Bio-based Polymers for Sustainable Packaging and Biobarriers: A Critical Review

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Barrier materials have an important role in various packaging applications, especially considering the requirements associated with protection and shelf life. Most barrier materials used in today's industry are either manufactured from oil resources or metals. Driven by the increase in environmental awareness, access to oil resources as well as legislation, new and environmentally benign alternatives are at the center stage of scientific and industrial interest. This article covers the use of wood-derived polymers and those produced from microorganisms, which display remarkable barrier properties. Wood-based products have received great attention for their air/oxygen resistance. As far as their properties, microorganism-derived biopolymers are comparable to conventional oil-based thermoplastics, but their cost may still be an issue. Both, wood and microorganism-derived biopolymers are challenged when moisture, grease and oxygen resistance are simultaneously required. Hence, multilayer structures and composites are needed to fulfill the most demanding requirements of packaging materials. Here we offer a review of these topics together with a discussion of their prospects.

Keywords: Biopolymer; Packaging; Barrier

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INTRODUCTION TO BIOBARRIER MATERIALS

Bio-based and biodegradable packaging materials have gained increased global attention. Among the drivers towards more sustainable packaging materials, the following ones stand out: growing environmental awareness (Andersson 2008; Mousavioun *et al.* 2010; Hermann *et al.* 2011; Philp *et al.* 2013), waste management and landfilling (Andersson 2008; Hermann *et al.* 2011; Johansson *et al.* 2012; Philp *et al.* 2013; Khan *et al.* 2014), resource insufficiency (Andersson 2008; Wu *et al.* 2009; Chung *et al.* 2013), the accumulation of plastics in the ocean (Philp *et al.* 2013), waste legislations, producer and consumer accountability (Andersson 2008), the need to reduce energy consumption (Mousavioun *et al.* 2010), and marketing trends (Weber 2000; Khan *et al.* 2014). In fact, compared to those sourced from fossil carbon, the use of bio-based polymers represents a solution that can effectively benefit from the above pressures, mainly owing to their sustainability, biodegradability, biocompatibility, availability, and non-toxicity (Rastogi and Samyn 2015); in addition, they bring about a possible reduction in overall carbon footprint (Greene 2014).

While the packaging industry is focusing on creating lighter products, to reduce raw material use, transportation costs, and waste volumes (Johansson *et al.* 2012; Vartiainen *et al.* 2014), consumers and producers are focusing on recyclable, environmentally-friendly, and non-fossil-based packaging solutions (Talja *et al.* 2011). As a component of packaging materials, paperboard provides the necessary mechanical strength. However, it needs to be combined with other materials to promote the required barrier performance (Andersson 2008; Rastogi and Samyn 2015). For instance, traditionally, paperboard packaging materials are coated with synthetic polymers that enhance their resistance to water, moisture, grease, oxygen, and odor (Talja *et al.* 2011). In this review, we use the term "biobarriers" to refer to the main components of the system if they are bio-based, either in their pure, blended, or composite forms. So far, fossil-derived synthetic polymers have been the preferred choice, owing to their beneficial properties and the relatively low price (Siracusa *et al.* 2015). In stark contrast to paperboard, however, most petrochemical-based polymers exhibit poor biodegradability and represent a challenge for their disposal and subsequent landfilling (Johansson *et al.* 2012). In 2015, Europeans generated 84.5 million tons of packaging waste, equivalent to 166.3 kg per inhabitant. The share of plastic packaging waste was 19%, resulting in 31.6 kg plastic packaging waste per inhabitant and 15.9 million tons in total. The share of other packaging materials were 41% paper and cardboard, 19% glass, 16% wood, and 5% metal (Eurostat 2015). The food product packaging sector represents a minor share of the total environmental impact of packed food units (Johansson *et al.* 2012; Grönman *et al.* 2013). The adoption of biopolymer alternatives to petroleum-based plastics potentially reduce carbon dioxide emissions by 30% to 70% (Lackner 2015).

The main objective of a package is to protect the product from the surrounding environment and to achieve this result in a sustainable manner (Gröndahl *et al.* 2004; Mikkonen and Tenkanen 2012). Packaging materials should provide mechanical, chemical, and biological protection (Khan *et al.* 2014). A suitable packaging should fulfill performance metrics and should be safe, enable long shelf life, reduce the loss of food (Khan *et al.* 2014; Sand 2016), and make the product more sustainable (Sand 2016). To fulfill these requirements, barrier materials should protect against oxygen, carbon dioxide, moisture (Gröndahl *et al.* 2004; Arora and Padua 2010; Johansson *et al.* 2012; Mikkonen and Tenkanen 2012), aromatic compounds (Arora and Padua 2010; Johansson *et al.* 2012; Mikkonen and Tenkanen 2012), water, micro-organisms (Mikkonen and Tenkanen 2012), and grease (Johansson *et al.* 2012). Some of the main functional properties of packaging materials are included in Fig. 1, relevant to the exposure to given agents. Generally, the most common challenges with biobarriers have been their low resistance to water, gases (Arora and Padua 2010), heat, and mechanical stress (Johansson *et al.* 2012), as well as their relatively high price (Song *et al.* 2009; Philp *et al.* 2013).

In this review, wood- and microbial-derived polymers are considered as biobarrier materials. Wood-based materials are prominent for their high potential and availability (Vaca-Garcia *et al.* 1998; Gandini 2008; Edlund *et al.* 2010). Fermentation-based biodegradable barrier materials, such as polylactide (PLA), poly(butylene succinate) (PBS), and poly(hydroalkanoates) (PHAs), are synthesized from bio-based sources and are available at industrial scales (Fortunati *et al.* 2012; Rabu *et al.* 2013; Bugnicourt *et al.* 2014; Rastogi and Samyn 2015; Siracusa *et al.* 2015). Other options for bio-based barrier materials, which are not considered in this review, are proteins (*e.g.*, whey, soy, gluten, collagen) and polysaccharides such as starch, alginate, and chitosan (Rastogi and Samyn 2015). While biopolymer processing is not covered in this review, we refer to the literature for discussion on the main technologies used to apply barrier coatings and films, including melt extrusion, dispersion, and solvent-based approaches, reported in

(Rastogi and Samyn 2015) and others. We start this review by introducing the terminology around the biobarrier field followed by a discussion on the main biobarriers, their properties, and future prospects.

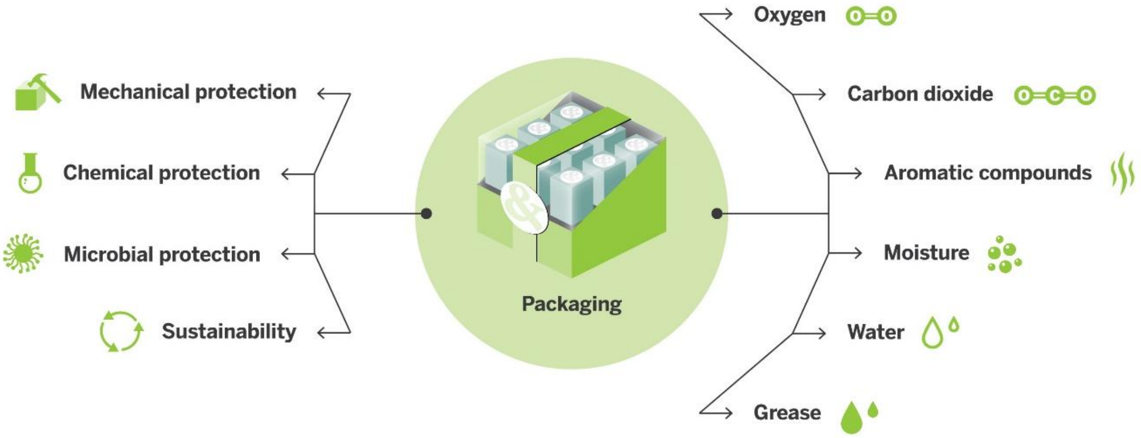

Fig. 1. Some of the desirable properties of packaging materials (left) in contact with different elements (right) and to meet a number of requirements, including cost effectiveness

TERMINOLOGY

Biobarrier terminology is important as far as the polymer composition and associated definitions. For example, not all biopolymers are produced from renewable biomass (Philp *et al.* 2013), not all bio-based polymers are biodegradable, and *vice versa* (Song *et al.* 2009). In this section, we briefly introduce the most relevant terminology.

Biopolymers

Along with the growing interest in biopolymers, their diversity, sources, and properties are ever expanding (Philp *et al.* 2013). Biopolymers can be generally considered to be (a) bio-based and biodegradable, (b) bio-based and non-biodegradable, and (c) petroleum-based and biodegradable (Fig. 2) (Philp *et al.* 2013; Lackner 2015; Rastogi and Samyn 2015). Traditional petroleum-based polymers are generally non-biodegradable, but there are some exceptions such as poly(ε-caprolactone) (PCL), polybutylene adipate terephthalate (PBAT), and poly(butylene succinate) (PBS) (Philp *et al.* 2013).

Bio-based Polymers

Bio-based polymers originate either entirely or partially from renewable biomass resources (CEN 2017; European Commission 2017). Renewable biomass resources include plants, micro-organisms, and animals (Song *et al.* 2009). Bio-based polymers can either be directly derived from renewable biomass resources (*e.g.*, cellulose), produced by chemical synthesis where renewable monomers are used (*e.g.*, PLA), or produced by micro-organisms (*e.g.*, PHAs) (Weber 2000; Weber *et al.* 2002; Shalini and Singh 2009; Rastogi and Samyn 2015).

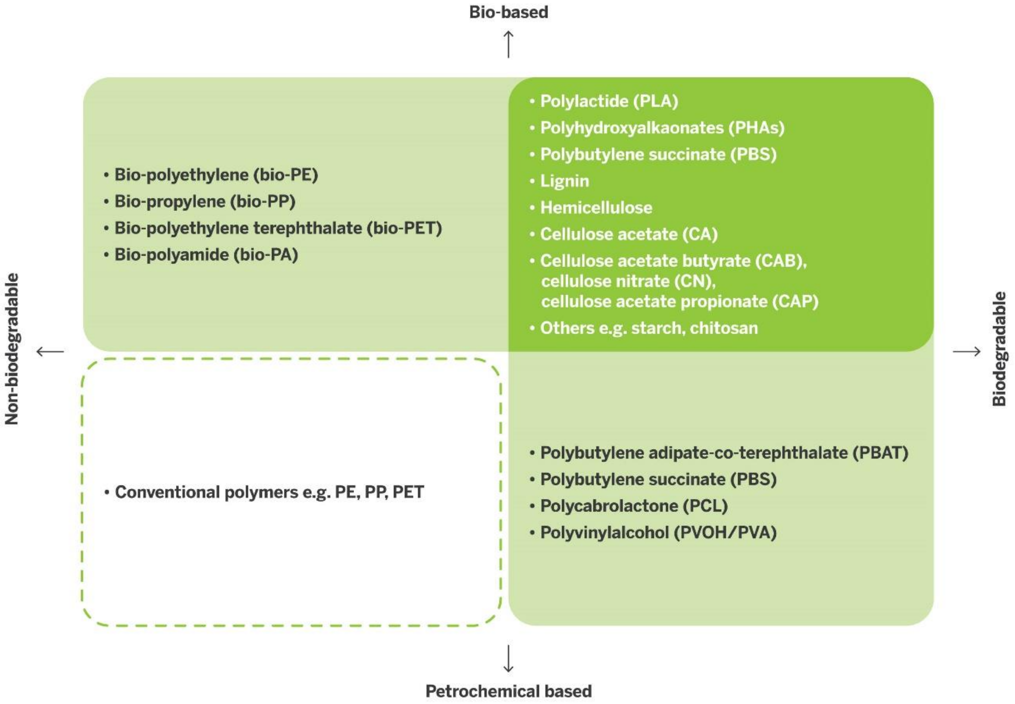

Fig. 2. Polymers and biopolymers shown according to their biodegradability and source (Puls *et al.* 2010; Xu and Guo 2010; Sabiha-Hanim and Siti-Norsafurah 2012; Philp *et al.* 2013; Lackner 2015; Yu *et al.* 2016)

The U.S. Department of Agriculture (USDA) has determined the minimum content of bio-based material for 109 different product categories (USDA 2017a). In the BIOPreferred program (USDA 2017b), the referenced products need to reach the specified minimum limit in order to be certified as bio-based (Greene 2014). Testing is required according to the ASTM D6866 standard (Greene 2014). The minimum relative content of bio-based material for disposable tableware made of or coated with plastic, for example, is 72% (USDA 2017a). Moreover, in addition to the BIOPreferred label, there are several other bio-based labels, such as OK biobased by Vincotte, which relates to the ASTM D6866 testing. In practice, the content of bio-based material can be determined by quantifying ^{14}C content, according to ASTM D6866-05 (2005). This is because fossil-based carbon does not include radiocarbon (^{14}C) due to its half-life of 5,730 years (Kijchavengkul and Auras 2008). There is no comparable ISO-standard test method for determining the content of bio-based materials currently available (Greene 2014).

Biodegradability

There are numerous standards available for biodegradability (Müller 2005; Kale *et al.* 2007; Rudnik 2012; Philp *et al.* 2013) from international (ISO, ASTM, CEN) and national (*e.g.*, DIN) standardization bodies (Rudnik 2012). The European Committee for Standardization (CEN) has determined that biodegradable material degrades into biomass, carbon dioxide, and/or methane, and water under the influence of micro-organism activity (Müller 2005; Hermann *et al.* 2011). Likewise, other definitions are found, *e.g.*, in the European Parliament and Council Directive 94/62/EC; that source states that biodegradable packaging waste is required to undergo physical, chemical, thermal, or biological decomposition, converting the material mainly into carbon dioxide, biomass, and water (Andersson 2008).

