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## Bringing New Function to Packaging Materials by Agricultural By-Products

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## Chapter 12

### 12. Bringing new function to packaging materials by agricultural byproducts

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#### Abstract

The development of functional additives for packaging polymers starting from byproducts of the agriculture and food industry is a very active research field. Different examples are discussed concerning the formulation of polylactides (PLA) in the aim to increase ductility and barrier properties or developing active packaging using byproducts of the vegetable oil industry and lignocellulosic materials. Moreover, the potential of the production of polyhydroxyalkanoates from agricultural byproducts is shown and recent results concerning their blending with auxiliary polymers in the aim to obtain packaging materials. Notwithstanding the renewable origin of such novel technological adjuvants for packaging materials, their safety must be ensured and they need to comply with existing regulations. The fundamental principles and means for risk management are summed up. When performance and safety is designed together, there is a high potential for the from agriculture and food industry to contribute to the development of new packaging systems safer for consumers and environment.

KeyWords: polylactide, polyhydroxyalkanoate, packaging, barrier properties, mechanical properties, Food Contact Materials, regulation, nanocellulose, vegetable oil industry, lignin

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## 12.1. Introduction

Due to the superior properties of thermoplastics, the packaging sector is the largest user of polymer materials. Polymers enable the production of lightweight materials, easily processed into packages with specific design and mechanical properties. The large use of those materials causes, however, several environmental issues, mostly linked to the risk of persistent pollution in the environment and the use of fossil resources. The development of biodegradable and biobased polymers is one of the answers to these questions. Combined with the use of renewable resources, it allows to step towards circular economy by bringing new value and agricultural production. In this perspective, agriculture and food industry can become suppliers of polymer materials and not only users of these materials.

Academic research brings the necessary expertise for screening potential (by)products and improving the functionality of these polymer materials. Indeed, new biodegradable and biobased resins lack sometimes technical properties for successful replacement of existing materials. This is a challenge to rise to and to invent novel strategies for building the desired function by the creation of original assemblies and morphologies. Furthermore, constraints such as availability, ecological impact and security of materials need to be respected.

Within this framework, examples will be discussed based on the experience of our laboratory concerning the development of novel packaging materials based on agricultural byproducts taking into account functional and security aspects. The main focus will be given on biobased polyesters, mainly polylactides (PLA), which account for the highest volume in packaging applications and polyhydroxyalkanoates (PHAs), which are actually emerging.

## 12.2. Formulation of polylactides

### 12.2.1. Introduction on PLA synthesis, properties, and degradation

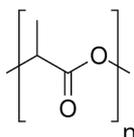


Figure 12.1. Chemical structure of PLA

The basic constitutional unit of PLA (Figure 12.1) is lactic acid. Lactic acid (2-hydroxy propionic acid) is an  $\alpha$ -hydroxy acid with an asymmetric carbon atom and exists either as L (+) or D(-) stereoisomer. The L- isomer is produced in humans and other mammals, whereas both the D- and L-enantiomers are produced in bacterial systems. The large majority of lactic acids

produced today is obtained by bacterial fermentation of simple sugars in L-conformation. The abbreviation of the polymer “PLA” stands for either for poly(lactic acid) or for poly(lactide), depending on the polymerization route. Poly(lactic acid) is obtained by direct polycondensation of lactic acid. Because of the difficulty to reach high molecular weights, this synthesis route is scarcely used. The majority of PLA is polylactides obtained by ring-opening polymerization (ROP) of lactides (Ducruet and Domenek 2015), a synthesis pathway first reported by Wallace Carothers in 1932 (Carothers et al. 1932). Three forms of lactide can be obtained by high-temperature distillation: L,L-lactide, D,D-lactide and D,L-lactide (meso-lactide). The type of lactide and the proper management of the ROP allows producing macromolecules with controlled stereochemistry (Stanford and Dove 2010). The stereocontrol of the macromolecular chain induces large changes in the thermal stability and crystallization behaviour of PLA. PLA with random distribution of enantiomers and containing more than 93 % of L-lactic acid is semi-crystalline, while PLA containing L-lactic acid between 50 and 93 % is amorphous. D-lactic acid, in high proportion, prevents PLA crystallization (Auras et al. 2004). In contrary, enantiopure PLLA and PDLA can form a stereocomplex due to stereoselective interactions (mostly van der Waals forces) locking the chains into a novel material with largely changed physical properties, for instance increased crystallization and melting temperature (Stanford and Dove 2010). PLA is an admitted Food Contact Material (FCM) in the European and North-American Legislations. It is generally formulated with some technological adjuvants, but at moderate level. Antioxidants and lubrication agents were evidenced (Gratia et al. 2015; Lalanne et al. 2010; Salazar et al. 2017). A summary of the major properties of PLA is presented in Table 12.1. PLA is efficient in maintaining food quality because of its high resistance to fatty food and barrier to aroma compounds (Salazar et al. 2014). It is however noteworthy that PLA has high affinity to aromatic molecules, which cause already at very low concentrations plasticizing and induced crystallization (Salazar et al. 2012).

Table 12.1. Main properties of PLA

			Reference
Density	1.24	g/cm <sup>3</sup>	(Auras et al. 2004)
Glass transition temperature Tg	55 – 60	°C	(Ducruet and Domenek 2015)
Melting temperature	140 – 180	°C	(Saeidlou et al. 2012)
- Stereocomplex	260	°C	(Stanford and Dove 2010)

Thermal decomposition temperature	360	°C	(Carrasco et al. 2010; Kopinke et al. 1996)
Elongation at break	5 – 10	%	(Domenek et al. 2018)
Young modulus	3500	MPa	(Domenek et al. 2018)
Yield strength	40 – 70	MPa	(Domenek et al. 2018)
Oxygen permeability 23 °C, 0 % RH	$2 - 3 \cdot 10^{-18}$	$\text{m}^3 \cdot \text{m}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$	(Sonchaeng et al. 2018)
Water vapour permeability 23 °C	$1 \cdot 10^{-14} - 1 \cdot 10^{-13}$	$\text{kg} \cdot \text{m}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$	(Sonchaeng et al. 2018)

PLA is a glassy polymer at room temperature. The melting temperature is dependent on the D/L ratio, being situated in a range between 140 and 180 °C. The stereocomplex melting temperature is shifted to much higher temperatures (**Table 12.1**). PLA presents brittle fracture behaviour with necking and stress whitening. The main deformation mechanism is shear banding and shear-band nucleated crazes. In the ductile deformation region after the necking, the preferred plastic deformation mechanism of PLA is then standard crazing (Domenek et al. 2018). Oxygen barrier properties of PLA are intermediate between high volume polymers such as poly(ethylene) (PE) and poly(ethylene terephthalate) (PET), while water vapour permeability is 10 to 1000 times higher compared to PET and PE.

The degradation of PLA can be abiotic, *i.e.* uniquely relying on chemical processes, or biotic, *i.e.* involving metabolic processes of microorganisms. Abiotic thermal degradation can occur during processing because aliphatic polyesters as PLA have limited thermo-stability. The degradation processes can already start at temperatures as low as 215 °C (Kopinke et al. 1996), but the fastest degradation kinetics are observed around 360 °C (Carrasco et al. 2010; Gupta and Deshmukh 1982; Kopinke et al. 1996). The mechanisms of the thermal degradation of PLA are rather complex, involving thermal hydrolysis by trace amounts of water, zipper-like depolymerisation, inter- and intra-molecular transesterification, and oxidative random main chain scission (Södergård and Stolt 2002). Those reactions can be accelerated by the presence of impurities or residual catalysts. Thermal hydrolysis and intramolecular transesterifications are the preponderant degradation route of PLA during processing, as has been evidenced by several authors (Taubner and Shishoo 2001; von Oepen and Michaeli 1992; Wang et al. 2008). Careful drying, minimizing process temperature and residence time are important process parameters for PLA extrusion. In particular, (Salazar et al. 2017) showed that the main degradation products of PLA formed during extrusion were lactides, alcohols, and aldehydes. They quantified several odorous compounds with low perception threshold, such as 2-methyl 2-propanol or acetaldehyde. The acetaldehyde concentration was however between 3.6 and 18 times lower compared to values obtained during PET production. Those compounds

disappeared during storage of PLA under ambient conditions and were not detectable any more after 2 months (Salazar et al. 2017). In practice, this means that PLA does not lead to perceivable alteration of organoleptic properties of foodstuff. A successful experiment testing the sensorial properties of chocolate packed in PLA films was reported by (Ruellan et al. 2016). Hydrolysis kinetics of PLA in the mild temperature conditions ( $T < 40\text{ }^{\circ}\text{C}$ ) of an agricultural environment are of high importance for the design of products used mulch films. Upon immersion, water molecules can penetrate only the amorphous phase, crystallites are excluded volume. Amorphous domains are therefore degraded first, PLA materials undergo thus bulk erosion starting from the surface (Hakkarainen et al. 1996). In the presence of water and a catalyst, ester hydrolysis occurs, bringing about decrease of molecular weight. The accumulation of oligomers with acid ends or lactic acid can have an autocatalytic effect on the ester hydrolysis. It can be shown that the degradation of bulk pieces in humid environment proceeds faster than the one of pieces immersed in water. In the latter case, acidic degradation products are leached out from the sample and washed away, which decrease the autocatalytic degradation process (Gerometta et al. 2019).

