packaging films. Results showed that despite decreasing the main properties of the PHBV films such as mechanical and barrier properties, the wheat straw and olive mills are promising materials to use as fillers in PHBV-based packaging materials in order to be applied in products with high respiration rates. Only a few works studied the use of raw or mildly pre-treated LCMs in bio-based packaging materials, however, this is one of the potentially interesting applications of lignocellulosic materials of low cost in packaging applications.

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Chapter 6

Food Applications of Lignocellulosic-Based Packaging Materials



6.1 General Aspects

Bio-based packaging materials are promising systems for improvement of the quality, shelf-life, safety, and functionality of foods. Nowadays, food packaging industries, which have increased quickly in the last twenty years, look for bio-based sources that can be used to replace or reduce the use of petroleum-based materials in order to guarantee sustainability, protect environment, and at the same time offer to consumers high quality foods with low amounts of chemical preservatives as well as an extended shelf-life. The utilisation of cellulose in the production of cellophane films and paper-based packaging materials is well known. However in the last years several, studies have been focused on the use of other sources of bio-based polymers, including LCMs for production of packaging materials with new characteristics [e.g. Poly(lactic acid)—PLA and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)—PHBV] aiming thus, their application in different food products. Other interesting group of packaging materials are the coatings, where the bio-based materials are applied as solutions directly on foods, forming a thin film around food products, or in a film, imparting additional properties to the packaging materials. Most of the commercial applications of bio-based materials based on LCMs in food packaging are in the form of coatings, being some examples presented below.

6.1.1 Coatings

Coatings made from bio-based sources provide significant advantages when compared to those produced from petroleum-based materials, due to their edible nature and biodegradability. Regulation regarding edible coatings to be applied on foods is defined by two essential elements. Firstly, “edible” implies that the film or coating,

including all of its components, must be safe to eat i.e. that they are generally recognised as safe (GRAS) and thus approved by the pertinent regulatory agencies to be used on foods. Secondly, they must be composed of materials with film-forming capacity, which after applied on a surface are able to form a thin film. Therefore, edible coatings are defined as continuous matrices that can be prepared from bio-polymers such as polysaccharides, proteins, lipids and other important components including surfactants and food-grade plasticizers. These coatings may be made from a unique bio-based material or a mixture of them (Cerqueira et al. 2016). Besides the coatings' composition, the adhesion and cohesion properties (see Chap. 4) and the characteristics of food surface (e.g. polarity), are of extreme importance for the successful use of coatings as packaging material.

Generally, these systems are designed to act as a barrier in order to protect the food against physical and mechanical impacts, chemical reactions and microbiological contamination (Fig. 6.1). Coatings can provide a barrier against moisture, oxygen, carbon dioxide and volatile compounds, which counteracts the weight loss, delays deterioration and prevents the loss of natural aroma of the products and other components (Lin and Zhao 2007). They can be used as potential carriers of additives and bioactive compounds such as anti-browning agents, antimicrobials, flavours, colourants, antibiotics and, antioxidants in order to maintain or even improve the nourishing and sensory features of foods (Cerqueira et al. 2009; Lin and Zhao 2007). Moreover, edible films and coatings are expected to provide a more attractive appearance, improve the food quality and safety, and simultaneously increase shelf-life (Pavlath and Orts 2009; Guilbert and Gontard 1995). Therefore, edible coatings can be important regarding the quality, safety, transportation, storage, and cover a wide range of fresh and processed foods such as meats, nuts, snacks, candies, vegetables and different fruits, among others. Despite being a well-known technology, this is a topic that continues to be of interest to the scientists and to the companies, which is clear from the number of publications and commercial products that appeared in the last 10 years.

Recently, a film made from Indian gooseberry puree, methylcellulose (MC) and Indian gooseberry extract (IGE) was used to produce active coatings to be applied on roasted cashew nut. The coating with 0.5% of IGE showed to be useful against roasted cashew nut deterioration (i.e. low peroxide formation) during storage at