Table 1. Biodegradability Standards (Philp *et al.* 2013; Greene 2014)*

Standard	Description	Final Disposal
AS 4736 -2006	Biodegradable plastics – biodegradable plastic suitable for composting and other microbial treatment	Compost
ASTM D5338 -98	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions	Compost
ASTM D6002 -96	Standard guide for assessing the compostability of environmentally degradable plastics	Compost
EN 13432 : 2000	Requirements for packaging recoverable through composting and biodegradation – test scheme and evaluation criteria for the final acceptance of packaging	Compost
ISO 14855: 1999	Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions – method by analysis of evolved carbon dioxide	Compost
ASTM D5988 -03	Standard test method for determining aerobic biodegradation in soil of plastic materials or residual plastic material after composting	Soil
ISO 17556: 2003	Plastics – determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved	Soil
ASTM D6691-01	Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium	Marine
ASTM D6692-01	Standard test method for determining biodegradability of radiolabeled polymeric plastic materials in seawater	Marine
ISO 15314:2004	Methods for marine exposure ISO 16221:2001 Water-quality – guidance for the determination of biodegradability in the marine environment	Marine
ISO 16221: 2001	Water quality — Guidance for determination of biodegradability in the marine environment	Marine
ISO 14851	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by measuring the oxygen demand in a closed respirometer	Marine*
ISO 14852	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium -- Method by analysis of evolved carbon dioxide	Marine*
ASTM D7081	Standard specification for non-floating biodegradable plastics in the marine environment	Marine*

Several publications are available on the topic of biodegradability standards (Müller 2005; Rudnik 2012; Philp *et al.* 2013). Among other issues, these publications describe the complexity of biodegradation process (Müller 2005; Rudnik 2012; Philp *et al.* 2013), including a comparison of different examination methods for polymer biodegradability (Rudnik 2012). Biodegradation tests are recommended to select according to the material's expected application as well as its end-of-life, which can take place in different environments, such as compost, soil, and fresh or marine water (Philp *et al.* 2013). A few general standards related to biodegradation in compost, soil or a marine environment are listed in Table 1.

Oxo-biodegradability often involves the effect of additives, such as metal salts (*e.g.*, manganese, iron, cobalt, nickel) that are added to plastics (*e.g.*, PE) to expedite the otherwise very slow degradation. The outcome of oxo-biodegradation relates to the generation of non-visible, micro-sized plastic and metal particles (Philp *et al.* 2013). Testing of these materials is described in the ASTM D6954-18 (2018) standard. The use of oxo-degradable polymers is banned in Germany (Kosior *et al.* 2006).

A few standards for addressing marine degradation exist. In general, plastics that are degraded in marine environments biodegrade and disintegrate into seawater within a certain period without causing any impact on the surrounding marine organisms. In addition, these plastics are required to pass marine toxicity tests, have a very low heavy metal content, and should be industrially compostable (ASTM D6400-12 2012) (Greene 2014).

Compostability

A compostable material is generally defined as a material that is biodegradable under aerobic conditions and converted into biomass, carbon dioxide, water, and inorganic compounds, in turn, without producing any toxic compounds and disintegrating during the fermentation phase (Mohanty *et al.* 2000; Kale *et al.* 2007; Philp *et al.* 2013). In addition, the compostable material, according to CEN norms, should not cause complications, neither to the composting process, nor to the compost itself (Weber 2000). Compostable polymers are considered as biodegradable, whereas biodegradable polymers are not necessarily compostable, which has higher demands, *e.g.*, of resulting biodegradation products (Weber 2000; Müller 2005; Kale *et al.* 2007), heavy metal content (European standard EN 13432 2000), disintegration within a certain time frame, and the requirement that they do not cause problems during the process of composting (Weber 2000). Philp *et al.* (2013) and Rudnik (2012) have presented multiple standards considering compostability in their publications. Polymers should be tested by relevant ISO, ASTM, and EN standards in order to meet the compostability criteria (Philp *et al.* 2013).

European standard EN 13432 for compostability of packaging is commonly used (Kosior *et al.* 2006; Philp *et al.* 2013). Test methods and certification refers to industrial composting (Kosior *et al.* 2006; Hermann *et al.* 2011). In industrial composting, the temperature (58±2 °C), humidity, composting cycles (3 months thermophilic and 3 months maturation phase), and aeration conditions are carefully controlled. In contrast, home composting conditions vary widely. In the case of home composts, temperatures are lower and may vary considerably throughout the seasons (Kosior *et al.* 2006; Song *et al.* 2009). Moreover, there is no international standard for home compostability (Kosior *et al.* 2006; Endres and Siebert-Raths 2011; Hermann *et al.* 2011), and industrially compostable products (EN 13432) may not perform acceptably in home composts (Song *et al.* 2009; Endres and Siebert-Raths 2011). A certification for home compostable product is available from Vincotte, "OK Compost Home". This certification follows the EN 13432 testing standard, except that the process takes a longer period of time (365 days instead of 180 days) and requires lower temperatures (20 °C to 30 °C instead of 58

°C) (Song *et al.* 2009; Endres and Siebert-Raths 2011; Hermann *et al.* 2011). Industrially compostable certifications, such as Din-Geprüft industrial compostable and OK Compost are following EN 13432 testing (Kale *et al.* 2007; Song *et al.* 2009; Hermann *et al.* 2011). There are also other certifications, *e.g.*, "Compostable", which are based on ASTM D6400-12 (2012) (Kale *et al.* 2007).

Legislation

The safety of packages and packaging materials are secured by a variety of laws and regulations. General product safety directive 2001/95/EC (European Commission 2001), food contact material regulation EC No 1935/2004 (European Commission 2004), the regulation considering manufacturing of food contact materials EC No 2023/2006 (European Commission 2006) (GMP Regulation), and the positive list of substances for plastic packaging materials EC No 10/2011 (European Commission 2011) are a few of the guidelines which food contact materials are required to fulfill (Leminen *et al.* 2013).

In addition, there are regulations and recommendations used globally for food contact materials (Leminen *et al.* 2013). They include those from the U.S. Food and Drug Administration (FDA), the Bundesinstitut für Risikobewertung (BfR) recommendations (Andersson 2008; Leminen *et al.* 2013) and Chinese Standards, *e.g.*, Food-Contact Use Paper, Paperboard and Paper Products GB 4806.8-2016 (2016), and GB 9685-2016 (2016) National Food Safety Standard: Standard for the Use of Additives in Food Contact Materials. Other regulations and national laws need also to be considered (Leminen *et al.* 2013).

The European Commission (May 2018) has published a proposal for a directive of the European Council on the reduction of the impact of certain plastic products on the environment. The goal is to prevent and reduce marine litter from single-use plastics and plastic fishing gear. Some products are being banned from the market, *e.g.*, plastic cutlery, straws, and plates, whereas the use of plastic cups and food containers need to be reduced by the Member States. Among these actions, there are other rules that Member States and their producers must fulfill (European Commission 2018). One example of a national ordinance, which is a driving factor for increasing the use of bio-based polymers, is the French ordinance Décret n° 2016-1170 (2016). It requires all disposable tableware (*e.g.*, cups and plates) to be home-compostable and produced from 50% renewable materials by January 2020. Furthermore, the required renewable content will be raised to 60% by January 2025.

Barrier Materials

In the European Union (EU) legislation for plastic materials, Regulation (EU) No. 10/2011, a functional barrier is defined as a layer that prevents substances from migrating from behind the barrier layer into the food.

To avoid confusion, this review considers the term "matter" to refer to both ideal and non-ideal gases, vapor, or liquid, whereas by "gas" we refer to gases, such as those in the atmosphere. Permeating matter displays two primary ways of transport through film material: either by transmitting through the entire thickness of a solid, homogeneous film, or by transmission through its defects, such as pores or pinholes. As porosity and pinholes resemble an unwanted heterogeneous film structure, this review will focus on the former case. Permeating matter undergoes three physical phenomena referred to as absorption, diffusion, and desorption (Paine and Paine1992; Auvinen and Lahtinen 2008; Nair *et al.* 2014).

Several types of barrier properties are measured to determine the exposure of a package's contents to ambient conditions. The most common barrier measurements include gas transmission such as oxygen, liquid, and vapor transmission, such as water and water vapor, and oil transmission, followed in test conditions typically by castor oil. The properties of the permeating molecule, the properties of the film material, and ambient conditions all influence the barrier properties. For instance, the size and polarity of the molecule, the polarity and crystallinity of the film material, the temperature, and relative humidity conditions influence the amount and rate of permeating matter. In principle, transmission is non-existent when the permeant molecule and the film material are insoluble in each other, and *vice versa*. In this case, the cohesive energy is high between the permeating molecule and film material, whereas a high solubility, in turn, indicates low cohesive energy (Auvinen and Lahtinen 2008).

Inside a polymer film, the molecular motion of permeating gas appears in small scale compared to the free space to another stochastically bouncing molecules. However, in the large scale there is a clear trend of molecular flow, which tends to equalize the difference in chemical potential between the sides of the film material. Thereafter, the large-scale motion of gas molecules from one side of a film material to the opposite side follows Fick's first law of steady state diffusion, as indicated in Eqs. 1 (concentration difference between film edges) and 2 (pressure difference between film edges). In steady state conditions, the absorption of permeating matter into the film from one side is the same amount of matter as its desorption out of the film from the other side, thus resulting in steady diffusion of matter inside the film. Equation 2 is obtained when adding Eq. 3 (Henry's law of solubility) to Eq. 1. Finally, Eq. 4 is a common permeation equation related to the relation of the gas coefficients (Paine and Paine 1992; Auvinen and Lahtinen 2008).

$$J = \frac{D(c_1 - c_0)}{l} \quad (1) \qquad J = \frac{P(p_1 - p_0)}{l} \quad (2) \qquad c = S\,p \quad (3) \qquad P = D\,S \quad (4)$$

In Eq. 4, J is the *steady state diffusion* [work/area], *e.g.*, [J/cm^2], P is the *permeation coefficient* [amount*material thickness/area*time*pressure difference], *e.g.*, [cm^{3}cm/cm^2 s Pa], D is the *dissolution coefficient* [area^2/time unit], *e.g.*, [cm^2/s], S is the *solubility coefficient*, *e.g.*, [cm^3 (STP)/cm^3 polymer], l is the *film thickness*, *e.g.*, [cm], c is the *concentration of dissolved gas*, *e.g.*, mL/L or M, p is the *partial pressure of a gaseous solute, e.g.*, Pa, p_1-p_0 is the *partial pressure difference between the permeating gas on one side and the other side of the film*, and c_1-c_0 is the *concentration difference between the permeating gas on one side and the other side of the film* (Piringer 2000a; Auvinen and Lahtinen 2008).

In steady state, given by Eqs. 1 to 4, the activation energy of diffusion is reached, thus allowing diffusion to occur. Equations 1 to 4 contain dimensionless coefficients, set by P, D, and S. The diffusion coefficient is a measure of the speed by which molecules pass through a given area of the film material, while the solubility coefficient is a measure of the molecules that pass through given area. Basically, the coefficients as such resemble ideal gas behavior, whereas for non-ideal gases, vapors, and liquids, the coefficients are corrected by applying to Eq. 4 the Arrhenius equation of activation energy (Paine and Paine1992; Auvinen and Lahtinen 2008). Moreover, Fick's second law of diffusion is related to unsteady state conditions. Before reaching steady state and constant diffusion, the permeating gas exhibits an unsteady state, accelerating diffusion after reaching the state of its activation energy. The reader is referred to Piringer (2000a,b) and Paine (1992) for more information.

Determining Barrier Properties

Methods such as water contact angle and the Cobb test (see standard ISO 535, 2014) are useful to assess the surface properties and wettability of the substrate onto which a barrier layer is applied. Most relevant, for quantitatively determining the extent of the four types of barrier properties, standardized and non-standardized methods are available. Relations such as Eqs. 1 to 4, are typically based on phenomena described by permeation or transmission and gravimetrical analyses. Several authors, including (Tunç and Duman 2010; Rastogi and Samyn 2015) have used gravimetric techniques to evaluate the water solubility of films, Eq. 5,

$$\text{Water solubility (\%)} = 100\,(W_1 - W_2)/W_1 \qquad (5)$$

where W_1 and W_2 represent the initial and undissolved dry matter weights (g) of films, respectively.

For water vapor permeability, there are both standardized and non-standardized test methods. The water vapor transmission rate (WVTR) represents the mass of water per surface area unit of barrier film, which permeates through the surface within a predetermined time interval and pressure difference, within a constant temperature and constant relative humidity. A typical unit of WVTR is $g{*}m^2{*}day^{-1}$ (Dufresne 2012; Rastogi and Samyn 2015). Han *et al.* (2010) calculated WVTR by combining Henry's Law and Fick's first law by using Eq. 6,

$$\text{WVTR (g/m}^2\text{*24 h)} = w/A \qquad (6)$$

where w represents the increase in weight (g) of the film in the measuring unit after 24 h and A is the area (m^2) of the exposed film. The unit can be also expressed as $cc.m^{-2}.s^{-1}$ (Siracusa *et al.* 2008).

Bilbao-Sainz *et al.* (2010) calculated water vapor permeability (WVP) by a "gravimetric modified cup method", following ASTM E96 (ASTM E96 / E96M-16 2016). They also defined adsorption desorption isotherms of water by using a dynamic vapor sorption analyzer (DVS).

Being the initiator of life on our planet, oxygen is the most bioactive and reactive gas of all atmospheric, gases. Therefore, it is essential to protect a package contents from oxygen to ensure its high quality and to promote a long-lasting shelf-life. For oxygen, there are a few methods of measurement. The most traditional one is the oxygen transmission rate (OTR) by using the MOCON instrument, according to ASTM D3985-17 (2017) standard. In this method, the barrier material is placed between two chambers at ambient atmospheric pressure in dry condition (RH < 1%). One chamber contains nitrogen and the other oxygen. The permeated oxygen is detected by a coulometric detector. The unit of OTR is given as $cc.m^{-2}.s^{-1}$ (Siracusa *et al.* 2008). Once the oxygen transmission rate is determined, the transmission rates of other atmospheric gases can be predicted by knowing the relationship between each other. For example, for nitrogen, the transmission rate is one-third of that of oxygen, while carbon dioxide permeates six times as fast as oxygen (Paine and Paine1992). However, an assigned quantity for carbon dioxide also exists, known as carbon dioxide transmission rate (CO_2TR), expressed as $cc.m^{-2}.s^{-1}$. Similar to WVTR and OTR, one area of importance for CO_2TR is in food packaging (Siracusa *et al.* 2008).