Biodegradability of polymers is a multifunctional property referring to end-of-life options of materials in different biological environments (industrial or home composting, anaerobic digestion, e.g.). According to the ISO EN 13423 it refers to a process where materials are degraded under the action of microorganisms into carbon dioxide, methane (only in anaerobic conditions), water, inorganic compounds, and new biomass. The kinetics of this degradation are dependent on the specific biodegradation conditions (temperature, water activity, presence of microorganisms and their nature, oxygenation, etc.) (Ruggero et al. 2019). Biodegradation can therefore involve in a first step chemical processes such as dissolution, hydrolysis and enzyme-catalysed degradation, but also oxidation, photolysis. In the case of PLA, an abiotic (catalysed) hydrolysis step seems to be always involved leading to the formation of oligomers, which are able to be assimilated by microorganisms, which will metabolize them to  $\text{CO}_2$  and water under aerobic conditions (Auras et al. 2004; Pitt et al. 1981). Biodegradation of PLA has been studied in soil, in sea water and in compost. The biodegradation kinetics vary as a function of the PLA characteristics (molecular weight, stereochemistry, crystallinity degree) and the environment. For example, in soil activation time can be very long, bringing about long degradation times of PLA if abandoned in natural environments. A field test in Greece showed complete disintegration of PLA only after one year, while it was accomplished in 60 days in industrial composting conditions involving temperatures higher than  $T_g$  (Haider et al. 2019). In

simulated composting conditions, such as liquid media, PLA mineralization by microorganisms can be completed after only 60 days (Ruellan et al. 2016).

### **12.2.2. Toughening PLA using agricultural by-products and their derivatives**

As shown in Table 12.1, PLA is a brittle polymer with relatively low toughness. This limits its applications in both, rigid and flexible packaging. Improving toughness using biobased and biodegradable substances is therefore a very active research field. Agricultural by-products can be a source of technical adjuvants, such as plasticizers, fibres, polymers for the formulation of blends. The influence of plasticizers on the mechanical properties of PLA has been extensively studied and recently reviewed (Ruellan et al. 2015a). Plasticizers essentially increase the free volume inside polymer matrixes and decrease the inter-chain interactions (Ruellan et al. 2015a), which eases slip of one macromolecule with respect to another, decreases the cooperativity volume (Araujo et al. 2019). The macroscopic consequence of these mechanisms is decreased glass transition temperature and increased elongation at break. Numerous monomeric and oligomeric plasticizers were tested, the most prominent of which are poly(ethylene glycol) (PEG) with variable molecular masses and citrate derivatives, such as acetyl tributyl citrate (ATBC) (Ruellan et al. 2015a). The transition of the brittle to ductile behaviour of formulated polymers is generally obtained when the plasticizer concentration is large enough to decrease the glass transition temperature near the mechanical testing temperature. To give an example, ductile PLA was obtained with ATBC concentrations higher than 15 wt% (Courgneau et al. 2011; Courgneau et al. 2012). An alternative possibility to increase toughness of polymers is the use of impact modifiers. Most impact modifiers are materials softer than the polymer matrix (for example rubbers). The role of the softer phase is to absorb the mechanical energy of an impact and to stop fracture propagation in case of formation of crazes or breaks. This latter effect can also be obtained by the inclusion of plasticizers at concentrations higher than the miscibility limit. In that case, the plasticizer phase separates and forms tiny droplets able to stop the fracture propagation (Ruellan et al. 2015c). For preserving claims on biodegradability and biobased carbon content in plasticized PLA, biobased and biodegradable molecules were extensively screened as plasticizers (Ruellan et al. 2015a). To give some examples, epoxidized soybean oil (Al-Mulla et al. 2010; Ali et al. 2009; Xiong et al. 2012; Xu and Qu 2009) or epoxidized palm oil (Al-Mulla et al. 2010; Silverajah et al. 2012a; Silverajah et al. 2012b) were tested with some success. Very interesting properties could be obtained using of deodorizer distillates, which are by-products of the vegetable oil industry. They can be easily introduced

in the PLA matrix by twin-screw extrusion. It was shown that deodorizer distillates from the palm oil refinery improved the elongation at break of PLA up to 180 %, while the  $T_g$  (45°C) remained higher than room temperature and the yield strength at 24 MPa (Ruellan et al. 2016; Ruellan et al. 2015b). This result is reported in Figure 12.2. The deodorizer distillates of the palm oil refinery contain different types of free fatty acids which crystallize at temperatures below and above room temperatures. The mixture of liquid and crystalline inclusions in PLA induced extensive crazing with numerous microcracks, the formation of which slowed down fracture propagation and yielded a large delay of specimen fracture (Ruellan et al. 2015b). The properties were stable during aging for 6 months (Ruellan et al. 2016). Overall migration tests at laboratory scale showed compliance with European legislation limits. The materials were fully biodegradable (Ruellan et al. 2016). Preliminary Life Cycle Analysis showed an advantage of using such byproducts over petrochemical plasticizers. Those results show that the use of agricultural byproducts compatible with current polymer processing technologies can mediate large property gains of PLA.

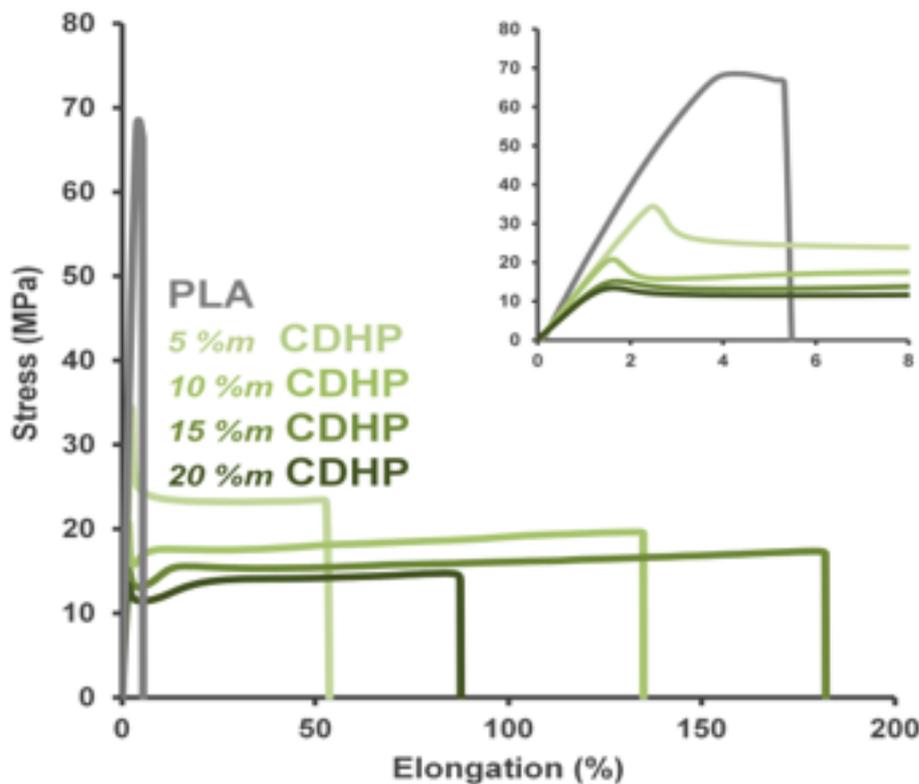


Figure 12.2. Tensile properties of PLA (grey line) and PLA formulated with palm oil deodorizer distillate (CDHP) at different concentrations (5, 10, 15, 20 wt%) (green lines). The insert zooms on the properties of the neat PLA. Adapted from (Ruellan et al. 2015b).