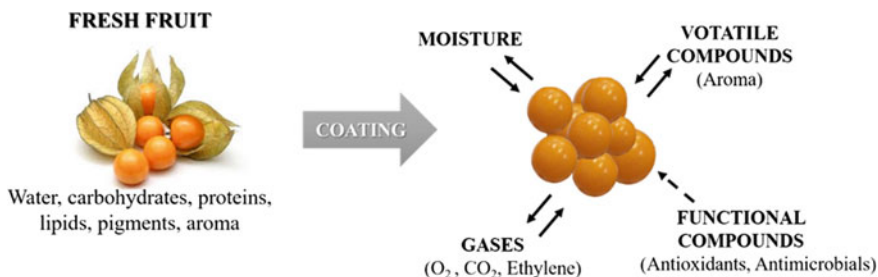


Fig. 6.1 Example of the application of bio-based edible coating on fresh fruits

ambient and accelerated conditions (i.e. 90 and 27 days of storage at 27 and 37 °C, respectively) (Suppakul et al. 2016). Edible coatings also showed the capacity to increase the shelf-life of products under cold storage. A film based on hydroxypropyl methylcellulose (HPMC), beeswax (BW), and food preservatives with antifungal properties (sodium methyl paraben, sodium ethyl paraben and sodium benzoate) was tested on cherry tomatoes during cold storage. Cherry tomatoes were artificially inoculated with *Alternaria alternata* being the shelf-life evaluated after stored at 5 °C for 21 days, followed by 4 days at 20 °C. Results showed that all antifungal coatings reduced the incidence and severity of *Alternaria* black spot on inoculated cherry tomatoes, being the coatings containing sodium benzoate the most effective. Moreover, these coatings were effective in reducing the weight loss and respiration rate, and in maintaining the firmness of cherry tomatoes (Fagundes et al. 2015). Edible coatings have also been used to increase shelf-life of fresh-cut fruits (Dhall 2013). A composite based on a mixture of Cashew gum and carboxymethylcellulose (CMC) was used as an edible coating on cut red guavas. Under the storage conditions (25–28 °C, and relative humidities (RHs) of 76.0 and 12.4%) during 12 days, the weight loss in coated samples was 38.5% lower than that in uncoated samples. At large, all coating formulations reduced water loss and colour changes of cut surfaces (Forato et al. 2015). On the other hand, Noshirvani et al. (2017) reported the use of chitosan, CMC and oleic acid composites as coatings of sliced wheat bread. For the development of an active coating, different amounts of antimicrobial ZnO nanoparticles were added to those coating solutions. Results indicated a decrease of microbial contamination for the coated sliced bread when compared with uncoated ones, and showed that in coatings containing 1 and 2% of ZnO nanoparticles no fungal growth happened during 15 days.

Some applications of commercial and non-commercial edible coatings containing bio-based materials derived from lignocellulosic sources are shown in Table 6.1.

6.1.2 Films

Most of the common applications in food packaging use films or trays as a way to involve/protect foods. While glass, paper and metal dominated the packaging materials at the beginning of the 20th century, plastics, mainly made from petroleum-based materials, reached the top of most commonly used materials at the beginning of the 21st century, mainly due to their versatility, price and lightweight. In the case of lignocellulosic-based materials, cellophane and paper are used in food packaging and are still today the most used materials to pack food products. Recently, new bio-based sources appeared in the food packaging industry showing the possibility of using renewable and biodegradable materials as packaging. Several examples were given (see Chap. 5) regarding the possibility of using LCMs as raw materials for the production of packaging with enhanced physicochemical properties. Nevertheless, only a few works have shown examples of the

Table 6.1 Use of lignocellulosic materials for the packaging production

Composition of bio-based packaging material	Type	Food	Main functions	References
NatureSeal® Ascorbic acid, calcium chloride, and hydroxypropyl methylcellulose	Coating/ Dipping	Fresh-cut fruits and vegetables	<ul style="list-style-type: none"> – Browning inhibition – Maintains taste, texture, and colour 	Natural-Seal (2017)
NatureSeal® Commercial anti-browning solution containing vanillin (derived from lignin materials)	Coating/ Dipping	Fresh-cut apples	<ul style="list-style-type: none"> – Carrier (antimicrobial agent) 	Vasantha Rupasinghe et al. (2006)
Semperfresh™ Sugar esters, vegetable oils, and plant cellulose	Coating/ Dipping Drenching Spraying	Bananas and cherries	<ul style="list-style-type: none"> – O₂, CO₂ and ethylene barrier – Control weight loss – Retains moisture – Maintains the natural colour 	Pace-International (2017)
Pro-long™ Esters of fatty acids, sodium salts of carboxymethyl cellulose and mono- and diglycerides	Coating/ Dipping	Bananas	<ul style="list-style-type: none"> – O₂ and CO₂ barrier – Delays the ripening initiation 	Banks (1983, 1984)
Carboxymethyl cellulose, polysaccharides from spent coffee grounds, plasticizer (glycerol)	Coating/ Spraying	Goldenberry	<ul style="list-style-type: none"> – O₂, CO₂ and ethylene barrier – Delays the microbial growth and weight loss 	Ballesteros (2016)
Xylan, cellulose, and cellulose derivatives	Film	Tortilla chips, dry biscuits, and potato flakes packed	<ul style="list-style-type: none"> – O₂, CO₂ and H₂O barrier 	Peelman et al. (2016)
Starch, plasticizer (glycerol/sorbitol), and microbial agent	Coating/ Dipping	Strawberry	<ul style="list-style-type: none"> – H₂O barrier – Carrier (antimicrobial agent) 	Garcia et al. (1998)
Hydroxypropyl methylcellulose	Coating/ Dipping	Apple	<ul style="list-style-type: none"> – O₂ and CO₂ barrier 	Cisneros-Zevallos and Krochta (2003)
Pea starch-based and grape seed extract (flavonoids and phenolics)	Film	Pork loins	<ul style="list-style-type: none"> – Bacteriostatic effect against meat microbial surface 	Corrales et al. (2009)