Although more seldomly measured compared to oxygen/air, water, and water vapor permeability, the fat/oil/grease barrier performance is very important in the food packaging industry (Lavoine *et al.* 2012). This is due to an inherently high fat content in many food products (Leminen *et al.* 2015). Moreover, a few different methods of measurement for grease and oil exist. According to Auvinen and Lahtinen (2008), the amount of grease or oil penetration into a film material depends on both internal and external factors. The internal factors govern properties such as the relation of saturated fats to unsaturated fats and the average length of fat chains; the external factors govern the temperature and the relative humidity. Several options for the measurement of oil absorption are available: the COBB-Ungern method (SCAN-P 37:77 1976), the Kit-test (TAPPI Test Method T 559 cm-12 2012), and the ASTM F119-82 (2015) standard test are some of the most commonly applied methods.

Other types of phenomena that need to be minimized in order to protect the package content are worth mentioning. In fact, the barrier film itself is not necessarily inert to the package's contents. Instead, it may release molecular species to the contained product. These can include volatile organic compounds (VOCs), including aromatic compounds, flavors, and fragrances. In EC No 10/2011 of the European Union (EU) legislation for plastic materials, the unit of migration is mg/kg. Here, migration loosely refers to mass transport through the barrier film, which affects food safety and quality, and involves direct contact with the package content and the package layer (Auvinen and Lahtinen 2008). In addition, pathogens, including various microbes and bacteria, such as *Escherichia coli* and *Staphylococcus aureus*, can harm the package content. Finally, given frequencies of light radiation can deteriorate the package content. UV light can cause harm to the package content by inducing oxidative rancidity. Likewise, fat-containing products tend to deteriorate when exposed to sunlight. In commercial packaging materials, a coating of aluminum foil is often used for protection against UV light (Paine and Paine1992; Kirwan 2005; Lavoine *et al.* 2012).

WOOD BASED BARRIERS

Wood consists mainly of cellulose (40% to 50%), hemicellulose (25% to 35%), and lignin (18% to 35%) (Pettersen 1984). These materials can be also isolated from various agro-based feedstocks (Laine *et al.* 2013) and, in fact, cellulose, hemicellulose, and lignin are the most abundant plant-based natural polymers (Klemm *et al.* 2005; Antonsson *et al.* 2008; Albertsson *et al.* 2011). Interesting properties from the barrier point of view have been discussed in several studies. In this section cellulose derivatives, nanocellulose, lignin, and hemicellulose are considered.

Cellulose Derivatives

Before adoption of petroleum-derived plastics, several commercially-produced cellulose plastics (cellulosics, cellulose chemicals, or cellulose derivatives) have been commonly used. From 1960s onwards, the superior performance and low cost of petroleum-derived plastics made them more attractive. Many large volume cellulose derivatives are still used today, in specific applications (Gilbert 2017). Cellulose derivatives are prepared from native cellulose, which is hydrophilic, yet water insoluble. Common cellulose derivatives are soluble in various industrial solvents, and this can be a great advantage for processing and for film development (Rastogi and Samyn 2015). The swelling tendency of cellulose, because of its hydrophilic and hygroscopic nature, limits its film-forming capability while it requires an energy-consuming drying process. The motivation to produce cellulose derivatives is to respond to the limitations of native cellulose (Rastogi and Samyn 2015), while maintaining the bio-based origin and characteristic biodegradability. Cellulose derivatives include cellulose ethers and cellulose esters (Brydson 1999; Kuusipalo *et al.* 2008; Granström 2009). Their preparation can be done by heterogeneous or homogeneous modification (Granström 2009), the former of which generally maintains the fibrous structure while the latter applies to organic solvents for derivatizing the cellulose backbone. There are several variables that affect the properties of cellulose derivatives, out of which the degree of substitution (DS), and the chain length, described by the degree of polymerization (DP) of the anhydroglucose monomers, are quite relevant. The DS relates to the average number of hydroxyl groups substituted per anhydroglucose units. Thus, the higher the DS, the more complete the reaction (Reese 1957). There are several properties that are dependent on the DS. Whereas viscosity indicates the average DP, associated with mechanical and rheological properties, the softness, hardness, and moisture absorption of the material depend strongly on the DS (Gilbert 2017). Moreover, the DS affects the biodegradability of cellulose ethers; a higher DS means a larger number of ether linkages and therefore lower biodegradability (Andersson 2008). Another important parameter is the purity of the cellulose used as raw material, as indicated by the relative mass fraction of pure cellulose (alpha-cellulose) (Burton and Rasch 1931). The more amorphous and the less crystalline the structure, the higher the rate of diffusion, being specific for different reagents (Gilbert 2017). In heterogeneous modification, the DS is significantly dependent on the location of the anhydroglucose unit in the fibrous structure (Thielking and Schmidt 2006; Andersson 2008). For improved results in cellulose modification, both the position of the modified anhydroglucose unit in the chain and in the fibrous structure as well as the positions of the substituents around the anhydroglucose ring and along the chain should be controlled (Fox *et al.* 2011; Gilbert 2017). Uniform distribution of reaction during cellulose structural modification is required for targeting advanced end-use properties. Regioselectivity is facilitated by homogeneous modification and associated solvents, while today’s heterogeneous modification relies on analytical methods and controlling regioselectivity (Fox *et al.* 2011). Cellulose derivatives have been reported to act as suitable matrix materials for cellulose nanocrystals, which in turn improve the water vapor barrier of cellulose derivatives, while acting together as a filler composite (Paunonen 2013).

Cellulose Ethers

The preparation sequence of cellulose ethers consists of an alkalization and an etherification step. The purpose of alkalization is to activate the hydroxyl groups of the cellulose polysaccharides, which yields alkali cellulose. In the subsequent etherification, the alkali concentration of the preceding alkalization step defines the final amount of substituents that shall replace the hydroxyl groups in the backbone of alkali cellulose. Therefore, the alkaline concentration regulates the DS of the polymer (Brydson 1999; Thielking and Schmidt 2006). The cellulose ethers presented in the following section can all be used as barrier materials (Rastogi and Samyn 2015). Except for hydroxypropyl cellulose (HPC), cellulose ethers are non-thermoplastic, which means that they do not provide heat-sealable coatings, although they can be cast as films and are water- and ethanol-soluble. Moreover, they inherently display modest moisture barrier and slow biodegradation, yet they possess a relatively resistance to oil and fat (Andersson 2008). For packaging purposes and compared to cellulose esters, cellulose ethers can be substituted regio-selectively since the substituents, the ethers, are located closer to the main group of the cellulose polysaccharide (Fox *et al.* 2011). However, while comparing with starch, Andersson (2008) concludes that cellulose ethers are expensive to produce in large-scale as coating materials due to their costly derivatization process associated with their recalcitrant crystalline structure.

Methyl cellulose

Methyl cellulose (MC) is a non-thermoplastic, water-soluble cellulose ether (Khan *et al.* 2010) with high oxygen barrier ability. As its hydrophilic nature would suggest, the water vapor barrier performance of MC is modest (Paunonen 2013). Liu *et al.* (2018) improved the water vapor barrier by grafting a coating of polyethylene-reinforced graphene oxide on a MC substrate. Lagarón and Fendler (2009) obtained a high water barrier by combining methyl cellulose with two types of fillers, either montmorillonite (MMT) or mica. A high water barrier by increasing MMT content was also found by Tunç and Duman (2010). MC is used as a viscosity modifier in fields such as food packaging and pharmaceutical industry, where it is applied as an edible film. In addition, MC is used as a thickener, emulsifier, and water-containing substance, and can be applied as a film or coating material (Paunonen 2013). It has been investigated for drug delivery, antimicrobial materials, and regenerative applications (Liu *et al.* 2018). A potential blend of polycaprolactone (PCL) and methyl cellulose (MC) was proposed by Khan *et al.* (2012), which exhibited low water vapor permeability.

Carboxymethylated cellulose

Carboxymethylated cellulose (CMC) is prepared by an alkali-catalyzed reaction aided by chloracetic acid. The CMC is a hydrophilic, non-thermoplastic, water-soluble polymer which displays decent thermal gelatinization. The hydrophilic nature of CMC has been reported to increase along with its DS, which in turn is linked to alkali concentration in the alkalization step used for preparation. Thus, the DS is directly proportional with the WVP, although after a certain alkaline concentration, the DS and WVP reach their maximum and start to decrease. In industry, including papermaking (Paltakari 2009), CMC is used as viscosity modifier, thickener, water-retention agent and as a structural or adhesive component. Likewise, in the packaging field CMC is used for edible films (Paunonen 2013). Mazhari Mousavi *et al.* (2017) coated nanocellulose (e.g. nanofibrillated cellulose, NFC) with CMC as an additive for paperboard. As a result, the barrier properties were improved. The CMC allowed a higher NFC solids content while also reducing NFC flocculation and blocking pores. He *et al.* (2008) demonstrated the procedure of producing CMC from paper sludge as a more cost-effective method than conventional CMC production methods, which utilize cotton linters as precursor material.

Hydroxypropyl cellulose

Hydroxypropyl cellulose (HPC) is a thermoplastic polymer that provides a good water vapor barrier and satisfactory grease resistance (Thielking and Schmidt 2006). It displays a liquid crystalline behavior with cholesteric, nematic, and smectic phases, which affect both its barrier and mechanical properties, the latter of which are strongly dependent on the measured direction (Andersson 2008). Leminen *et al.* (2015) studied HPC-based dispersion barrier coatings on paperboard to improve its oil resistance. He postulates that HPC is the only both edible and film-forming thermoplastic cellulose derivative, which makes it especially interesting for multi-component dispersion coatings. HPC formulates readily as gel because of its low DS and abundant hydroxyl groups that form strong hydrogen bonds. The film-forming properties of HPC are relatively good, yet the resulting oil barrier is sufficient only for fast food packaging. HPC can be used in coatings as a film-forming material, thickener, binder, and as a suspending agent (Andersson 2008). Johnson *et al.* (2008) mixed fillers of cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC) into HPC matrix material.

Hydroxypropyl methyl cellulose

As with most cellulose ethers, hydroxypropyl methyl cellulose (HPMC) is non-thermoplastic, and therefore it cannot form heat-sealable coatings (Paunonen 2013). However, it has been commonly used as barrier material in coatings (Rastogi and Samyn 2015). It displays moderate resistance to fat and oil, yet one of its drawbacks is its poor mechanical film integrity (Bilbao-Sainz *et al.* 2011). Its moisture barrier properties have been reported to improve considerably when introducing fatty acids (Andersson 2008). Coma *et al.* (2001) improved the moisture barrier with fatty acids as well as reduced the resistance of HPMC films against the bacteria *Listeria innocua* and *Staphylococcus aureus*. The etherification step of HPMC consists of methylation, in which pure MC is produced by reacting alkali cellulose with methyl chloride, either in its liquid or gaseous forms. The grades produced in this preparation display a DS between 1.7 and 2.3. Among the several applications, the most popular use of HPMC in industry is as a protective colloid used in the production of vinyl chloride (Thielking and Schmidt 2006). HPMC films are reported for their potential applications in the food industry due to environmental appeals, low price, as well as their flexibility and transparency (Bilbao-Sainz *et al.* 2011). Mahadevajah *et al.* (2016) studied the mechanical and barrier properties of HPMC films by applying various combinations of plasticizers. Larsson *et al.* (2017) applied HPMC at different concentrations in films of cellulose nanofibrils and nanocrystals. However, increasing the content of HPMC did not improve water vapor barrier. Bilbao-Sainz *et al.* (2011) used HPMC as a film matrix for microcrystalline cellulose (MCC), in which MCC improved the moisture barrier compared to a pure HPMC film.

Cellulose Esters

From the advent of petroleum-based plastics around 1950 and until today, the cellulose esters are some of the most applied thermoplastics. In the 1990s there was a large interest in biodegradable cellulose esters (Gilbert 2017). High oxygen barrier properties while applying cellulose ester to fillers have been reported (Dou *et al.* 2013; Uddin *et al.* 2016), yet water vapor barrier properties are limited. Cellulose esters are produced by reacting an organic or inorganic acid substituent with the three hydroxyls of an anhydroglucose unit (Kuusipalo *et al.* 2008). The preparation sequence of cellulose esters is in principle the same as that of cellulose ethers, yet instead of alkalization and etherification it involves acidification and esterification. Similar to alkalization, the purpose of acidification is to activate the hydroxyl groups of the anhydroglucose units. The extent of activation depends on the acid concentration (Granström 2009). In the subsequent esterification step, the substituent is an acid that corresponds to the final cellulose ester (Brydson 1999).

Cellulose acetate

In the preparation of CAs, acetic acid anhydride, together with a catalyst of zinc chloride or sulphuric acid, acts as a reagent to substitute the hydroxyls of the cellulose backbone in esterification (Kuusipalo *et al.* 2008). Found in applications in fields such as molding and extrusion (Gilbert 2017), cellulose acetate (CA) is currently the most commonly applied thermoplastic cellulose derivative. Likewise, many of the applications of CA and its forms are found in the food packaging industry, being used as rigid wrapping films (Paunonen 2013). Cellulose acetate can exist in several forms, some of the most common ones being cellulose acetate butyrate (CAB), cellulose triacetate (CTA), and cellulose acetate propionate (CAP). Out of these forms, CAB displays the lowest water absorption. However, the value is still high compared to its counterparts in today's industry, vinyls, such as polyvinyl chloride (PVC). Several biodegradable CAs have been introduced in the 90s. They were marketed as Bioceta® and Biocellat®, the products of the former including eco-friendly hair brushes, *etc*. Likewise, the blends of CA have been marketed under the name Biodegrade® by FKuR. They are food-contact approved and applicable for injection molding and extrusion (Gilbert 2017). Uddin *et al.* (2016) found promising results as far as high oxygen barrier and interfacial adhesion, while combining CA with graphene oxide in order to produce a CA-based oxygen barrier material for biodegradable packaging applications. Dou *et al.* (2013) reported a drastic improvement in oxygen barrier by combining CA and layered double hydroxide nanoplatelets (LDH), after which thermal annealing treatment was carried out. Moreover, there have been several attempts to apply CAs as antimicrobial films, as well as matrix material for nanocellulose fibers (NCF) motivated by the solubility of CAs to organic solvents (Paunonen 2013). Kabiri and Namazi (2014) reported a maximum decrease of 47% in WVP with 0.8% of graphene oxide (GO) on a matrix of nanocrystalline cellulose acetate, where CA was used to link graphene oxide fillers with cellulose nanocrystals. Likewise, Grunert and Winter (2002) combined trimethylsilylated cellulose nanocrystals from bacterial cellulose (BC) with CAB acting as matrix material.