### 12.2.3. Increasing barrier properties of PLA with agricultural by-products

Gas barrier properties of polymers are an important use property from many applications, in particular for food packaging. The sorption/diffusion model (Graham 1864) rules the permeability (P) of gas and vapors in polymers, establishing that P is the product of two fundamental contributions, the diffusion coefficient (D) and the solubility coefficient (S), *i.e.*  $P=D \cdot S$ . The permeability is therefore influenced by different intrinsic factors of a given polymer, such as the free volume fraction (FFV) of the polymer, the glass transition temperature (T<sub>g</sub>), the Cohesive Energy Density (CED), the molecular orientation, the copolymerization. Furthermore, the inclusion of impermeable structures in the polymer matrix increases the tortuosity of the diffusive pathway, which macroscopically decreases D. The excluded volume of the impermeable structures decreases also the available volume for penetrant sorption, which macroscopically decreases S.

The increase of the tortuous pathway of diffusion inside PLA was largely investigated (Sonchaeng et al. 2018). Two different approaches were used: (i) increasing the polymer crystallinity, since the crystallites are impermeable to small molecules (Colomines et al. 2010; Guinault et al. 2012; Nassar et al. 2017), and (ii) adding nanofillers. Although most studies concerned mineral nanoparticles (Sonchaeng et al. 2018), some results were obtained employing agricultural products from lignocellulosic biomass (Espino-Pérez et al. 2018; Espino-Perez et al. 2016; Fabra et al. 2016; Sanchez-Garcia and Lagaron 2010).

The crystallization of PLA does not improve in all cases the gas barrier properties, in some configurations even adverse effects can be obtained. This counterintuitive result is caused by the formation of dedensified amorphous phases in the vicinity of PLA crystallites, which constitutes an accelerated pathway for diffusion (Guinault et al. 2012; Nassar et al. 2017; Varol et al. 2020). Dedensified phases are formed preferentially upon crystallization of PLA from the glassy state at low temperatures, conditions which favour coupling between amorphous and crystalline phase of the polymer (Nassar et al. 2017; Righetti and Tombari 2011). The annealing of PLA with regards to improved barrier properties needs thus to be carried out at high temperatures (>110 °C) on ideally nucleated materials (Nassar et al. 2017).

The second technology for increasing barrier properties is the use of nanofillers. In particular, bionanocomposites of PLA were developed using cellulose nanostructures. Nanocelluloses can be obtained from different sources of lignocellulosic biomass. Although most of the nanocelluloses produced today come from the paper making industry, many reports exist showing the production of nanocelluloses from by-products of the food and agriculture industry. For example, they can be successfully obtained from barley husks and agave bagasse

(Espino et al. 2014), or banana residues (Alzate-Arbelaez et al. 2019). Cellulose microfibrils (MFC) have nanosize diameters (2-20 nm depending on the origin) and a fibre length in the micrometer range. The crystalline parts of MFC can be isolated by several mechanical and chemical treatments, affording cellulose nanocrystals (CNC) or nanowhiskers. Dimensions of CNC range from 200 nm up to 1-2  $\mu\text{m}$  in length and about 8-50 nm in diameter (Habibi 2014). Nanocelluloses have very high oxygen barrier properties in the dry state. The oxygen permeability ( $P(\text{O}_2)$ ) can be in the order or one to two magnitudes lower than the one of the widely used polymer poly(ethylene vinyl alcohol) (Fukuzumi et al. 2009). (Sanchez-Garcia and Lagaron 2010; Sanchez-Garcia et al. 2008) compared the effect of the same content of MFC and CNC on  $P(\text{O}_2)$ . The addition of 5 wt.% of MFC had no effect over gas barrier properties while 5 wt% of CNC led to a decrease in oxygen permeability. (Espino-Perez et al. 2013) reported similar results. The main difficulty in using CNC or MFC for barrier applications is their swelling in environments with a water activity higher than 0.6. The swelling decreases substantially the barrier properties (Fukuzumi et al. 2013). Surface grafting techniques were developed to decrease this water sensitivity of CNC with some success. A sample result is reported in the Figure 12.3, which displays the water sorption isotherm of native CNC and surface grafted CNC. In the range of low water activities, both sorption isotherms were essentially superposed. The native CNC showed an upswing of the water mass uptake at activities  $> 0.6$  due to granule swelling and water condensation. The surface grafting of CNC produced a shift of the upswing towards higher water activity and less mass uptake (Espino-Perez et al. 2016).

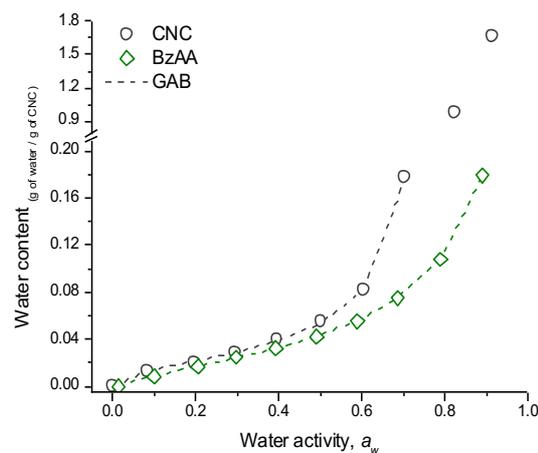


Figure 12.3. Water sorption isotherm of CNC powders (black circles) and powders of CNC bearing surface grafts of benzyl acetic acid (BzAA, green diamonds). Adapted from (Espino-Perez et al. 2016).

Swelling phenomena give rise to non-Fickian diffusion, a phenomenon which is often overlooked. PLA and CNC films and their composites are subject to polymer relaxation driven non-Fickian water diffusion (Davis et al. 2013; Espino-Pérez et al. 2018). In the case of films thinner than 80  $\mu\text{m}$ , relaxation phenomena can be observed at experimental times longer than two hours and the relaxation driven component can be preponderant (Figure 12.4) (Almeida et al. 2020; Espino-Pérez et al. 2018). Recently, a mathematical model was developed able to separate Fickian transport kinetics and polymer relaxation driven transport. With the help of this model, characteristic relaxation times can be obtained and used for the optimization of the transport properties of nanocomposites in presence of swelling penetrants (Almeida et al. 2020).

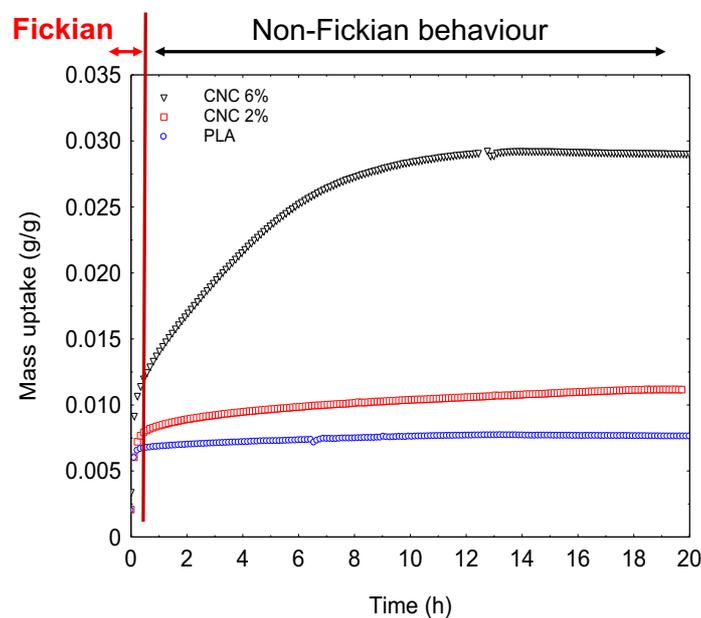


Figure 12.4. Non-Fickian water vapour mass uptake of PLA/CNC nanocomposites at different CNC concentrations (2 and 6 wt%). Adapted from (Espino-Pérez et al. 2018).

In conclusion, high gas barrier properties and in particular high oxygen barrier properties are needed in food packaging for the protection of oxidation sensitive goods. Biobased materials such as nanocelluloses have very interesting potential in this respect, but they need to be shielded from water vapor. This challenge is yet to be raised to.