(continued)

Table 6.1 (continued)

Composition of bio-based packaging material	Type	Food	Main functions	References
Polysaccharides	Coating/ Dipping	Frozen meat	<ul style="list-style-type: none"> – Prevents moisture loss – Avoids deleterious oxidative changes 	McHugh and Avena-Bustillos (2011)
Methyl cellulose and hydroxypropyl methylcellulose	Film	Marinated whole chicken strips (films applied prior to breading and frying processes)	<ul style="list-style-type: none"> – Prevents moisture loss – Reduces the fat absorption during frying process 	Holownia et al. (2000)
Starch and dextrin	Coating	Nuts, snacks, and cereals	<ul style="list-style-type: none"> – Integrity maintainers, appearance enhancers, and seasoning adhesives 	Krochta et al. (2005)

applications of these bio-based packaging materials (based on lignocellulosic materials) in food products. Table 6.1 presents some examples, and others are discussed in detail below.

Peelman et al. (2014) showed the possibility of using PLA and cellulose-based multilayer package as main materials for modified atmosphere packaging (MAP) for foods. Rumpsteak, ham sausage, filet de saxe, grated cheese and pre-fried fries were MAP-packed at 4 °C. Results showed sufficient gas-barrier to guarantee the shelf-life of MAP-packed food products, even when materials with lower barrier properties were used (i.e. cellulose/starch multilayer). The bio-based materials performed well on the industrial packaging machines; however, the mechanical properties did not allow holding high food amounts. Other work developed an active composite film based on chitosan, CMC and ZnO nanoparticles (ZnO-NPs), which was used in the preservation of soft white cheese. Results showed that the use of the packaging led to an increase of the shelf-life of the white soft cheese at 7 °C during 30 days with the decreasing of the microbial load. In fact, the prepared bio-nanocomposites displayed good antibacterial activity against gram-positive (*Staphylococcus aureus*), gram-negative (*Pseudomonas aeruginosa*, *Escherichia coli*) bacteria and fungi (*Candida albicans*) (Youssef et al. 2016).

One interesting approach is the functionalization of paper-based packaging aiming an improved functionality of the materials. One example was presented by Battisti et al. (2017) that coated raw paper films with biopolymeric solutions based on gelatin cross-linked with transglutaminase enzyme, containing glycerol as the plasticizer, and citric acid as the antimicrobial and antioxidant agent. The application of a coating on paper led to films with lower water vapour permeability values. Those authors used these active films in beef and showed that it is possible to have a lower microbial population at the end of the 4th day of storage, and had greater stability to lipid oxidation during the entire period of storage if the active coating is used. The active paper film held the desirable red colour of the beef and significantly decreased lipid oxidation when compared with beef packaged in the uncoated control paper. The coated paper films also protected the beef against moisture loss during storage.

Several studies showed that it is possible to use lignocellulosic materials in food packaging, however, only paper and cellophane seem to be commercial options at this moment (in the case of films). More studies are needed to show the advantages of using e.g. microfibrillated cellulose films or bio-based packaging with the incorporation of cellulose nanocrystals or lignin in the protection of food products. Possibly the way will be to show their capacities, not only regarding the increase of shelf-life by decreasing gas permeability or applying a modified atmosphere, but also by using other strategies such as the use of active compounds that can be blended in these materials and not in petroleum-based ones.