Cellophane

Cellophane exhibits potential barrier properties (Tome *et al.* 2011). Cellophane, regenerated cellulose in film form, is produced in the viscose process together with rayon fibers (Alén 2011; Paunonen 2013). Tome *et al.* (2011) studied the permeability of atmospheric gases, such as oxygen, and water vapor barrier properties of cellophane by esterifying with fatty acids. As a result, an improvement of 50% in water vapor barrier and 8% in oxygen barrier was reached. These studies encourage further investigation on the barrier properties of cellophane, which is biodegradable and fully suitable in food packaging. However, cellophane use has diminished given the emergence of several other alternatives for packaging. Environmental effects associated with carbon disulfide and other by-products of the viscose process are also important factors; however, cellophane itself is 100% biodegradable, a reason for its popularity as a food wrapping.

Nanocellulose and Nano-lignocellulose

There are several main reasons for the barrier properties of films comprising micro- or nanofibrillar cellulose or nanocrystalline cellulose. The degree of crystallinity, the length-to-width ratio of fibrils, the surface polarity, and the internal cohesion of the fibrillar suspension all play a role (Lagaron *et al.* 2004; Dufresne 2012; Hubbe *et al.* 2017). The uptake of moisture from surroundings is a significant drawback of nanocellulose, while facilitating other superior barrier properties (Lindström and Aulin 2014). As is typical with hydroxyl group-abundant biopolymers, nanocellulose exhibits low water-resistance and high water vapor permeability (Hubbe *et al.* 2017). Principally, crystallinity is beneficial in terms of barrier properties, because it is more difficult for molecules to penetrate the crystalline areas (Siró and Plackett 2010). As such, crystallinity is beneficial in terms of water resistance and water vapor barrier. Moreover, heat treatment improves wet strength, rendering the film denser, possibly due to the aggregation of adjacent cellulose chains, and less porous, which is beneficial in preventing leakage (Österberg *et al.* 2013; Hubbe *et al.* 2017). Sharma *et al.* (2014) showed that when heating films of nanofibrillated cellulose (NFC) for 3 h at 175 °C, the water vapor permeability was reduced by 50% (Nair *et al.* 2014), whereas Xia *et al.* (2018) reported a ten-fold decrease in WVTR while comparing 3 h post-treated TEMPO-oxidized nanofibrillated cellulose (TONFC) films to untreated TONFC films. Likewise, for a treated film OTR values of 0.007 and 0.584 $mL.\mu m.kPa^{-1}m^{-2}day^{-1}$ were measured at room temperature and relative humidity (RH) of 50% and 80%, respectively. The result for RH 80% is 100 times lower than most plastic films, such as PET or PVC. The results are in line with Österberg *et al.* (2013) who indicated OTR values that improved by hot-pressing NFC films. Feng *et al.* (2015) reported variations in the properties of bacterial cellulose (BC), depending on the drying method used. This was highlighted by a water-holding capacity obtained by freeze-drying half that obtained by oven-drying, with values of 6000% and 12,000%, respectively. Likewise, while comparing NFC with CNC, Peng *et al.* (2013) noticed differences in crystallinity and thermal stability from different drying methods. As a result, for NFC, spray-drying displayed the highest combination, in terms of thermal stability and crystallinity, whereas the conclusion was ambiguous for CNC. According to Xia *et al.* (2018), the barrier-enhancing effects of heat on NFC are explained by both increase in crystallinity and reduction in porosity. The increase in crystallinity by heat treatment was also found by Peng *et al.* (2013), who discussed various drying methods for NFC. The higher crystallinity leads to lower oxygen permeability, while water vapor permeability is reduced simply by increased material density.

The larger the length-to-width ratio and the surface area of fibrils, the higher the fibril entanglement and the longer the path for molecules need to travel through the barrier material (Dufresne 2012). The mechanical fibrillation is used to manufacture micro- or nano-fibrils, which influences the barrier properties by affecting fibril dimensions (Kangas 2014). The mechanical fibrillation step involves a few alternative disintegration methods, as presented in Fig. 3. The influence on barrier properties correlate with the reduction of length-to-width ratio and surface area of the fibrils during the mechanical fibrillation (Dufresne 2012; Kangas 2014). As expected, this reduction is greater as the number of steps or passes, is increased (Siró and Plackett 2010). However, mechanical fibrillation also tends to decrease crystallinity (Siró and Plackett 2010), which is a drawback when aiming for superior barrier properties.

Nanocellulose and reinforced composites

Nanocellulose possesses a high capacity for interacting with fillers when blended in a polymer matrix, leading to exceptional mechanical strength. These properties are enhanced by the high aspect ratio of nanofibers, as well as the inherent reactivity of cellulose. Given suitable structural conditions in the blend, one form of interaction of NFC with a filler is by generating a rigid percolation network. The percolation network has been cited in many publications (Dufresne 2013). Moreover, superhydrophobic paper has been topical and with high potential demand (Rastogi and Samyn 2015). Arbatan *et al.* (2012) successfully coated NFC together with precipitated calcium carbonate (PCC) as two separate layers on filter paper while applying the dip-coating method. In addition, they applied alkylene ketene dimer to render the paper superhydrophobic.

Nanocellulose/biopolymer blends

Lindström and Aulin (2014) raised the issue of compatibility between a thermoplastic and non-thermoplastic material, which would need to be tackled prior to industrial-scale implementation. The difficulty of blending nanocellulose with thermoplastic, hydrophobic materials, such as PLA, has been discussed. Attempts to resolve this issue have so far involved the application of surfactants or emulsions. To date, the challenge has not yet been resolved. Nair *et al.* (2018) presented a solution in the form of nanocellulose fibrils with high lignin content (NCFHL), which were wet mixed with PLA. A strong compatibility was found between the fibrils and PLA. In addition, the NCFHL fibrils increased the mechanical, thermal, and water vapor barrier properties. Song *et al.* (2014) applied a blend of nanocellulose fibrils and polylactic acid (NCF/PLA) on paper by a cast-coating process. To disperse it conveniently in the hydrophobic PLA, NCF was rendered hydrophobic by grafting hydrophobic monomers *via* free radical polymerization. Consequently, the WVTR of paper was reduced. We note, however, that to render them hydrophobic or compatible with a hydrophobic matrices, the surface treatment of nanomaterials, such as nanocelluloses, which have a very high area per unit mass, imply a high treatment cost. Jonoobi *et al.* (2010) improved the processability of NFC while blending it with PLA. The improvement was due to the enhanced mechanical and thermal properties. The improvement in storage modulus of the blend was attributed to nanofibers restricting PLA segmental mobility. Espino-Pérez *et al.* (2013) obtained a satisfactory composite, despite some thermal stability issues, by blending cellulose nanocrystals (CNC) with PLA by grafting with n-octadecyl isocyanate. As a result, this hydrophobic, long-chain aliphatic molecule was noted to decrease WVTR, yet OTR remained unchanged.

Nano-lignocellulose

Nano-lignocellulose (NLC) or ligno-nanocellulose, is a form of nanocellulose produced from mechanical pulp, as displayed in Fig. 3. Mechanical pulp typically contains more lignin than chemical fibers. Therefore, the prepared nanocellulose also inherently contains lignin. Due to the presence of lignin, the mechanical properties of NLC are somewhat lower than those of chemical pulp nanocellulose (Osong *et al.* 2014). One benefit of using NLC instead of chemical pulp nanocellulose is the more economical production of mechanical pulp compared to that of chemical pulp (Osong *et al.* 2016). According to Spence *et al.* (2010), the presence of lignin increased water vapor permeability, due to increased porosity that compensates its hydrophobic nature. However, hot-pressing appears to increase material density and thereafter impart an improved oxygen barrier and surface hydrophobicity. Rojo *et al.* (2015) reported a reduction in oxygen permeability and surface wettability due to increase in material density as a consequence of hot-pressing of NLC films. Likewise, while adding lignin, the reduced wettability was found to correlate with a decrease in the dispersive component of NFC surface energy.

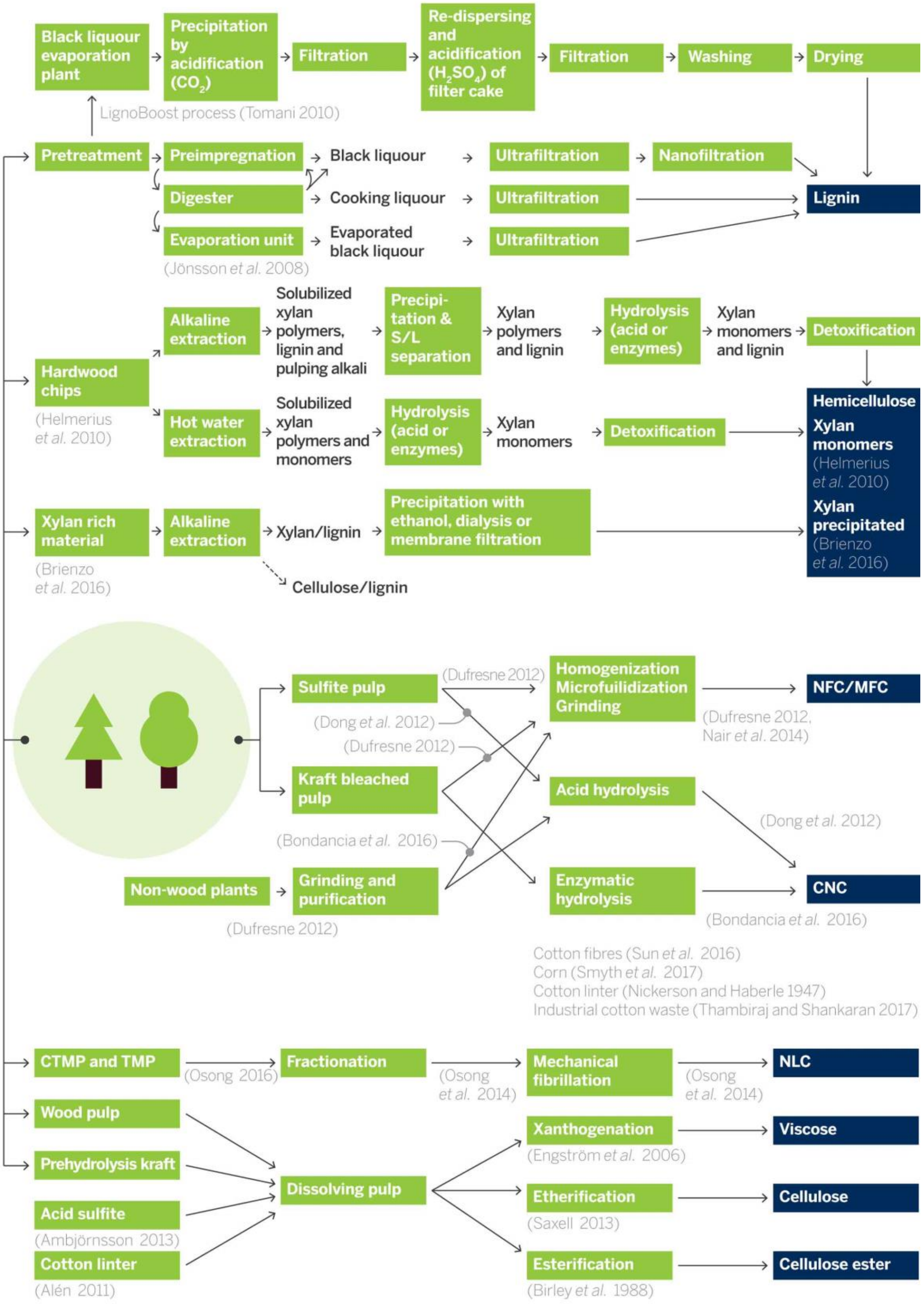

Fig. 3. Schematic illustration of some of the processes and precursors used to produce from wood biopolymers and materials that can be used as biobarriers (see references provided for more details).

Despite the significant growth in the number of publications related to nanocellulose fibrils during the latest decade, it is notable how little emphasis has been given on the upscaling of nanocellulose production and the associated economic aspects. Recently, extensive reviews on these challenges for both cellulose micro- and nanofibrils (De Assis *et al.* 2018) and CNC (de Assis *et al.* 2017) were published. Several technical challenges in the behavior of NFC should be resolved prior to implementing industrial production. Some products are already produced by applying NFC as raw material (De Assis *et al.* 2018). Accordingly, Lindström and Aulin (2014) articulated a few practical challenges that might limit the implementation of nanocellulose in packaging applications. One key challenge is to blend hydrophilic nanocellulose with hydrophobic matrices: until today, most advancements are related to demonstrations of surfactant and emulsion-based systems to improve nanocellulose dispersion in a matrix and achieve improved overall properties. Another key challenge relates to the prevention of unwanted hornification and shrinkage, an issue that has not been fully addressed to date. In terms of conventional pulp, the extent of hornification relates to the content of hemicelluloses (Östlund *et al.* 2010), which suggests that hemicelluloses influence the hornification of NFC. A third key challenge relates to the tendency of nanocellulose to absorb moisture from air, given its hygroscopic nature, which tends to compromise other advantageous properties. This issue can be addressed by applying nanocellulose in the form of dense, layered structures within which a high density of hydrogen bonding and the tight packing reduces related interactions. Likewise, combining nanocellulose with other materials, such as PLA or lignin can reduce its hygroscopic nature. A fourth key challenge relates to the drying of nanocellulose, as it typically exhibits high water-holding capacity and high swelling ability. In addition, one challenge relating to upscaling, also pointed out by Lindström and Aulin (2014) is the inherently high viscosity of NFC, which might affect pumping and transport (Hubbe *et al.* 2017; Kumar 2018). Furthermore, according to Kangas (2014), there are a few more issues related to the industrial implementation of nanocellulose. The possibilities of nanocellulose are indicated by the variety of potential applications, for example, to replace oil-based products in packaging, such as polyethylene and polypropylene (Piringer and Baner 2000), and their ability to add new functionalities, such as electroconductivity and printability (Guo 2017; Kumar 2018). A current drawback is the uncertainty in the costs and production scale. Despite these factors, the interest continues to grow at an accelerated pace (Kangas 2014). Some recent attempts to accelerate the use of nanocelluloses for the manufacture of continuous films include a laboratory-scale coating (Kumar 2018) and a pilot-scale SUTCO machine to produce surface-treated nanocellulose films (Peresin *et al.* 2012), to name only a few.