#### 12.2.4. Lignin as source for antioxidants and active packaging

An alternative or supplementary means to protect oxidation sensitive foodstuff during shelf-life is the use of active packaging. This technology consists in the inclusion of antioxidant molecules in the packaging material. Generally, active packaging films rely on migration of

the antioxidant in the foodstuff. However, some evidence exists in literature that it is possible to develop materials with antioxidant surface activity (Crouvisier-Urien et al. 2016; Domenek et al. 2013; López-de-Dicastillo et al. 2012). In that context, lignin, an abundant and low-priced by-product of biorefinery processes based on lignocellulosic biomass (bioethanol, paper making), is an interesting source of raw materials. Lignin is a polyphenolic copolymer constituted of three subunits (coumaryl, coniferyl and syringyl alcohols), arranged in a hyper-branched structure and containing reactive free phenolic hydroxyl groups. Furthermore, lignins contain often additional free phenolic acids (e.g. ferulic acid). Phenolics are well-known antioxidants due to the ease of proton abstraction and the stabilization of free radicals in the quinone resonance structure. The antioxidant activity of lignin is already largely documented (Naseem et al. 2016). A drawback of lignin in the field of active packaging is that lignin cannot form films by itself. It needs to be included in a polymer matrix, which raises compatibility issues between lignin and the carrier polymer. PLA was investigated as a carrier polymer. (Domenek et al. 2013; Yang et al. 2016a; Yang et al. 2015b). An interesting result concerned the extrusion processing of lignin/PLA blends. The thermal treatment led to lignin degradation and liberation of free phenolic acids. This enhanced the antioxidant activity of the PLA/lignin films, which shows that such materials can be potentially developed using existing polymer processing technology (Domenek et al. 2013). In response to aggregation issues of lignin in the carrier polymer, fabrication methods of lignin nanoparticles were developed and different types of compatibilizers between lignin and PLA were experimented (Yang et al. 2015a; Yang et al. 2016a). A very interesting result was obtained combining CNC as dispersants and lignin nanoparticles in PLA. The resulting materials had enhanced strength and antioxidant and antimicrobial properties (Yang et al. 2016a). Among alternative carrier materials for lignin the use of is very promising. Chitosan is a derivative of chitin, which is an abundant by-product of the fishing industry (crustacea shells) (Crouvisier-Urien et al. 2016; Crouvisier-Urien et al. 2017; Yang et al. 2016b). Chitosan and lignin are incompatible polymers since chitosan is much more polar than lignin. Therefore aggregates are formed upon dispersion (Baumberger et al. 1998; Núñez-Flores et al. 2013), the size of which can however be decreased using lignin nanoparticles or high-shear or high-pressure processing methods (Crouvisier-Urien et al. 2017; Yang et al. 2016b). Figure 12.5a-c shows the impact of high-pressure homogenization on the decrease of the size of lignin aggregates in chitosan and its impact on the antioxidant activity of the blends. The homogenization treatment did not impact the overall radical scavenging activity of the films, as can be observed by the superposition of the RSA kinetics (Figure 12.5d-e), but changed the importance of the contribution of dissolved lignin residues. High-shear and

high-pressure treated lignin included more small molecules likely to be extracted into the contacting medium, where they develop antioxidant activity. Lignin can thus have antioxidant activity on the film surface and via the extraction of active compounds in the foodstuff (Crouvisier-Urien et al. 2017). Both mechanisms can be used for developing active packaging, but the safety of the materials needs to be very carefully instructed.

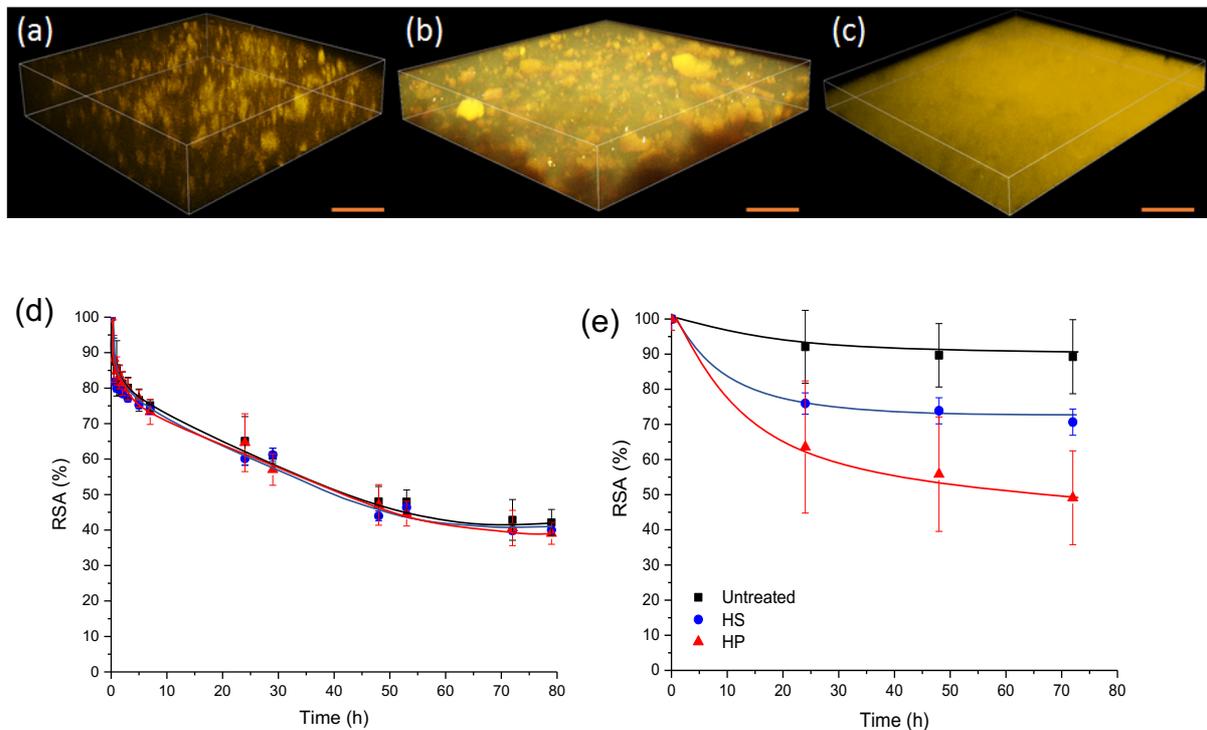
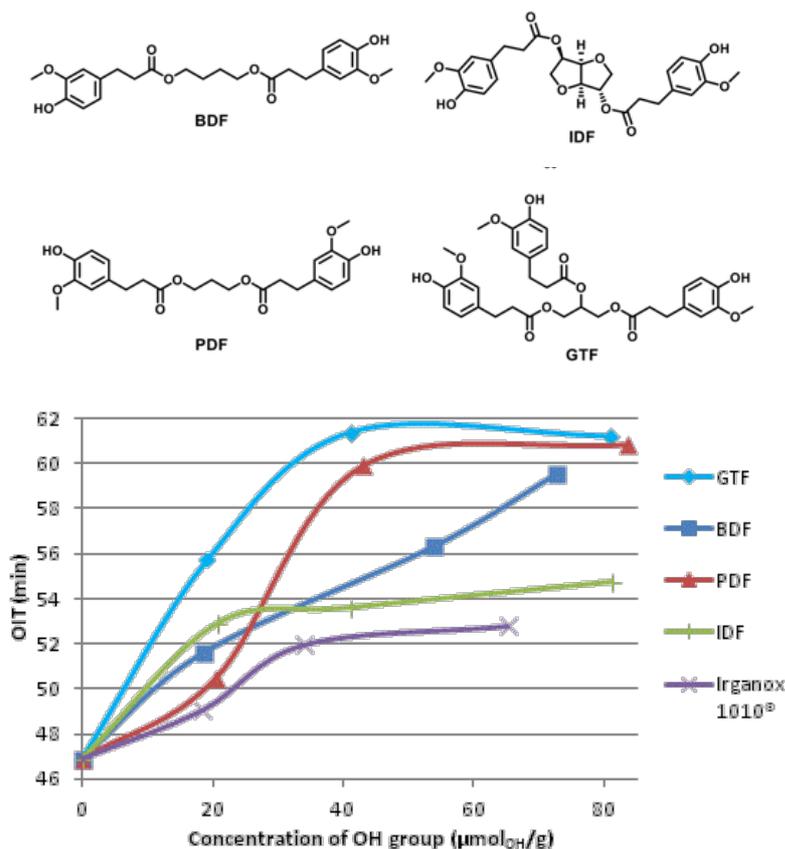


Figure 12.5. Effect of high-shear (HS) and high-pressure (HP) treatment on lignin aggregates and antioxidant activity of chitosan films. Fig. 12.5 a-c) 3D reconstruction from two photon fluorescence microscopy observations performed at 750 nm excitation with 563-588 filter selection for chitosan-lignin film for the (a) untreated, (b) HS treated and (c) HP treated lignin. The scale bar represents 40  $\mu\text{m}$ . Fig. 12.5 d-e) Reduction of the Radical Scavenging Activity (RSA, %) determined by the DPPH method and representing the kinetics of the decrease of the concentration of free radicals (DPPH $\cdot$ ) in ethanol/water solution: (d) overall kinetics of films submersed in an ethanol/water solution containing the free radical DPPH $\cdot$ . Including untreated, HP treated and HS treated lignin, (e) analysis of the radical scavenging activity of lignin residues released from these films (n = 6). The lines are to guide the eye. Adapted from (Crouvisier-Urien et al. 2017).