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Chapter 7

Conclusion and Future Trends



7.1 Conclusion

Materials, such as cellulose at micro- and nano- scales, hemicellulose and lignin from different lignocellulosic sources have attracted a great attention of the scientific community due to their astonishing intrinsic properties. In the last years, their use in the reinforcement of bio-based and other petroleum-based packaging materials have shown to be a good approach to improve mechanical and barrier properties. Besides, the application of lignocellulosic resources in bio-based packaging materials has highlighted their potential use to help improving properties and overcoming some of the challenges of the commercial packaging materials. Their renewable nature, biodegradability and availability are of great importance for the different types of applications. Consequently, these bio-based polymers are rapidly emerging as sustainable alternatives to conventional synthetic and petroleum-based materials, being it highly desired in many diverse areas for high-value applications. These materials could indeed be an answer to society regarding filling some lacks on the most diverse sectors, such as food packaging industry.

However, many obstacles and challenges need to be overcome, including the industrial-scale extraction of purified components from lignocellulosic materials (LCMs) and their utilisation and incorporation in packaging production processes. The high costs of LCMs extraction at a large-scale as well as the variability of the LCMs used (can vary from one plant species to another or even between the same specie since to soil and climate conditions influence their chemical composition) to obtain the purified materials (i.e. cellulose, hemicellulose and lignin) are some of the problems. Other important issues are the environmental and social impacts related to some extraction methodologies and the need of adapting the actual packaging production processes to be used with those materials. Therefore, although many advances have been made in this field, more research efforts are still needed.

The use of bio-based materials in some specific applications where, for example, the edibility or biodegradability is needed, make LCMs an excellent alternative for food applications. It is also expected in the future that lignin and hemicellulose increase their application possibilities, and it is obvious that cellulose derivatives and micro- and nano-structures obtained from cellulose will easily reach the market as indicated by the already existing companies that sell these materials for packaging. Nevertheless, there are still progresses that will need to take place before industrial applications can become practicable.

7.2 Future Trends

It is expected that the use of LCMs will foster the bio-economy by using by-products and residues from agroindustry to create new multifunctional materials and structures for bio-based packaging applications. One of the key points is the extraction/recovery of pure materials. The use of greener technologies for the pre-treatment and recovery of LCMs could solve the issues regarding the chemicals generated and the energy expended during those pre-treatments. One of the examples is the use of eutectic solvents for the extraction and solubilisation of lignin, which can be obtained with very specific characteristics (Alvarez-Vasco et al. 2016).

It is clear that lignocellulosic-based materials could be used in the development of new materials and composites, becoming a great opportunity to reduce the use of petroleum-based materials in packaging production. One of the big challenges of using LCMs in bio-based packaging is their miscibility and compatibility with other materials. Also, the methodology used for processing and production of these bio-based packaging materials is of great importance in order to obtain a final product with the desired properties. In the packaging production process, innovative methodologies (electrohydrodynamic processing and vibration atomization) can be used for a successful functionalization of bio-based packaging properties, as well as an easy processing of lignocellulosic-based materials in packaging (i.e. multilayer, nanofibers) (Cerqueira et al. 2016). Other of the game changers can be the modification and development of new nanostructures using these LCMs. Fibres and particles at nanoscale are being used to reinforce bio-based packaging, showing to be a good approach to overcome the usual limitations of the tensile and barrier properties of bio-based packaging. The nanosize of these materials leads to a large surface area-to-volume ratio that influences their physical and chemical behaviour. Furthermore, the presence of those nanostructures can provide new functionalities to the material, such as hydrophobicity, active properties (including antimicrobial, antioxidant, or UV light absorption capacity), or be used to encapsulate bioactive compounds and add them in packaging materials, envisaging the delivery of active compounds. Several examples are available in the literature where cellulose-based materials were used to encapsulate various active compounds aiming at the development of active packaging (with antioxidant and antimicrobial activities and

barrier to UV) (Gutiérrez et al. 2012; Noronha et al. 2014; Muppalla et al. 2014; Lavoine et al. 2014). Moreover, lignin, which presents antioxidant and antimicrobial capacities, can be used in the development of active packaging, at the same time that the physical properties of them are enhanced (Domenek et al. 2013). Lignocellulosic materials may also be used to develop intelligent packaging materials, e.g. aiming at the detection of physicochemical and microbiological changes in the packaged product (Shukla et al. 2015; Khan et al. 2016). This will help to guarantee the safety of the foods at the moment of their consumption. These new developments aiming at the incorporation of lignocellulosic materials will help to increase the capacity of the packaging industry to produce and supply all the main industries using bio-based packaging.

As a final point, it is important to a company, when considering to replace conventional petroleum-based by bio-based packaging or by petroleum-based packaging incorporating lignocellulosic-based materials, to understand how the properties of these materials will interact and influence the shelf-life of foods. This must be considered together with their possible adverse impacts in all parts of the lifecycle, in order to understand if the selected materials are sustainable and economically affordable.

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