Hemicelluloses

Hemicelluloses can be found in plant cell walls between cellulose microfibrils. Hemicelluloses have been separated from wood and various agro-based materials (Albertsson *et al.* 2011; Mikkonen and Tenkanen 2012; Laine *et al.* 2013). The content and the composition of hemicelluloses are dependent on the origin and location in the plant (Albertsson *et al.* 2011; Mikkonen and Tenkanen 2012). Depending on the species, wood contains 20 wt% to 30 wt% of hemicelluloses: hardwood contains slightly more hemicelluloses than softwood. The hemicelluloses in hardwood are mainly xylans, while a lesser amount consist of glucomannans. The main hemicelluloses in softwood, on the other hand, are glucomannans, while a considerably lower amount consist of xylans (Jääskeläinen and Sundqvist 2007; Mikkonen and Tenkanen 2012).

In kraft pulping, hemicelluloses are isolated from hardwood chips and from hardwood black liquor (Talja *et al.* 2011). Hemicelluloses can also be isolated as a co-product from several production processes, such as the production of dissolving pulp, nanocrystalline cellulose (CNC), nanofibrillated cellulose (NFC), and sugar for biofuels (Mikkonen *et al.* 2015). Hemicelluloses could be recovered also by filtrating wastewater streams (Edlund *et al.* 2010). However, hemicelluloses are less-commonly used in industrial scale relative to starch and cellulose (Mikkonen and Tenkanen 2012). A couple of examples from hemicellulose isolation processes are presented in Fig. 3.

Hemicelluloses as such are hydrophilic. The hydrophilicity enables good resistance towards oil and grease (Mikkonen and Tenkanen 2012; Laine *et al.* 2013). Challenges in hemicellulose-based films involve their hygroscopicity and mechanical properties (Saadatmand *et al.* 2013; Chen *et al.* 2016). The high internal cohesion leads to the film-forming properties of xylan to be relatively poor (Talja *et al.* 2011; Vartiainen *et al.* 2014). Nevertheless, hemicelluloses are chemically modifiable due to their free hydroxyl groups. Plasticizers are typically used to improve the flexibility of hemicellulose-based films (Hansen and Plackett 2008; Laine *et al.* 2013; Chen *et al.* 2016). Suitable plasticizers for this purpose include xylitol, sorbitol, glycerol (Hansen and Plackett 2008; Vartiainen *et al.* 2014) and bio-based polymers such as carboxymethyl cellulose (CMC), lignin (Chen *et al.* 2016), and alginate (Vartiainen *et al.* 2014).

Hemicellulose-containing pulp has been a preferred conventional practice in the paper industry to provide a higher yield and to enhance mechanical properties. Hemicelluloses have also been utilized in the food industry, *e.g.* as a sweetener, thickener, and an emulsifier (Gröndahl *et al.* 2004). For example, xylan has been used industrially as a raw material for chemicals (Talja *et al.* 2011). Hemicelluloses have a great potential to be utilized also as bio-based barrier coatings: the raw material is easily available, and suitable application methods include air brush, bar, and curtain coaters (Gröndahl and Bindgård 2014). Due to the encouraging oxygen, grease, and taint resistance of hemicellulose-based films, dry food packaging could be a suitable application. Nevertheless, further improvements with respect to the mechanical properties are required in order to utilize hemicellulose-based barrier materials in application fields, such as food packaging. Mikkonen and Tenkanen (2012) have published a comprehensive article on the use of xylan and mannans in food packaging materials.

Researchers have reported promising oxygen barrier properties with hemicellulose-based films (Hansen and Plackett 2008; Edlund *et al.* 2010; Laine *et al.* 2013; Saadatmand *et al.* 2013). Laine *et al.* (2013) achieved a significantly lower oxygen permeability level by using xylan-based barrier material than with a coating of polyethylene terephthalate (PET). In addition, the same xylan-based barrier functioned as a mineral oil barrier. Acetylated galactoglucomannan (AcGGM) has a promising resistance level towards oxygen, yet it is sensitive to moisture. Hartman *et al.* (2006) produced benzyl-galactoglucomannan (BnGGM) films, which were less sensitive to high-moisture conditions than unmodified AcGGM films, consequently maintaining their oxygen barrier properties. Moreover, galactoglucomannan (GGM) has been shown to have a low resistance towards carbon dioxide, which is desirable in some packaging applications (Mikkonen and Tenkanen 2012). However, there is a need to improve GGM's tensile strength and elongation at break properties (Mikkonen *et al.* 2008). There have been studies about the permeability of aroma compounds into different hemicellulose-based films including birch xylan, GGM and konjac glucomannan (KGM), with promising results being achieved (birch xylan coated paper < KGM < GGM) (Mikkonen and Tenkanen 2012).

Hemicellulose/mineral composites

Several studies have been conducted with different hemicellulose composites to obtain enhanced barrier properties (Johansson *et al.* 2012; Mikkonen and Tenkanen 2012). Talja *et al.* (2011) produced glycerol plasticized birch xylan/nanoclay (bentonite) composite coating, which was found to enhance WVTR and aroma barrier properties due to the addition of nanoclay. Nanoclays have the potential to improve barrier properties against gas, water vapor, and aromas due to their feature of making rambling diffusion paths for the molecules. Excellent oxygen barrier performance (< 0.18 cm^{3}µm/m^{2}dkPa) was achieved by using oat spelt arabinoxylan (AX) mixed with sorbitol and 50 wt% cellulose nanocrystals. Spruce galactoglucomannan (GGM) displays resistance towards oxygen, although the oxygen resistance did not improve with the addition of cellulose nanocrystals. The same phenomenon was noticed in water vapor properties. The moisture resistance of oat spelt AX films increased by adding cellulose nanocrystal, whereas the cellulose nanocrystal addition did not improve moisture resistance of GGM-based films. Nanofiller additions have also been studied in the perspective of enhancement of mechanical properties (Mikkonen and Tenkanen 2012).

Hemicellulose/biopolymer blends

The mechanical properties of hemicelluloses depend on the chemical structure, relative humidity, and possible additives, *e.g.*, plasticizers (Mikkonen and Tenkanen 2012). Many studies have investigated the mechanical properties of hemicellulose-based films and their improvement through the addition of another polymer (Mikkonen *et al.* 2008; Mikkonen and Tenkanen 2012), fillers, or by crosslinking.

Mikkonen *et al.* (2015) achieved improved oxygen and water vapor resistance of hydroxypropylated birch xylan (HPX) with an addition of an external plasticizer (sorbitol). Likewise, Gröndahl *et al.* (2004) reported high oxygen barrier properties with aspen glucuronoxylan with 35 wt% of sorbitol. Hemicellulose-based coatings, while blended with a crosslinking agent or a hydrophobizing agent, improved their resistance to oxygen, aroma, and grease in parallel to the improvement of their water vapor resistance. However, due to their hydrophilic nature, hemicellulose-based films are sensitive to changes in RH. An increase in the amount of plasticizer, such as glycerol or sorbitol, reduced the moisture uptake of GGM films at lower RH (Mikkonen and Tenkanen 2012). Crosslinked (5% citric acid) and plasticized HPX films achieved promising grease, mineral oil, oxygen, and water vapor barrier properties. The WVTR was comparable with that of commercial PLA films (Vartiainen *et al.* 2014). A light barrier is an important property in food packaging to maintain the quality of the packaged good. The GGM was found to act as an UV light barrier (Mikkonen and Tenkanen 2012). Improved tensile strength of GGM was achieved by blending with KGM (Mikkonen *et al.* 2008; Mikkonen and Tenkanen 2012).

Lignins

Lignin is an amorphous polyphenolic macromolecule with functional groups (Mousavioun *et al.* 2010; Gordobil *et al.* 2014), including hydroxyl phenylpropane

(Gullichsen 2000). The main precursors of lignin are coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol (Alén 2000; Vanholme *et al.* 2010).

The origin and the type of processing of lignin influence its composition, which can vary considerably among different types of sources (Alén 2000; Domenek *et al.* 2013; Hult *et al.* 2013a; Gordobil *et al.* 2014). Lignins can be found in the cell walls of plants (Gullichsen 2000; Yu *et al.* 2016) and are classified as softwood, hardwood, and grass lignins (Alén 2000). The content of lignin in softwoods is normally higher than in hardwoods. For example, the lignin content of pine (*Pinus sylvestris*) is approximately 25% to 30% (dry weight), whereas in birch (*Betula pendula*) it is 20% to 25% (Jääskeläinen and Sundqvist 2007).

Major quantities of lignin can be obtained as a byproduct of pulp production (Pouteau *et al.* 2004; Gandini 2008), whereas another noteworthy source of lignin is the bioethanol industry (Yu *et al.* 2016). A common extraction method of lignin is precipitation from black liquor by acidification (Jönsson *et al.* 2008). A few examples from lignin production routes can be seen in Fig. 3. Currently, most of the technical lignin from the pulp industry is burnt as fuel in recovery boilers (Pouteau *et al.* 2004; Gandini 2008; Domenek *et. al.* 2013; Hult *et al.* 2013a,b; Gordobil *et al.* 2014). However, there are serval commercial and semi-commercial facilities to produce lignin. Stora Enso, one of the largest kraft lignin producer in the world, has a lignin production of 50,000 tons annually (Upton 2018). The great availability of this complex polymer is one of the main reasons why it is such an interesting raw material (Gandini 2008). In addition, lignin has a great potential for chemical modification into specialty products (Antonsson *et al.* 2008; Hult *et al.* 2013a,b).

Technical lignins are rather dark-colored, while the lignin in the wood is nearly colorless. In some applications, the dark color of lignin needs to be removed. Decolorization methods have been presented, *e.g.*, UV irradiation in a tetrahydrofuran (THF) solution and blocking of the free phenolic hydroxyl groups followed by oxidation (Wang *et al.* 2016).

The formation of films with technical lignins is a great challenge due to its brittleness and rigidity. However, the required thermoplastic properties can be improved by chemical functionalization (Hult *et al.* 2013a,b; Li *et al.*, 2018). Esterification of lignin improved its moisture and oxygen resistance. A piece of paper coated with two layers (3.9 g/m^2 each) of tall oil fatty acid (TOFA) esterified softwood lignin resulted in a 70% reduction in WVTR as well as improvements in OTR (Vartiainen *et al.* 2014). Lignin films and coatings have been fabricated, *e.g.*, with a bar coater (Hult *et al.* 2013a), and solution casting methods (Bhat *et al.* 2013; Shankar *et al.* 2015). Possible application fields for lignin have been presented to include emulsifiers, binding dispersing agents (Jönsson *et al.* 2008; Watkins *et al.* 2015), thermosets, paints, dyes (Watkins *et al.* 2015), wet strength additives (Jönsson *et al.* 2008), chelating agents for heavy metal removal (Toledano *et al.* 2010; Kaewtatip and Thongmee 2013), flame retardant (Kaewtatip and Thongmee 2013), and antioxidants (Kaewtatip and Thongmee 2013; Shankar *et al.* 2015). Lignin and its blends have been reported to provide both gas (Hult *et al.* 2013a,b) and UV light barrier properties, as well as to work as an antimicrobial barrier (Yu *et al.* 2016; Rai *et al.* 2017). Due to these features, lignin-based films have been considered suitable for food packaging applications (Shankar *et al.* 2015; Rai *et al.* 2017).

Lignin/biopolymer blends

In spite of native lignin being generally hydrophobic, its hydrophobic nature is not sufficient to provide paperboard with a hydrophobic barrier (Antonsson *et al.* 2008). However, the derivatives, blends, and composites of lignin have achieved promising results as far as water resistance (Antonsson *et al.* 2008; Spiridon *et al.* 2010; Bhat *et al.* 2013; Hult *et al.* 2013a,b). Furthermore, while examining acetylated lignin blended with PHB, lignin was found to lower the crystallinity of PHB and to enhance its thermal stability in TGA analysis by increasing $T_{5\%}$ 22 °C, $T_{50\%}$ 19 °C, and $T_{\max}$ 17 °C (Bertini *et al.* 2012). In addition, Mousavioun *et al.* (2010) studied PHB/bagasse soda lignin (up to 40 wt%) blends. Soda lignin enhanced the overall thermal stability of the PHB matrix. Kovalcik *et al.* (2015) made films from poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBHV) together with lignin (up to 10 wt%). The addition of lignin enhanced the thermo-oxidation stability as well as oxygen and carbon dioxide resistance of the films. These films were recommended to be used as packaging materials (Kovalcik *et al.* 2015). Shankar *et al.* (2015) studied agar/lignin films where the lignin content was 1wt% to 10wt%. The authors noticed a positive difference in water vapor barrier, UV-light barrier, and mechanical properties compared to the neat agar films. They proposed food packaging film end-use for the agar/lignin films due to their UV-light barrier properties (Shankar *et al.* 2015). Antimicrobial activity against Gram (+)ve and Gram (-)ve bacteria of chitosan/lignin films has also been examined. Clear activity against the bacteria was detected and found suitable for active food packaging applications (Rai *et al.* 2017).