Antioxidants are furthermore important technological adjuvants of plastics and rubbers, because the addition of antioxidant phenolics is the most convenient and effective way to keep polymers, such as polyolefins and polyesters, from oxidative damages during melt processing,

aging and weathering. For this purpose, the employment of natural antioxidants, such as lignin-derived *p*-hydroxycinnamic acids (*p*-coumaric acid, ferulic acid and sinapic acid) is often hindered by their low thermal stability. Thermal stabilization can be obtained by derivatization. In that aim, a novel synthesis method following the principles of green chemistry using a *Candida antarctica* lipase B was developed. This enzyme can catalyze transesterification reactions of *p*-hydroxycinnamic acids with biobased diols (1,2-ethylene glycol, 1,3-propanediol, 1,4-butanediol, glycerol and isosorbide) in organic solvents or directly in the reactants without solvent under mild conditions (Pion et al. 2014; Reano et al. 2016b). The obtained macrobisphenols showed thermal stability at temperatures higher than 280 °C (Pion et al. 2013). The analysis of the structure/activity relationships informed on the optimal structure with regards to antiradical and antioxidant activity (Reano et al. 2015). The highest antiradical activities were obtained with saturated esters and sinapic moieties. The saturated ferulic acid-based bisphenols had slightly lower activity, but ferulic acid is easier available than sinapic acid (Reano et al. 2015). Ferulic acid-based compounds were tested in PP and poly(butylene succinate) (PBS) against the commercial benchmark Irganox<sup>®</sup> 1010 (tetrakis-(methylene-(3,5-di-*t*-butyl-*p*-hydroxycinnamate))methane, CAS 6683-19-8), a widely used petrochemical antioxidant. Figure 12.6 sums up the results of the Oxygen Induction Time (OIT) of mixtures of PBS and the bisphenols at different concentrations. The highest OIT was obtained with tris-*O*-dihydroferuloyl glycerol (GTF), and all biobased molecules were more efficient than Irganox<sup>®</sup> 1010 (Reano et al. 2016a). In PP, the results were not favorable for the biobased molecules, because of their low solubility in the very apolar polymer matrix. This problem can be solved, by adapting the polarity of the molecules. For that, a new class of bisphenols based on the glycerol derivatives was designed using fatty acids from vegetable oils. They showed high antiradical power and thermal stability, which makes them potent antioxidant additives for polyolefins (Hollande et al. 2018). The endocrine disrupting activity of the bisphenols was tested in vitro and no estrogenic activity was observed (Hollande et al. 2018). To sum up, lignins are a very promising raw material for high added value substances. They can either be used with only minor preparation or serve as a starting material for chemicals synthesis in the aim to produce novel antioxidants or active packaging materials.



**Figure 12.6.** Antioxidant properties of ferulic acid-based antioxidants (upper part) tested by the Oxygen Induction Time (OIT) (thermogravimetric test) in poly(butylene succinate) recorded as a function of concentration of free phenolic hydroxyls. Irganox<sup>®</sup> 1010 is the petrochemical benchmark. Adapted from (Reano et al. 2016a).

### 12.3. Blending of polyhydroxyalkanoates (PHAs)

In the last decades, numerous studies addressed the development of PHAs and some applications of PHAs exist today in the biomedical field, taking advantage of the biocompatibility of PHAs. PHAs feature high biodegradability in natural environments (even in sea water) (Dilkes-Hoffman et al. 2019). They have some promising properties for larger scale applications in the field of plastics, mainly linked to their high crystallinity, which are high barrier properties to gases compared to other bioplastics and high heat deflection temperature (HDT) (Laycock et al. 2014). Today, the major hurdles for materials applications are a lack of mechanical properties and low thermal stability during plastics processing. The latter point can be partly solved by the use of chain extenders which allow crosslinking of PHA

chains during the processing and therefore maintaining molecular weight or blending strategies, such as blending PHAs with other biodegradable polymers.

### 12.3.1. Introduction on PHAs

Polyhydroxyalkanoates (PHAs), discovered already in the 1920s by Maurice Lemoigne, are fully biodegradable thermoplastic polyesters which are produced by microorganisms as carbon and energy storage compounds in the presence of excess carbon and limited macronutrients, such as oxygen, nitrogen or phosphorus. Depending on the length of number of carbons of the monomer unit, they can be classified in short chain length or medium chain length PHAs. The most prominent group is short-chain-length PHAs, mainly represented poly(3-hydroxybutyrate) P(3HB) and the copolymer P(3HB-co-3HV) (Figure 12.7) (Laycock et al. 2014; Pakalapati et al. 2018).

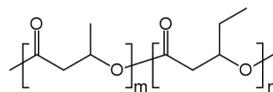


Figure 12.7. Chemical structure of PHBV

The general fabrication process consists in a two-step fermentation, where the first step consists in the microbial growth until obtaining high cell densities and the second step in macronutrient limitation to trigger PHA production and intracellular accumulation. The downstream processing consists in breaking down the microbial cells to liberate the PHA granules and their purification by solvent or surfactant-based extraction techniques. This process is relatively cost-intensive as compared to standard polymer synthesis. Apart from the costs linked to downstream and purification, degrees of freedom for cost reduction are the type of fermentation, pure cultures needing sterile conditions or mixed cultures in non-sterile environments, and the choice of fermentation substrates (pure sugars, byproducts, wastes) (Laycock et al. 2014; Pakalapati et al. 2018).

The pure culture process under sterile conditions of P(3HB) was first patented in 1959 by Grace and Company (Baptist 1965). This process is still in use and the few commercially available PHAs grade are synthesized *via* pure culture fermentation using in most cases *Cupriavidus necator*. PHA production based on mixed cultures offers a viable solution with decreased processing costs, because microbial consortia are stable without aseptic conditions (Laycock et al. 2014). Synthesis of PHAs in mixed cultures was first observed in 1974 in waste water treatment plants designed for biological phosphorus removal (Wallen and Rohwedder 1974). A

supplementary advantage is that mixed cultures are able to adapt to various complex feedstocks, opening the door for cost reductions by using agricultural by-products.

### 12.3.2. Use of agricultural byproducts of PHA production

Production of PHA requires the use of a carbon source as fermentation substrate. However, the cost of the carbon source greatly contributes to the overall cost of PHA production and can be as high as 40% of total operating cost (Leong et al. 2017; Posada et al. 2011). Using carbon sources coming from waste or byproducts of agriculture and food industry is an appealing solution for cost reduction. Furthermore, revalorization of wastes is a possibility to step towards a more circular economy. The change of the carbon source can have but large impact on the productivity of the microbial culture. A tradeoff needs to be reached between cost of fermentation substrates and PHA productivity. This topic has consequently received large industrial and academic interest. For example, (Kumar et al. 2016) used four types of food industry wastes including hydrolysates of pea-shell, apple pomace, potato peels and onion peels. They were tested for PHA production individually or mixed with of pea-shell in different ratios. The authors found that all hydrolysates were suitable for the growth and PHA production by *B. cereus* EGU43 and *B. thuringiensis* EGU45. While biowaste combinations allowed to achieve high PHA yield. The combination of potato peels (PP) and pea-shell (PS) achieved the highest PHB yield but was dependent on the PS:PP ratio where PS:PP 1:2 and 2:1 produced 20 and 405 mg/L of PHB, respectively. Addition of glucose was effective to enhance PHB yield but varied upon PS:PP ratio from 485 to 335mg/L at 1:2+1% glucose supplementation and 2:1+1%G, respectively. In another example, waste water from different fruits and vegetables processing plants were used at carbon sources for PHBV with very high HV content (up to 35 mol%) (Elain et al. 2016),(Lemechko et al. 2019).

Vegetable oils represent another source of inexpensive carbon source to synthesis PHAs at lower cost than carbon source of high purity. Their interest as feedstock is linked to their chemical composition which includes esters of glycerin and high rate of monocarboxylic acids. Olive oil, corn oil and palm oil are reported to be effective to produce the homopolymer poly(3-hydroxybutyrate) using *Cupriavidus necator* H16 (Fukui and Doi 1998). Virgin and waste sesame oil could be successfully used as carbon source for PHBV production by *C. necator* H16 (Taniguchi et al. 2003). Similarly, waste frying oil could be used to to synthesis PHB with homopolymer concentration similar to PHBV from glucose (Verlinden et al. 2011).

Another promising way to obtain PHAs at lower cost comes from microalgae. Microalgae are part of a heterogeneous group of microorganisms, photosynthetic, eukaryotic or prokaryotic, and gram negative (Olaizola 2003). Their photosynthetic behavior offers the ability to use light as source of energy and inorganic nutrients for growth and to synthesize valuable compounds. Species, culture conditions and extraction methods still need to be defined to take full advantage of microalgae as viable source to produce PHAs (Costa et al. 2019).

### 12.3.3. Physical-chemical properties of PHAs

PHAs are rubbery materials at room temperature (glass transition temperature,  $T_g$ , of PHB is typically 5 °C), wherefore they are in literature often compared to polyolefin. Even if the tensile strength is comparable of the yield stress to polypropylene (PP) or polyethylene (PE) (elongation of break typically 400 for PP and 600-700 for LDPE), the elongation at break is largely inferior (Table 12.2). Typically, PHAs attain less than 5 % of maximum elongation, which makes them extremely brittle materials. Also, their impact strength is low, fracture propagating readily through the material. The reason is most likely the occurrence of very large spherulites with poor coupling between crystalline and amorphous phases. The use of nucleating agents for decreasing spherulite sizes was shown to be a successful means for increasing slightly mechanical properties (Laycock et al. 2014). Moreover, physical aging kinetics is fast, bringing about rapid embrittlement of the polymers. The embrittlement is also favored by cold crystallization of PHA, because their cold crystallization temperature is near room temperature (Gérard 2013). The most commonly used PHBV, contains 3 mol% HV and shows a Young Modulus of about 2.9 GPa, a tensile strength of 38MPa and very poor elongation at break of about 3%. The thermo-mechanical properties of PHBV can be tuned by increasing the percentage of HV in PHBV copolymer (Anjum et al. 2016), but even at high 3HV ratios the polymer remains relatively brittle (Table 12.2). PHBV have also a narrow processing window and degrade rapidly upon melting, they have a low shear viscosity and melt elastic strength, which impacts negatively their processability in blow extrusion (Anjum et al. 2016; Cunha et al. 2016). This is strongly limiting the industrial application, because most flexible packaging and thin films are obtained by blow extrusion.

Table 12.2. Thermo-mechanical properties of different PHBV copolymers

Polymer	3HV content (mol%)	Young Modulus GPa	Tensile strength MPa	Elongation at break %	T <sub>m</sub> (°C)	T <sub>g</sub> (°C)	Reference
P(3HB)	0	3.5-4	40	3-8	173-180	5-8	(Anjum et al. 2016)
P3(HB-co-3HV)	3	2.6	32	3.5	167	N/A	(Corre et al. 2012)
	9	1.9	37	N/A	162	N/A	(Anjum et al. 2016)
	15	0.5	11	9	142	-5	(Lemechko et al. 2019)
	35	0.04	1.2	13	150	-12	

#### 12.3.4. Formulation and blending of PHAs with polyesters and PLA

A widely used strategy to improve the thermomechanical properties of brittle polymers consists in blending them with a more ductile material to combine polymer properties in a synergetic way. Moreover, this route can help reducing material costs, since blending a high-cost material with a low-cost polymer will decrease the total cost. Most polymers are immiscible and this leads to phase separation. Depending on blend ratio, different morphology can be developed. When one polymer is in majority, this will lead to a nodular structure where droplets of the minor polymer are dispersed throughout the continuous matrix. When both polymer ratios are close, a co-continuous phase morphology will develop starting from a system-specific threshold ratio. Immiscible blends exhibit two T<sub>g</sub>, corresponding to the properties of each polymer. Only one T<sub>g</sub> will be observed for miscible polymers. In partially miscible blends a shift and/or broadening of the T<sub>g</sub> of both or only one component can be observed approaching both T<sub>g</sub> towards each other. The use of a ductile material is expected to improve the toughness of the overall material. Miscible blends often show an enhancement in modulus and strength over unblended constituent due to specific interactions between both polymers. A positive synergistic effect on mechanical properties of immiscible blends can be obtained, but surface compatibility must be ensured to avoid poor tensile and impact strength (Robeson 2007).

PHBV and PBS obtained by melt-blending showed, although immiscible, significantly enhanced moduli compared to that of the neat PBS and increased elongation at break compared to neat PHBV (Phua et al. 2015).

In particular, the blending of PHAs with poly(lactide), PLA, has received interest, because of the already existing commercial applications of PLA. Blends were tested for the biomedical field (He et al. 2014; Shabna et al. 2014), for mulch films (Dharmalingam et al. 2015), for textiles (Szuman et al. 2016), and for technical applications such as packaging (Boufarguine et al. 2013; Martelli et al. 2012; Tri et al. 2013; Zembouai et al. 2014). The interest of using immiscible blends between PLA and PHB or PHBV is that the PHA can accelerate crystallization kinetics of PLA (Tri et al. 2013) and increase the elongation at break typically up to 40 % (Boufarguine et al. 2013; Gerard et al. 2014; Modi et al. 2013) and up to 60 % with optimized morphologies (Boufarguine et al. 2013). Ternary blend of PLA, PHBV and PBS afforded a good stiffness-toughness balance by improving the toughness and flexibility of PLA (Zhang et al. 2012). The failure mode changed from brittle fracture of the neat PLA to ductile behavior. In that study there was partial miscibility between PHBV and PLA but limited compatibility of both polymers with PBSA. The authors suggested that the optimum performances were obtained for a composition PHBV/PLA/PBSA of 60/30/10 (Zhang et al. 2012). Blends and multilayers were also used to increase the barrier properties of PLA. The dispersion of 10% of PHBV lamellas in PLA induces a decrease of gas permeability, which is slightly more pronounced than, with only 1 thick layer of PHBV in PLA. Indeed the helium permeability decreased from  $120 \times 10^{-18} \text{ (m}^3\cdot\text{m)/(m}^2\cdot\text{s}\cdot\text{Pa)}$  to 77.6 and  $74.3 \times 10^{-18} \text{ (m}^3\cdot\text{m)/(m}^2\cdot\text{s}\cdot\text{Pa)}$  with 3 and 129 layers, respectively (Boufarguine et al. 2013).

To overcome the negative effects induced by immiscible polymer blends, compatibilization is usually used to improve the mechanical properties due to enhanced interfacial adhesion, which helps stress transfer across the interface. Moreover, the morphology will tend to finer structures with a large decrease in nodule size by preventing coalescence between particles as illustrated in Figure 12.8. Immiscible polymer blends can be compatibilized by *in-situ*/reactive compatibilization by a third component which contains a reactive functional group (i.e., anhydride, epoxy, etc.) which will react with blend constituents (Utracki 2002). PHBV/PBS (80/20) compatibilized *via* *in-situ* reactive extrusion using dicumyl peroxide (DCP) as radical initiator improved already at a DCP content of 0.5 wt% dramatically the mechanical properties compared to not compatibilized blends (Ma et al. 2012). The morphology was much finer. The strain-stress behavior changed from a brittle to a ductile behavior with an elongation at break increased from 8 to 400 %. This improvement was attributed to the formation of PHBV-*g*-PBS copolymer, which was assumed to be located at the interface between the polymers and thus act as compatibilizer (Ma et al. 2012). DCP was also used for the compatibilization of PLA/PHBV (Dong et al. 2013). DCP improved the melt strength of the blends through partial

crosslinking which was further confirmed by improved melt viscosity. The blends had enhanced impact strength and impact toughness from about 13 to 20 kJ.m<sup>-2</sup> after addition of 0.5wt% DCP in PHB/PDLLA (70/30) blend (Dong et al. 2013).