Antioxidants can be used in active packaging and as a product protector against oxygen and gas. In this context, owing to the polyphenolic structure of lignin, its antioxidant behavior has been examined (Gordobil *et al.* 2014; Ye *et al.* 2016). Domenek *et al.* (2013) studied antioxidant activity of two different alkali lignins blended with a PLA matrix. As a result, the oxygen barrier properties were improved while the mechanical properties decreased slightly (Domenek *et al.* 2013). Indeed, some PLA/lignin blends have resulted into decreased mechanical performance, including tensile strength and elongation. Furthermore, Chung *et al.* (2013) enhanced the UV barrier properties of PLA by blending in 10 wt% of synthesized lignin-g-PLA copolymers. Moreover, Gordobil *et al.* (2014) studied two types of lignins at different content blended together with PLA. In the study, commercial alkaline lignin and almond shell extracted lignin were acetylated and compared. Finally, the addition of both lignins enhanced thermal stability, yet the crystallinity of PLA remained unchanged. Both acetylated lignins seemed to inhibit the hydrolytic degradation of PLA. In terms of mechanical properties, the elongation at break was enhanced with the addition of lignins, yet the other mechanical properties did not improve. If the lignin was not acetylated, the mechanical properties decreased (Gordobil *et al.* 2014).

Lignin has been reported to improve thermal stability, tensile strength, and hydrophobicity in starch-lignin blends. However, it has also been reported to impair elongation and transparency (Spiridon *et al.* 2010; Miranda *et al.* 2015). Indeed, lignin has been used as a filler in thermoplastic starch (TPS) blends. It has been reported to enhance mechanical and thermal properties, as well as moisture resistance (Gordobil *et al.* 2014). In addition, lignin has been reported to enhance plasticity in starch/lignin blends, to reinforce cellulose and to work as a compatibilizer in cellulose/starch blends. Bhat *et al.* (2013) improved the properties of starch-based films thought the addition of 1% to 5% lignin. The main improvement was in water and water vapor resistance and in the heat seal-ability of the film. The film was seen suitable for food packaging applications. Wu *et al.* (2009) studied cellulose/starch/lignin films and found that the content of both lignin and cellulose influence the mechanical properties of the film.

Unmodified lignin decreased the mechanical properties when blended together with thermoplastics (Chung *et al.* 2013). More specifically, lignin addition into polyolefins decreased the elongation at break, while had no effect on tensile strength. Blends with more compatible polymers, *e.g.*, polyesters, can result in enhanced strength, stress at yield, and Young's modulus (Pouteau *et al.* 2004). Modifications, such as esterification, etherification, and graft polymerization, enhance several properties of lignin/thermoplastics –dispersions (Chung *et al.* 2013). Likewise, the usage of additives (*e.g.*, plasticizers) have been reported to improve the reinforcing effect of lignin (Pouteau *et al.* 2004).

BARRIERS BASED ON MICROORGANISM-DERIVED BIOPOLYMERS

PLA, PBS, and PHAs are all biodegradable thermoplastic polyesters, and each of them can be produced from biomass-based raw materials by fermentation (Gorrasi *et al.* 2008; Xu and Guo 2010; Bhatia *et al.* 2012; Bugnicourt *et al.* 2014; Harmsen *et al.* 2014). These potential biopolymers ARE bio-based alternatives to petroleum-based thermoplastics (Bhatia *et al.* 2012; Bugnicourt *et al.* 2014; Rastogi and Samyn 2015). All of these biopolymers are found in industrial scale production (Rizzarelli and Carroccio 2009; Rabu *et al.* 2013; Bugnicourt *et al.* 2014). The production routes of these materials are presented in Fig. 4.

Different blends and composites have been studied both in order to improve mechanical, chemical, and thermal properties and to reduce the cost of these polymers (Dufresne *et al.* 2003; Lin *et al.* 2011; Bhatia *et al.* 2012; Gorrasi *et al.* 2014). In the following sections, PLA, PBS, and PHAs are introduced, together with their different blends and composites.

Polylactide

Polylactide (PLA) is a broadly available aliphatic and thermoplastic biopolyester (Liu 2006; Rhim *et al.* 2009; Bugnicourt *et al.* 2014; Rastogi and Samyn 2015) that was commercialized in the early 90s (Tang *et al.* 2012; Rabu *et al.* 2013). PLA is obtained from lactic acid, which is a bacterial fermentation product of starch-rich products, *e.g.*, corn, sugarcane (Yu *et al.* 2006; Gorrasi *et al.* 2008; Rhim *et al.* 2009; Papageorgiou *et al.* 2010; Tang *et al.* 2012; Rabu *et al.* 2013; Reddy *et al.* 2013), sulphite liquors, agro-wastes (Rastogi and Samyn 2015), or food industry wastes (Andersson 2008). It has been reported that with 1.6 kg of sugars, 1.0 kg of PLA can be obtained (Reddy *et al.* 2013). Lactic acid (LA) is the building unit of PLA and it exists as L- and D-lactic acid enantiomers. The most common stereoisomers of PLA are poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA) (Farah *et al.* 2016). The PLA can be produced *via* lactic acid polycondensation or *via* lactide ring-opening polymerization (Rhim *et al.* 2009; Rabu *et al.* 2013). The principles for the production process are presented in Fig. 4. Commercial, high molecular weight PLA is produced *via* the ring-opening method (Andersson 2008; Papageorgiou *et al.* 2010).

PLA is biodegradable yet also compostable and recyclable (Andersson 2008; Picard *et al.* 2011; Golden and Handfield 2014). PLA has good mechanical (Yu *et al.* 2006; Arora and Padua 2010; Papageorgiou *et al.* 2010; Bhatia *et al.* 2012) and moisture barrier properties (Weber *et al.* 2002; Liu 2006; Shalini and Singh 2009), great transparency and printability (Arrieta *et al.* 2014a), and it has shown promising results as a barrier of hydrophobic aroma compounds (Ducruet *et al.* 2011). PLA has great processability (Rhim *et al.* 2009; Arrieta *et al.* 2014a; Golden and Handfield 2014; Rastogi and Samyn 2015) with several techniques, for example by extrusion, thermoforming (Picard *et al.* 2011) and blow molding (Turalija *et al.* 2016); in addition to these applying techniques bar coating and solution casting have been used (Rastogi and Samyn 2015). Commercialized PLA is currently used for several packaging applications (Weber *et al.* 2002) and food service products (Andersson 2008; Fortunati *et al.* 2012; Rabu *et al.* 2013; Reddy *et al.* 2013).

Challenges in PLA utilization include its high brittleness (Harada *et al.* 2007; Andersson 2008; Kuusipalo *et al.* 2008; Rhim *et al.* 2009; Vroman and Tighzert 2009; Ducruet *et al.* 2011; Bhatia *et al.* 2012; Ojijo *et al.* 2012; Tang *et al.* 2012; Chung *et al.* 2013; Gordobil *et al.* 2014), relatively low thermal stability (Yu *et al.* 2006; Rhim *et al.* 2009; Vroman and Tighzert 2009; Fortunati *et al.* 2012; Tang *et al.* 2012; Chung *et al.* 2013; Gordobil *et al.* 2014), poor gas barrier properties (Andersson 2008; Rhim *et al.* 2009; Arora and Padua 2010; Picard *et al.* 2011; Johansson *et al.* 2012; Chung *et al.* 2013; Gordobil *et al.* 2014; Rastogi and Samyn 2015), low resistance against UV light (Chung *et al.* 2013) and, relatively high cost (Arora and Padua 2010; Papageorgiou *et al.* 2010; Bhatia *et al.* 2012; Chung *et al.* 2013; Golden and Handfield 2014; Gordobil *et al.* 2014; Gorrasi *et al.* 2014). In addition, the degradation rate of PLA is rather slow (Golden and Handfield 2014; Farah *et al.* 2016; Turalija *et al.* 2016) and reactive side-chain groups are desirable for this purpose (Golden and Handfield 2014; Farah *et al.* 2016).

In order to improve properties or to lower the price of the product, efforts have been made by blending and developing composites with other polymers and fillers (Bhatia *et al.* 2012) as well as other additives, such as thermal stabilizers and plasticizers (Gorrasi *et al.* 2014). For example, the brittleness of PLA has been addressed by plasticization, blending with tough polymers, and rubber toughening (Nampoothiri *et al.* 2010). Plasticization with 10-20 wt% ester-like plasticizers, such as poly(ethylene glycol, PEG), is effective but lowers the stiffness. When added up to 10 wt%, impact modifiers, such as ethylene-based copolymers, reduce the brittleness and maintain acceptable levels of stiffness. The main disadvantage has been their non-biodegradability, which have limited their use in large volumes. Biodegradable options for impact modifiers of PLA have been introduced, including poly(ε-caprolactone, PCL), poly(-butylene succinate, PBS) and poly(-R-3-hydroxybutyrate, PHB). The amount required to reach acceptable toughness has been reported to be 20 to 40wt% (Notta-Cuvier *et al.* 2014). The PLA based coatings are widely used in food-packaging where food safety is the major driver, for example, the migration of additives and toxicological properties of the blend need to be checked (Johansson *et al.* 2012).

PLA/filler composites

Many studies have involved layered silicates and reported to improve gas barrier properties by 50% to 60% (23 °C, RH 50%). However, for products with a high barrier demand, the improvement is not enough (Johansson *et al.* 2012). Several other filler options have been studied in addition to layered silicates, such as metal oxides (*e.g.*, TiO_2, ZnO), carbon nanotubes, and metal nanoparticles (*e.g.*, Ag, Au) to achieve improvements, for instance, in mechanical, thermal, gas barrier, antibacterial, and UV barrier properties (Papageorgiou *et al.* 2010; Gorrasi *et al.* 2014).

Several researchers have reported improvements in barrier and mechanical properties of biodegradable materials by 1.0 wt% to 5 wt%, by adding montmorillonite (MMT) (Sanchez-Garcia and Lagaron 2010). Picard *et al.* (2011) mixed PLA together with 4 wt% organically modified montmorillonite (OMMT), subsequently achieving enhance gas barrier properties. Ojijo *et al.* (2012) studied the blend of (PLA/PBSA)-organically modified clay composite. The ratio of polymers was kept constant at 70:30 (PLA/PBSA), while organically modified clay content was varied between zero wt% and 9 wt%. As a result, an improvement of 29% in elongation was obtained by a blend of PLA/PBSA/2 wt% organically modified clay compared to plain PLA. Moreover, other mechanical properties were also good in the blend, and reduction in thermal stability was only moderate (Ojijo *et al.* 2012). Rhim *et al.* (2009) investigated how different nanoclay types and concentrations in PLA films influence the mechanical, barrier, and antimicrobial properties of the film. The behavior varied among the types of nanoclays and concentrations. Promising improvement against water vapor (6% to 33% decrease) was noticed with organically modified clay. However, tensile strength and elongation decreased due to the filler addition (Rhim *et al.* 2009). While blending 5 wt% of organo-modified mica-based clay grade with PLA, Sanchez-Garcia and Lagaron (2010) achieved 54% lower water permeability, 55% lower oxygen permeability, a 75% decrease in UV light transmission (wavelength 250 nm), and a 32% reduction in visible light transmission (wavelength 650 nm) than with neat PLA. Gorassi *et al.* (2014) obtained upgraded water vapor barrier properties by mixing 6 wt% and 12 wt% of silane-treated halloysite nanotubes (HNT) with PLA matrix. Filler content was the main factor influencing the barrier properties. One filler option is the main byproduct, gypsum, from the PLA production. Gypsum is a calcium sulfate and can improve the mechanical properties of PLA. Furthermore, the filler size and content had the biggest influence on the water vapor resistance of a PLA/calcium sulfite hemihydrate biocomposite (Gorrasi *et al.* 2008). A good compatibility between PLA and modified kaolinite have been achieved, which resulted in improved oxygen resistance (50%) (Arora and Padua 2010). Due to the addition of nanoclays, PLA/nanoclay and PLA/PCL/nanoclay films have been reported to have improved oxygen and water vapor barrier properties (Andersson 2008).

Fortunati *et al.* (2012) achieved a 34% improvement in water vapor barrier properties with PLA matrix together with 1 wt% surfactant modified cellulose nanocrystals (s-CNC). In addition, they obtained good gas barrier properties and low overall migration levels in solvent casted PLA/s-CNC and PLA/unmodified cellulose nanocrystal (pristine, CNC) biocomposite films. Active food packaging materials from PLA, together with 1.0 wt% CNC and 1.0 wt% silver (Ag) nanoparticles, indicated a 46% reduction in the oxygen transmission rate. Similar improvement was obtained with a biocomposite of PLA/5wt% CNC/1wt% Ag. Fortunati *et al.* (2013) have reached acceptable levels in overall migration with PLA-based CNC/Ag-biocomposites, but they noticed that silver was easily released from them. By applying alcohols, Turalija *et al.* (2016) modified PLA surface properties to make it more hydrophilic and antimicrobial. Glycerol and polyethylene glycerol, chitosan, and silver nanoparticles were also considered. Enhancement in hydrophilicity with alcohols and chitosan decreased the water contact angle from 70° to 40-45°. Silver was applied on PLA-based films by plasma deposition. Turalija *et al.* (2016) noticed increased hydrophilicity and a noteworthy enhancement in the antimicrobial properties of PLA-based films with silver.

PLA/30 wt% flax fiber composites with different additives, *e.g.*, kraft lignin, have also been studied. Good impact strength was achieved with (NaOH-treated) flax fiber addition, further enhanced with < 3wt% addition of pine kraft lignin (however, higher addition levels weakened the mechanical properties of the composite) (Johansson *et al.* 2012).

PLA/ biopolymer blends

PLA's crystallinity was increased by mixing 25 wt% of poly(hydroxybutyrate) (PHB) and 5 wt% CNC. In addition, PHB enhanced the oxygen and water barrier properties, although it simultaneously impaired the transparency of PLA (Arrieta *et al.* 2014a).

PLA/starch blends have been a topic of study (Yu *et al.* 2006; Johansson *et al.* 2012; Tang *et al.* 2012). Starch is a renewable and biodegradable hydrophilic polymer, which has been a common material in bioplastics (Yu *et al.* 2006). In order to reduce price and to enhance biodegradability, the aim has been to blend PLA together with starch (Johansson *et al.* 2012; Tang *et al.* 2012). Several studies have been carried out with different starches and additives, such as native corn starch together with a plasticizer, corn starch *vs.* high-amylose corn starch and gelatinized starch with water/glycerol (Tang *et al.* 2012). About 30 wt% to 50 wt% starch has been blended with PLA, subsequently causing a reduction in mechanical properties, such as in tensile strength and strain at break (Johansson *et al.* 2012). The crystallization rate of PLA has been increased with talc (1 volume %) and with starch (1.0 to 40% volume) addition. However, there are challenges involving the hydrophobic nature of PLA and the hydrophilic nature of starch, thus causing weak cohesion to each other and resulting in poor properties without additives or compatibilizers (Yu *et al.* 2006).

Blending of enantiomeric polymers was reported to enhance thermal properties. Blending poly(L-lactide acid) (PLLA) together with poly(D-lactide acid) (PDLA) improved thermal stability compared to PLLA or PDLA alone. They achieved a 50 °C higher melting temperature by making the blend of PLLA/PDLA (Yu *et al.* 2006). The L and D isomers also have an effect on the crystallinity and mechanical properties of the polymer. High crystallinity can be achieved with L-form and amorphousness with copolymers of D and L isomers (Andersson 2008).

PLA has been blended and copolymerized with biodegradable poly(caprolactone) (PCL) to decrease brittleness and improve the mechanical properties (Tang *et al.* 2012), such as impact strength. The PLA-based urethane blend was reported to increase impact strength when used as an additive. In comparison, PLA/ poly(butylene adipate-co-terephthalate) (PBAT) enhanced impact strength when the concentration on PBAT was 20 wt%. Harada *et al.* (2007) mixed PLA with PBS (90/10 wt%) by using a reactive processing agent, lysine triisocyanate (LTI). As a result, the impact strength was enhanced, from 18 kJ/m^2 to 50-70 kJ/m^2 at a LTI loading of 0.5 wt% (Harada *et al.* 2007).

Poly(butylene succinate)

Poly(butylene succinate) (PBS) is one of the most promising environmental-friendly aliphatic polyesters, which offers a great alternative for common polyolefins (Bhatia *et al.* 2012; Phua *et al.* 2012; Wang *et al.* 2013; Charlon *et al.* 2015). PBS was developed in Japan in the early 1990´s by Showa Polymer (Vroman and Tighzert 2009; Phua *et al.* 2012). The PBS is commonly produced from succinic acid and 1,4-butanediol

(BDO) (Xu and Guo 2010; Bhatia *et al.* 2012). PBS can be manufactured fully or partially from renewable resources (Xu and Guo 2010), even though currently it is polymerized partially fossil based monomers in the industrial scale (Yim *et al.* 2011). The major steps for PBS production are included in Fig. 4. Renewable succinic acid is manufactured by bacterial fermentation. Possible raw materials include, for example starch, glucose, xylose (Xu and Guo 2010), or agricultural waste (McKinlay *et al.* 2007). By similar means, renewable BDO can be produced *via* the fermentation of sugars (Harmsen *et al.* 2014). Currently, the prevalent production method of BDO is still from oil-based feedstocks (Yim *et al.* 2011).

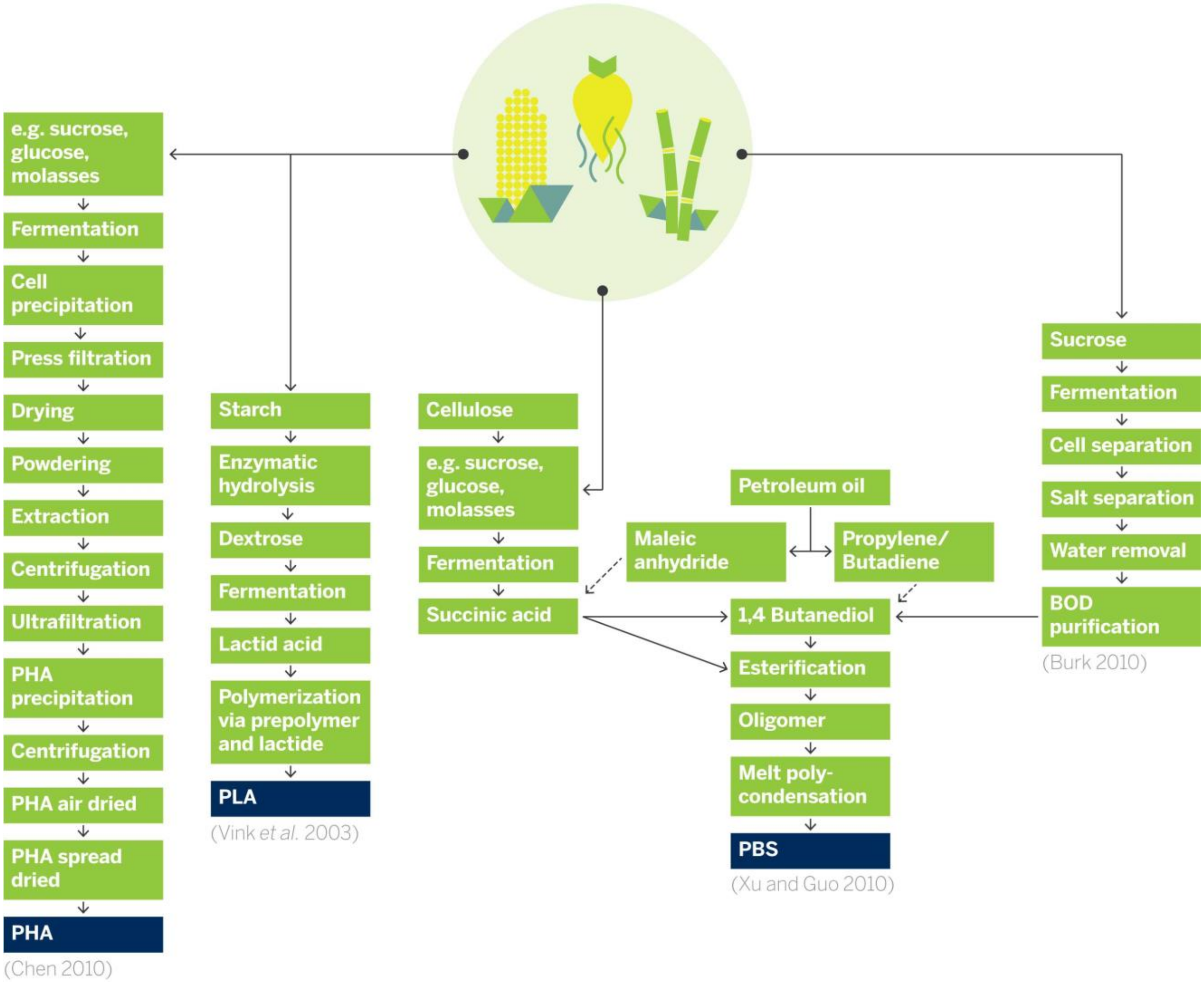

Fig. 4. Block diagram to illustrate the production of biobarriers from biomass fermentation (see Burk 2010; Chen 2010; Xu and Guo 2010)

The PBS exhibits good mechanical strength, great processability with traditional polyolefin processing equipment (Wang *et al.* 2013), high elasticity and a reasonably high thermal and chemical resistance (Lin *et al.* 2011; Bhatia *et al.* 2012; Phua *et al.* 2012). In addition to biodegradability in soil and aquatic environments, PBS is also compostable (Nam *et al.* 2011). Kanemura *et al.* (2012) observed that both the recycling of PBS is possible as well as the mechanical properties of PBS improve after reprocessing. A typical way to produce PBS film and coating is by melt extrusion casting (Wang *et al.* 2013).

It might occur that, for high barrier demand products, the soft PBS material is not effective enough (Lin *et al.* 2011; Phua *et al.* 2012; Charlon *et al.* 2015). Moreover, the gas barrier properties of PBS are barely sufficient for gas sensitive products (Lin *et al.* 2011; Phua *et al.* 2012; Zhou *et al.* 2016). Melt viscosity and a relatively high price are also limiting the use of PBS (Lin *et al.* 2011). Furthermore, PBS has been studied as component in composites or blends, for example, to improve gas barrier (Bhatia *et al.* 2012; Boonprasith *et al.* 2013; Charlon *et al.* 2015; Zhou *et al.* 2016), mechanical, and thermal properties (Lin *et al.* 2011).

PBS/filler composites

PLA/PBS/nanoclay is a good example of related composites, where a lower oxygen permeability level is obtained through the addition of the clay. PBS (20 wt%) was found to increase the water vapor permeability (WVP) of PLA (80 wt%). Thus, the addition of nanoclay offered an 18% improvement in WVP (Bhatia *et al.* 2012). PBS/thermoplastic starch (TPS) blend with added nanoclays decreased the OTR and WVTR values significantly (Boonprasith *et al.* 2013). The improvement of gas barrier by adding clays or nanoclays relates to the tortuous path the gas molecules need to travel through the barrier (Zhou *et al.* 2016).

Lin *et al.* (2011) blended 2 wt% and 5 wt% of cellulose nanocrystals (CNC) and starch nanocrystals (SN) separately with PBS. They improve the strength and elongation properties of the PBS matrices by both fillers. PBS/2 wt% CNC enhanced tensile strength by 11% and elongation by 17%, while PBS/5 wt% SN enhanced tensile strength by 8% and elongation by 28% (Lin *et al.* 2011). Someya *et al.* (2004) investigated different types of organo-modified montmorillonites blended with PBS. They found out that organo-modified montmorillonites promoted crystallization of PBS and therefore acted as nucleating agent. The addition of 3 wt% organo-modified montmorillonites resulted greater tensile and flexural modulus and weaker the tensile strength with most of the clay-types (Someya *et al.* 2004).

Moreover, PBS has been blended with agro-fillers, such as wood and rice husk flour, wheat straw, and bagasse. Kim *et al.* (2005) studied the PBS/agro-filler blends in filler concentrations of 10, 20, 30, and 40 wt%, by preparing a blend of PBS/rice husk flour and PBS/wood flour. As a conclusion, the mechanical properties deteriorated when filler content was increased, whereas the reduction of filler particle size caused the tensile strength properties to increase moderately. Moreover, the tensile strength of the wood flour filled blend was higher than in the rice husk flour filled blend. Liu *et al.* (2009) studied the biodegradability of PBS/jute fiber composites. The composites containing 10, 20, and 30 wt% of jute fibers degraded faster than the plain PBS film or the plain jute fiber. The most significant weight loss (62.5% in 180 days) in a compost soil burial test was performed by the PBS/10 wt% jute fiber composite (Liu *et al.* 2009). Nam *et al.* (2011) studied PBS/alkali-treated coir fiber composites with a coir fiber concentration of 10 wt% to 30 wt%. As a result, they found the highest improvement in mechanical properties with an alkali-treated coir fiber concentration of 25 wt%. In the particular composite, the tensile strength, tensile modulus, and the flexural modulus increased by 54%, 141.9%, and 97.4%, respectively, in contrast to plain PBS.

Poly(butylene succinate-co-adipate)

Poly(butylene succinate-co-adipate) (PBSA) is a random copolymer of PBS. Due to its flexibility of polymer chains and lower crystallinity and, it is more sensitive to biodegradation than PBS (Ray *et al.* 2007a,b). Ray *et al.* (2005) blended PBSA together with (3, 6, and 9 wt%) organically-modified clay to improve the mechanical properties (stiffness, and elongation), thermal stability of PBSA. The same authors investigated a PBSA/ organically modified synthetic fluorine mica (OSFM) blend (Ray *et al.* (2007a). An improvement in mechanical properties, such as in elastic modulus, as well as in thermal stability was noted. Ray *et al.* (2007b) also studied the morphology of a blend of 5 wt% organo-modified montmorillonite in poly(propylene) PP/PBSA (80:20) matrix. After the clay addition, the blend displayed a co-continuous structure and a lower viscosity ratio of the blend matrices. Likewise, improvements were noticed in mechanical, thermal, and rheological properties. Chen and Yoon (2005) produced twice-functionalized organoclays (TFC) and blended them with PBSA. They reported to increase the linear storage modulus of the blend compared to the organoclay /PBSA blend. In addition, PBSA/TFC blends displayed an improved tensile modulus and strength at break.

PBS/biopolymer blends

PBS has been blended with several bio-based polymers, such as cellulose, cellulose acetate, cellulose whiskers, starch, starch nanocrystal, chitosan, silk, plant- and red algae fibers, PLA, and PHAs (Lin *et al.* 2011). The PBSA/ starch blend (5 wt% to 30 wt%) has been investigated. In the study, it was found that starch addition did not considerably decrease mechanical properties, although the addition noticeably increased the degradation properties of the blend, starting from 5 wt% addition. Starch /PBS and starch/PBSA blends have been used in food packaging applications, for instance, as biodegradable biscuit trays or films (Tang *et al.* 2012).

Poly(hydroalkanoates)

Poly(hydroalkanoates) (PHAs) are a diverse group of linear thermoplastic biopolyesters (Liu 2006; Thellen *et al.* 2008; Bugnicourt *et al.* 2014). PHAs are naturally synthesized *via* bacterial fermentation under physiological stress (Liu 2006; Misra *et al.* 2006; Esteban *et al.* 2008; Johansson *et al.* 2012; Bugnicourt *et al.* 2014; Rastogi and Samyn 2015). PHA is obtained from the bacteria by extraction, which is followed by drying and powder or resin formation (Kuusipalo *et al.* 2008). The PHAs function as bacterial carbon and energy storage and their concentration can be from a marginal amount up to more than 80% of their cell dry mass, depending on the bacteria (Valentin *et al.* 1999; Esteban *et al.* 2008; Koller 2014). Sugar and glucose are common fermentation raw materials for the industrial production of PHAs. In addition to carbohydrates, lipids, such as vegetable oil and glycerin, have also been considered (Bugnicourt *et al.* 2014). Different types of wastes and wastewaters have been used for the production of PHAs (Bugnicourt *et al.* 2014; Rastogi and Samyn 2015). Some main processes used for PHA production are shown in Fig. 4.