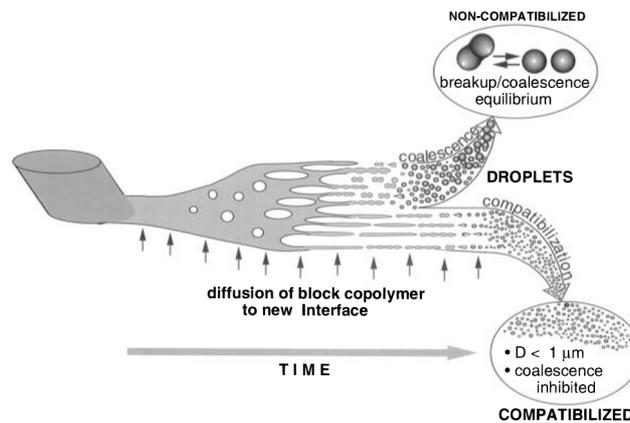


Figure 12.8. Schematic of morphology development during melt blending. As pellets or powder of the minor phase soften, layers peel off. These stretch out into sheets which break up into fibers and then droplets. Reprinted with permission from (Macosko et al. 1996). Copyright (2020) American Chemical Society.

## 12.4. Safety of formulated biobased and biodegradable Food Contact Materials

### 12.4.1. General principles and binding regulations

**US legislation** The biological origin of the polymer or its ability to be degraded by microorganisms does not preclude the obligation of testing the suitability of the proposed material for food contact. According to section 201(s) of the FD&C Act (FEDERAL FOOD, DRUG, AND COSMETIC ACT, last revision June 24, 2019), possible contaminants originating from food contact materials (food contact substances are defined specifically in section 401(s) of the FD&C Act) are called indirect additives and correspond to any substance, which may reasonably become a component or otherwise affects the characteristics of any food. Substances that are generally recognized by experts, qualified by scientific training and experience, to be safe under the conditions of its intended use are exempted. With this respect, incorporating food components into the packaging material as filler, plasticizer, adhesive, or antioxidant could be exempted from any restriction and preferable to the use of alternative synthetic substances. However, because a pesticide chemical residue in or on a raw agricultural commodity or processed food requires a specific approval, the safety of agricultural by-products and possibly of by-products originating from food production should always be established.

Scientific procedures include the application of scientific data (analytical, calculations, simulations, or other scientific studies), information, and methods, whether published or unpublished, as well as the methods to evaluate the toxicology and the chronic exposure of consumers. In short, if it is impossible in the present state of scientific knowledge to establish with complete certainty the absolute harmlessness of the use of any by-product, a safety assessment should be carried out. In determining safety, the probable ingestion of the substances originating from the considered by-products must be considered, as well as its cumulative effect of the substance in the diet, considering any chemically or pharmacologically related substance or substances in such diet.

**EU legislation** The EU framework is built on very similar foundations (safety requirements for the manufacturing, processing, and distribution of food contact materials), but with different conditions of application. General safety requirements lay down by Regulation (EC) No 1935/2004) apply to any of the seventeen groups of materials identified by the EU Commission, and for which specific measures exist already or could be applied in the future (see Annex I of Regulation 1935/2004/EC). As a general rule, all food contact materials and articles should be manufactured in compliance with good manufacturing practice (further defined in Regulation (EC) No 2023/2006), so that, under normal and foreseeable conditions of use, they do not transfer their constituents to food in quantities that could endanger human health, bring about an unacceptable change in the composition of the food, or a deterioration of its organoleptic characteristics. Such rules do not exist for today for materials incorporating by-products originating from agriculture or food production. They are aimed at strengthening the self-assessment and responsibility of the manufacturers, processors, and distributors of food contact materials and components.

The concept of specific measures is essential in the EU legal system as it encourages the harmonization at EU level generally towards the highest standard among all member states. The adoption of such specific measures lies with the European Commission, which may adopt such measures but is not obliged to do so. In most cases, specific measures are adopted via the “regulatory procedure with scrutiny” in which the European Parliament plays a scrutiny role. Without being exhaustive, the specific measures include the list of authorized substances (positive list), purity standards and special conditions of use for positively listed substances, specific and/or overall limits on the migration of certain constituents into the food, basic rules for checking compliance with the harmonized rules, authorization procedure for substances not yet in the positive list. In short, what is not accepted should not be used without asking for an

authorization at the European Food Safety Authority (EFSA). As a general rule, EFSA has six months to issue its opinion as to whether, under the intended conditions of use of the material or article in which it is used, the substance complies with the general safety requirements of the framework Regulation 1935/2004/EC. If the opinion is favorable, EFSA will publish an opinion including the designation of the substance and its specifications, recommendations or restrictions of use, an assessment of the analytical method, and/or calculation method used for risk assessment. From 2004 to 2015, EFSA has evaluated 348 substances (Karamfilova and Sacher 2016).

**Specific measures and specific migration limits in the EU** The level of harmonization at the EU level is far from being complete. Specific measures exist so far only for plastics and recycled plastics, ceramics, regenerated cellulose film, active and intelligent packaging. For other groups of materials such as rubbers, silicones, textiles, paper and board, printing inks, adhesives, coatings and varnishes, waxes, and wood, such measures may exist at national level. The principles of safety assessment for plastic materials used alone or in multilayers are summarized in Figure 12.9. For accepting a new substance, the level of the studies depends on the expected level of migration, that is to say on the level of mass transfer to the food in contact. Once the substance is accepted, the level of migration must be lower than the overall migration limit ( $60 \text{ mg}\cdot\text{kg}^{-1}$  or  $10 \text{ mg}\cdot\text{dm}^{-2}$ ) and the eventual specific migration limit (SML). The value of the SML is inferred from toxicological data and a conservative chronic exposure scenario for an adult of 60 kg ingesting 1 kg of food packed in  $6 \text{ dm}^2$ . SML can be verified by migration testing or by migration modeling (Zhu et al. 2019b).

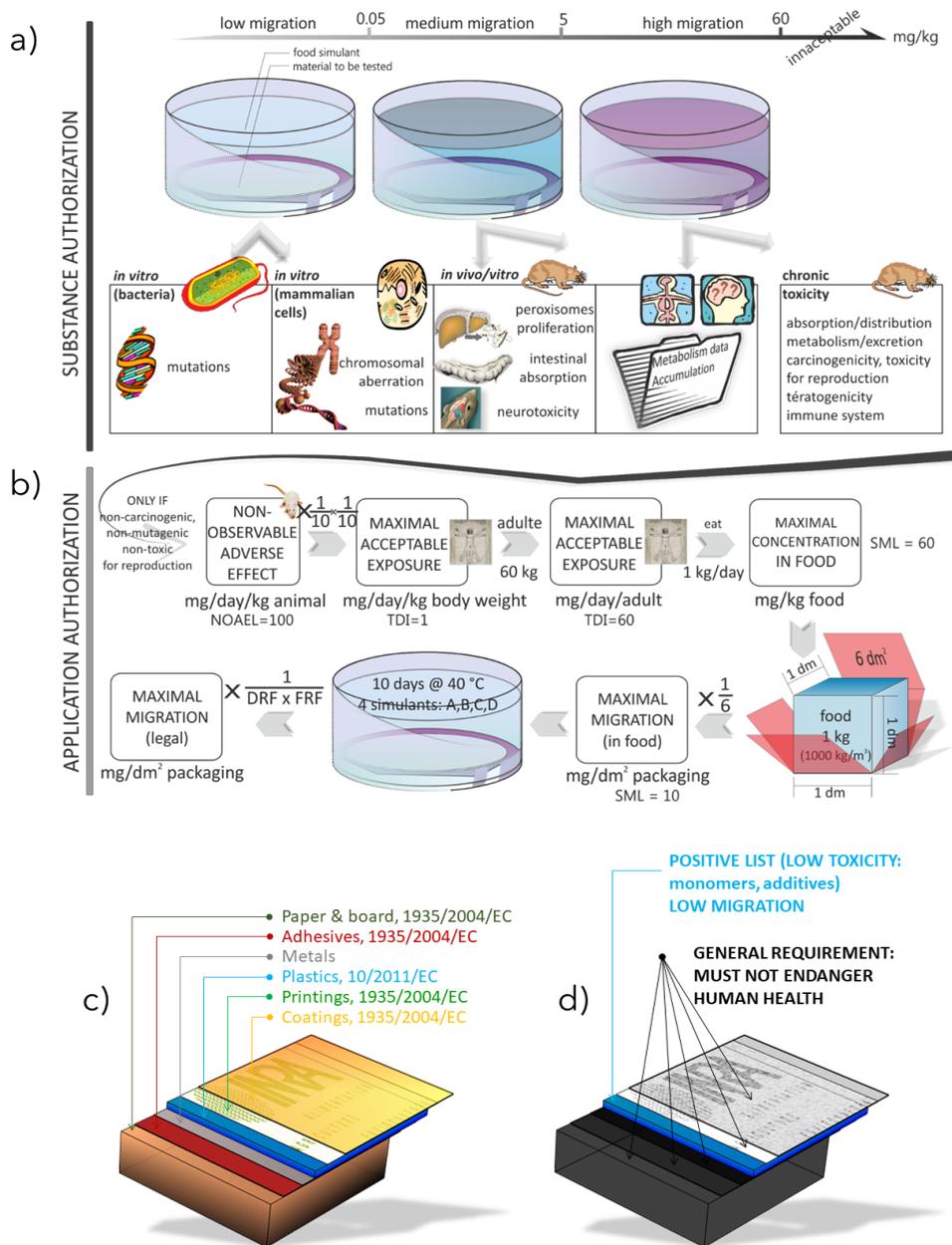


Figure 12.9. Principles of safety assessment applied in EU (a) for the authorization of new substances, (b) for the verification of specific migration limits, (c-d) principles in multimaterials (here a laminate intended to be in contact with food). DFR = Simulant D Reduction Factor, FRF = Fat Reduction Factor, NOEL = Non-Observable Adverse Effects Level, TDI=Tolerable Daily Intake.

**Overall migration limits (OML) in the EU** OML provide a global assessment of the inertia of food contact materials by assessing the total amount of non-volatile substances transferrable to the food. OML testing is achieved out by weighting the packaging before and after packaging. The methodology is not sufficiently accurate to be related to specific migration limits, and the standard conditions (OM1..OM7) are not any more related to time and

temperature conditions used to determined SML. The overall migration limit for plastics is 60 mg·kg<sup>-1</sup> for children or infants and can be replaced by the limit of 10 mg·dm<sup>-2</sup> in other cases.

**Table 12.3.** Test conditions for evaluating overall migration limits

Test code	Food contact conditions	Test conditions
OM1	Any food contact at frozen and refrigerated conditions	10 days at 20 °C
OM2	Any long-term storage at room temperature or below, including heating up to 70 °C for up to 2 h, or heating up to 100 °C for up to 15 min.	10 days at 40 °C
OM3	Any contact conditions that include heating up to 70 °C for up to 2 h, or up to 100 °C for up to 15 min, which are not followed by long-term room or refrigerated temperature storage	2 h at 70°C
OM4	High-temperature applications for all food simulants at temperature up to 100 °C	1 h at 100°C
OM5	High-temperature applications up to 121 °C	2 h at 100 °C or at reflux or alternatively 1 h at 121 °C
OM6	Any food contact conditions with food simulants A, B, or C, at temperatures exceeding 40 °C	4 h at 100 °C or at reflux
OM7	High-temperature applications with fatty foods exceeding the conditions of OM5	2 h at 175 °C
OM8	High-temperature applications without storage as alternative to OM1, OM3, OM4, OM5, and OM6	Food simulant E for 2 h at 175 °C and food simulant D2 for 2 h at 100 °C
OM9	High-temperature applications with long-term storage as alternative to OM1, OM3, OM4, OM5, and OM6	Food simulant E for 2 h at 175 °C and food simulant D2 for 10 days at 40 °C

Food simulants: A (10% ethanol), simulant B (3% acetic acid), simulant C (20% ethanol), simulant D1 (50% ethanol), and simulant D2 (vegetable oil).

### ***Sensorial evaluation***

The risk of deterioration of organoleptic characteristics needs to be verified, in particular, for bio-sourced and biodegradable components of the food packaging. The risk of aging, hydrolysis, and interactions with food are particularly high at all stages of its processing, storage, and final use. No specific guidance has been proposed to perform sensorial tests, but it is recommended to perform the evaluation on the food in worst-case conditions rather than on food simulants. The tests should be carried out in a way to detect off-flavors, bad taste or odors. Triangular tests are the most used by the industry (two samples are identical) as they enable the evaluator to identify easily false positive.

#### **12.4.2. What is acceptable according to EU rules for thermoplastics**

Though it has been constructed initially for synthetic substances, Regulation (EC) No 10/2011 for thermoplastics evolved progressively to integrate bio-sourced additives, monomers and more recently polymers obtained by fermentation. Criteria of purity prevail and currently, the concept of GRAS (generically recognized as safe substances) does not hold. For plastics obtained by microbial fermentation recovered with or without subsequent solvent extraction, it is stated that “potential health risk may occur from the migration of non- or incompletely reacted starting substances, intermediates or by-products of the fermentation process. In this case, the final product should be risk assessed and authorized before its use in the manufacture of plastic materials and article”. Among the 885 positively listed initial substances, 314 additives or monomers can be obtained by fermentation, but only one polymer (3-hydroxybutanoic acid-3-hydroxypentanoic acid, copolymer, *i.e.* PHBV) has been authorized. Current authorization requires this polymer to be produced by the controlled fermentation of *C. necator* (formerly *Alcaligenes eutrophus*) (strain H16 NCIMB 10442) with mixtures of glucose and propanoic acid as carbon sources.

In the general case and without prior authorization, by-products and bioproducts could be used in finished products under the same conditions, which have been accepted in general terms for recycled material. Materials or articles could incorporate non-listed substances, when they are present behind a plastic functional barrier, preventing them to migrate in detectable amounts. The limit of detection is set to 0.01 mg·kg<sup>-1</sup> and it excludes any mutagenic, genotoxic or reprotoxic substance as well as aggregates or molecular systems intermediate between dispersed solutes and nanoparticles. It is finally emphasized that other specific measures are not yet adopted at EU level and the complete requirements for multimaterial and/or multilayer materials and articles should be verified on a case-basis for each member state, based on their own national provisions.

#### **12.5. The design of materials incorporating by-products, bioproducts or polymers obtained by fermentation**

The evaluation by EFSA, FDA and other bodies of biobased and biodegradable materials used alone or as components shows various risks summarized in Table 12.4. The burden to find a compromise between many characteristics including risk assessment, food shelf-life, environmental impact, processing and retailing conditions can be found by using rapid

engineering methods of packaging design. Failure Mode Effects and Critical Analysis (Nguyen et al. 2013) has been successfully applied to packaging design along with rapid environmental prototyping methods (Zhu et al. 2019a). The methods are particularly capable to tackle the risk of cross-contamination in presence of complex supply chains (Nguyen et al. 2019; Nguyen et al. 2017). The software and databases parts of open-source projects (Vitrac 2015; Vitrac and Nguyen 2018) and a European initiative for massive online courses (Vitrac 2019).

**Table 12.4.** Critical risk associated to the use of by-products, bioproducts or polymers obtained by fermentation

<b>Issue</b>	<b>Possible corrective action</b>
Lack of control on the purity of raw materials: presence of residues	Specific control plan, purification, avoiding uncontrolled sources in fermentation, adding a functional barrier
Extensive of chemical solvents	Solvent substitution, extraction at solid state, solvent drying
Strong sensitivity to humidity (e.g. the properties in humid conditions differ from those in dry ones)	Restriction to dry food, avoiding frozen and chilled conditions, avoiding cooking and heating conditions
Rapid hydrolysis or oxidation during storage	Controlling storage time and temperature before use; food products with short shelf-life; dry food.
Strong interactions with the fat content of food	Restriction to dry food, non-processed food, over packaging
Lack of barrier properties to adhesive and ink components	Avoiding printing and laminates.
Plasticized formula with high risk of migration	Avoiding the use of plasticizers, high temperature

## 12.6. Conclusion

The discussed examples show that numerous studies were already carried out in the field of valorization of agricultural byproducts for increasing functionality of packaging materials, and that those approaches can have equal or higher performance than actually used technologies.

The development of functional additives for packaging polymers or packaging polymers themselves starting from byproducts of the agriculture and food industry holds high potential for the transition of the manufacturing industry towards increased use of renewable resources and the possibility for agriculture and food industry to develop novel value-added substances. Agricultural and food industry, today users of packaging materials and the included chemicals could thus become suppliers of those products. This would close the circle of fabrication, utilization, recycling and re-fertilization of soils by biodegradation for the production of new biomass used to prepare new packaging materials. This would be clearly a step towards circular economy.

However, many technological hurdles need yet to be overcome to develop the academic experiences to industrially viable products, such as standardization and quality management of raw materials which are today wastes, scale-up of production processes, and very importantly ensuring safety of the raw materials and packaging. Safety and legislative requirements need to be considered in the early steps of development, to design a novel generation of packaging safer for consumers and environment.

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