There are various monomer components enabling versatile properties and application fields of PHAs (Valentin *et al.* 1999; Liu 2006; Koller 2014). In addition to the structural variations, the fermentation process and its carbon source also affect the properties of PHAs (Liu 2006). The dominant and simplest polymers from the group of PHAs are poly(ß-hydroxybutyrate) (PHB) (Dubief *et al.* 1999; Liu 2006; Yu *et al.* 2006;

Tang *et al.* 2012; Arrieta *et al.* 2014a; Bugnicourt *et al.* 2014; Follain *et al.* 2014; Rastogi and Samyn 2015) and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Pardo-Ibáñez *et al.* 2014).

PHAs have been shown to be renewable and biodegradable under anaerobic and aerobic environments and are compostable biopolymers (Bugnicourt *et al.* 2014). PHA is a promising oxygen, water vapor, and UV-light barrier material (Bugnicourt *et al.* 2014; Rastogi and Samyn 2015). Compared to PLA, PHAs provide a better UV light barrier (Arrieta *et al.* 2014a). In addition, PHAs display better WVTR properties compared to other common extrudable biopolymers, such as PLA and PBS (Kuusipalo *et al.* 2008). Furthermore, there have been studies about the biodegradability of PHAs compared to other biopolymers, and this order was reported as PHB > PBS > PLA (Bugnicourt *et al.* 2014). PHAs display good film formability and coating ability (Tang *et al.* 2012). PHAs have been processed by several different techniques, such as extrusion, injection (Bugnicourt *et al.* 2014; Koller 2014) and compression molding (Rastogi and Samyn 2015), thermoforming (Koller 2014), solvent and spin casting (Thellen *et al.* 2008). PHBV-coated paperboards have been reported to handle creasing and to be heat sealable to itself and to paperboard within a temperature range of 190 °C to 230 °C (Andersson 2008). PHAs have been utilized as surface-sizing agents on paper with promising results on mechanical properties and the water resistance of the paper (Rastogi and Samyn 2015). PHB has also been used in other applications, *e.g.*, food and other types of packaging (Weber *et al.* 2002), in the manufacture of ropes, bank notes, and cars (Reddy *et al.* 2013) and in biomedical products (Misra *et al.* 2006).

Challenges of PHAs involve, for example, the production cost (Valentin *et al.* 1999; Weber *et al.* 2002; Dufresne *et al.* 2003; Liu 2006; Andersson 2008; Gandini 2008; Kuusipalo *et al.* 2008; Mousavioun *et al.* 2010; Tang *et al.* 2012; Bugnicourt *et al.* 2014), low acid and base resistance, poor thermal processability (Rastogi and Samyn 2015), and the fact that the raw materials that are currently used compete with food sources (Bugnicourt *et al.* 2014). The PHAs have weak thermal stability above the melting point (~175 °C), although this aspect can be controlled by using additives (Johansson *et al.* 2012). Due to PHAs’ tendency to be brittle, they are often blended with additives or other polymers (Bugnicourt *et al.* 2014). Moreover, there is potential for improvement in terms of the gas barrier properties of PHAs (Andersson 2008; Tang *et al.* 2012). PHAs have been blended with other polymers and fillers to enhance their properties and to reduce the cost (Dufresne *et al.* 2003; Yu *et al.* 2006; Mousavioun *et al.* 2010).

PHAs/filler composites

Sanchez-Garcia and Lagaron (2010) investigated PHBV/organomodified clay composite. Compared to neat PHBV, its composite with 5 wt% clay resulted in a reduction of permeability levels to water (by 76%), to oxygen (by 32%), and to oil (limonene) (by 78%). The PHB/nanoclay composites have been studied but challenges still exist in the formation of the composite material due to PHB degradation behavior and instability. Improvements in mechanical and thermal properties have been achieved by combining nanoclay with PHB (Tang *et al.* 2012).

Pardo-Ibáñez *et al.* (2014) improved the barrier properties of PHBV by adding keratin fibers. The PHBV with 1.0 wt% of keratin fiber blend improved water, limonene, and oxygen barrier properties as well as elastic modulus compared to pure PHBV. Dufresne *et al.* (2003) applied cellulose flour (up to 70 wt%) as reinforcement filler into a PHBV polymer matrix in order to reduce its price while still maintaining its biodegradability. They observed poor interaction between the filler and PHBV, poor mechanical properties, and an increased degree in crystallinity. Nevertheless, the mechanical properties were enhanced at higher temperatures (above glass–rubber transition of PHBV). Dubief *et al.* (1999) studied nanocomposites, where the matrix polymer was poly(β-hydroxyoctanoate) (PHO) and nanofillers were starch microcrystals and cellulose whiskers. As a result, the addition of nanofillers enhanced the mechanical properties of the matrix polymer. The PHB has been used in plasticized PLA/CNC nanocomposite to increase the crystallinity of PLA. Consequently, the resulting composites were transparent and compostable (Arrieta *et al.* 2015).

PHAs/biopolymer blends

The mechanical and thermal properties as well as the processability of PHB were enhanced by low and high molecular weight plasticizers. By adding 20 wt % plasticizer (blend of dioctyl phthalate and di-2-ethylhexylphthalate), Erkske *et al.* (2006) achieved enhanced strength, elongation, and decreased brittleness. In addition, the melting temperature was lowered and, overall, the processing window was expanded considerably. The authors also added 20-60 wt% of starch to a PHB/ plasticizer blend. The elongation and strength properties of the composite decreased by increasing the starch content, whereas water vapor barrier increased (the optimal starch content 25 to 40 wt%).

PHB has been blended with starch-adipate and grafted starch-urethane derivatives, resulting in limited mechanical properties (Tang *et al.* 2012). In another study, PHB was blended with starch acetate (SA) to change the crystallization, *e.g.*, lower temperature and enthalpy of non-isothermal crystallization of PHB. PHB/SA blends were found to be immiscible (Zhang *et al.* 1997).

PHB was blended with cellulose propionate (CP), which resulted in higher ductility. The components of the PHB and CP blend were miscible. Likewise, a miscible blend of PHB and cellulose acetate butyrate (CAB) expanded the processability of the system by lowering the degree of crystallinity and the melting temperature. Additional studies have considered chitin and chitosan blended with PHB (Yu *et al.* 2006). Ikejima and Inoue (2000) compared PHB/chitin and PHB/chitosan blends and found an improvement in the biodegradability compared to neat chitosan and chitin. In addition, they observed that 25wt% PHB containing PHB/chitin blend degraded more rapidly than neat PHB or chitin as a result of decreased crystallinity of PHB.

A PHB/poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHHx) blend was found to strengthen the elongation at break significantly when the PHBHHx content in the blend was increased from 40% to 60% (Zhao *et al.* 2003). The PLA/PHB films were brittle and rigid without plasticizing with, for example, poly(ethylene glycol) (PEG). The PLA/PHB based films in the Arrieta *et al.* (2014b) study displayed a compostable character. Abdelwahab *et al.* (2012) studied PLA/PHB blends with a plasticizer (5 wt% and 7 wt%). The elongation at break increased by the addition of the plasticizer. Olkhov *et al.* (2003) investigated PHB/poly(vinyl alcohol) (PVA) blends, where the PHB content varied from 0% to 100%. The highest water vapor permeability was observed when the PHB content was 40 wt%.

PROSPECTS

Barrier materials have an important role in different types of packaging applications, considering the protection from the environment and shelf life that they provide. Conversely, in some instances, the barrier material protects the environment from the product. Several barrier materials in today's industry are manufactured either from oil resources or metals. Driven by both the increase in environmental awareness, as well as the resource scarcity, novel and environmentally benign alternatives have been sought. This review covered wood and fermentation-based materials, which display interesting barrier properties and offer a potential for utilization in packaging.

Wood-based products have received great attention in a wide variety of fields. Hemicellulose-based barriers have been reported to display resistance against oil, grease, aroma and oxygen. Moreover, hydrophilic hemicelluloses offer promising barrier properties, and are easily modified. For polysaccharides streams, the main challenges include their mechanical properties, processability, and low water resistance. A relatively weak heat stability and narrow processing window may be challenging, and lower running speeds may be needed compared to oil based alternatives. Also, the adhesion may be challenging, depending on the substrate. Derivatives of cellulose render it soluble in various solvents that are widely used in industry. Their thermal properties and facile application on surfaces are great advantages. However, a more detailed discussion is needed, especially if focused on processing of eco-friendly barrier films at speeds relevant to industrial production.

A few essential variables are critical when considering cellulose derivatives and structure-property-process relationships for upscaling novel cellulose derivatives. These variables include the degree of substitution that is linked with water vapor permeability. The reaction conditions of cellulose derivatives regulate their DS, DP, and final properties, which include film-forming and barrier properties. There is interest for developing novel cellulose derivatives, due to a trend aiming for methods to replace petroleum-based packaging materials. Firstly, there have been suggestions for blends with other materials that compensate the poor WVP and enhance other barrier properties. Simultaneously, novel cellulosic solvents may bring promise, together with homogeneous modification methods, for increased regioselectivity leading to improved and more end-use-specific properties of the cellulose derivatives.

The interest towards lignin has been based on its availability and cost as well as its possibilities for chemical modification. Considering potential barrier applications, the properties of interest in lignin include its antioxidant behavior and UV-light resistance. However, challenges with technical lignins involve its poor film-forming properties and dark color.

There have been several publications covering heat treatment of nanocellulose. The crystallinity is important for oxygen permeability, whereas material density is decisive for water vapor permeability. In addition, the combination of hydrophobic, thermoformable matrices with nanocellulose is under study, and some promising solutions exist regarding compatibility, but also challenges, such as the low WVP of nanocellulose. The economic aspects and upscaling potential in nanocellulose production has been reported, and a few nanocellulose-containing end-use products are already commercialized. Nevertheless, several challenges remain to be resolved prior to large-scale industrial production, such as the hygroscopic tendency of nanocellulose to absorb moisture from its surroundings, swelling, and others.

PLA, PBS, and PHAs are commercial, biodegradable biopolymers, with characteristics that are comparable to conventional petroleum-based thermoplastics. The challenge in considering these polymers is their relatively high price, low production volumes, and the more challenging processability compared to that of conventional polymers, *e.g.*, polyolefins. In addition, the most common bio-based raw materials for PLA, PBS, and PHAs production compete with food. However, different waste-streams, wastewaters and agro-wastes, have been studied as an alternative feedstock. The PLA, PBS, and PHAs offer adequate mechanical and barrier properties for many applications, specially for packaging. Nevertheless, in order to enable a more extended use of these biopolymers in the packaging industry, the price level should be comparable to that of conventional polymers. This means the need for cheaper raw materials, more efficient production processes, thinner barrier layers, or the development of cost-efficient blends or composites. Another powerful accelerator could be a change in the legislation considering packaging materials, *e.g.*, similarly to European directive of single use plastics or French ordinance Décret n° 2016-1170 (2016).

For both wood-based or microorganism-based biobarriers, the incorporation of inorganic and mineral nano- and microparticles offer interesting prospects, for example, to develop antibacterial, thermal resistance and other properties (Hoseinnejad *et al.* 2018; Wang *et al.* 2018). For instance, high-barrier and fully biodegradable food packaging materials have been achieved by coating PLA with glycol chitosan-clay nanocomposite (Habel *et al.* 2018). Likewise, major advances have been made with compositions to achieve UV protection (Niu *et al.* 2018) as well as scavenging and releasing activities, all relevant to food and pharmaceutical packaging, to extent the shelf life, for diagnostic, identification and communication (quality tracking, brand protection, *etc*.). This topic has been reviewed recently (Janjarasskul and Suppakul 2018) and is a subject of current research. In all these contexts, safety and regulatory aspects need careful attention.

While this review did not discuss the topic in detail, an interesting solution to biodegradability, to improve the properties of packaging materials, and to enhance barrier effects, is the use of multicomponent polymers and blends. This includes the synthesis of systems via interpenetrating networks (Bai *et al.* 2015). For related purposes, various compatibilizers, including those that can be adopted during melt processing, have been discussed (Muthuraj *et al.* 2018). Along similar ideas, proteins have been proposed as compatibilizer and eco-friendly dispersant in composites comprising cellulose nanofibrils and PLA (Khakalo *et al.* 2018). Another aspect of interest is the possibility to make patterned biobarriers, which can be useful to engineer surfaces in advanced applications (Guo *et al.*, 2018). Finally, the so-called “solvent welding” is being researched to tune the surfaces of biobased films, expanding the scope of properties and offering a possibility to facilitate multilayered structures (Reyes *et al.* 2019)

CONCLUSIONS

Packaging materials are selected by end use requirements and they can be combined to fulfill given target properties. No single bio-based material will satisfy all potential markets or applications. Existing petroleum-based barrier solutions comprise products that have been developed over the course of several decades. The use of bio-based materials is not as matured and needs further development. Growing interest in designing packaging concepts include multilayer structures. PLA, PBS, and PHBs are becoming material alternatives for green, food packaging while wood-derived materials, including hemicelluloses and nanocelluloses are in the earlier stages of their consideration.

ACKNOWLEDGEMENTS

The authors are grateful to Terhi Saari and Sai Li for their excellent guidance and discussions on the content. Katja Vakula and Miska Savolainen are thanked for their help in visualizations used in the figures. H2020-ERC-2017-Advanced Grant "BioELCell" (788489) is acknowledged for funding support (O.J.R).

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Article submitted: December 5 2018; Peer review completed: January 27, 2019; Revised version received and accepted: February 9, 2019; Published: February 19, 2019.
DOI: 10.15376/biores.14.2.Helanto