

EDITOR

Pierfrancesco Morganti

Dermatology Unit, University of Campania “Luigi Vanvitelli”, Naples, Italy;

China Medical University, Shenyang, China;

Director of the R&D Nanoscience Centre MAVI, MAVI Sud Srl, Aprilia (Lt), Italy.

Editorial Office

MDPI

St. Alban-Anlage 66

4052 Basel, Switzerland

For citation purposes, cite each article independently as indicated below:

LastName, A.A.; LastName, B.B.; LastName, C.C. Chapter Title. In *Bionanotechnology to Save the Environment. Plant and Fishery's Biomass as Alternative to Petrol*; Pierfrancesco Morganti, Ed.; MDPI: Basel, Switzerland, 2018; Page Range.

ISBN 978-3-03842-692-9 (Hbk)

ISBN 978-3-03842-693-6 (PDF)

doi:10.3390/books978-3-03842-693-6

Cover image courtesy of Pierfrancesco Morganti.

© 2019 by the authors. Chapters in this volume are Open Access and distributed under the Creative Commons Attribution (CC BY 4.0) license, which allows users to download, copy and build upon published articles, as long as the author and publisher are properly credited, which ensures maximum dissemination and a wider impact of our publications.

The book taken as a whole is © 2019 MDPI under the terms and conditions of the Creative Commons license CC BY-NC-ND.

Flexible Food Packaging Using Polymers from Biomass

Maria-Beatrice Coltelli, Vito Gigante, Patrizia Cinelli and Andrea Lazzeri

Abstract: The use of polymers from biomass in the production of flexible packaging is an important challenge to give an answer to both the reduction of oil-derived materials and the increase of waste production. Oil-derived materials are now employed in recyclable packaging, but, although the management of waste recycling is improving, it cannot allow the complete mechanical recycling of the plastic fraction. It would be important to optimize the system by replacing packaging difficult to be recyclable, such as multi-layer flexible packaging mainly based on the use of polyolefines, with alternative packaging consisting of biodegradable materials, thus managing its disposal by considering composting. In the present paper, a classification of polymeric materials available from biomass for flexible packaging is reported. Moreover, the biodegradable and renewable materials investigated or yet employed in this sector are described. In addition, some insights on the actual production of flexible packaging is given, to describe also what technical specification the polymers from biomass should have to replace commodities. Finally, the perspectives in the field of flexible packaging for polymers from biomass are discussed.

1. Polymeric Materials from Biomass

As material scientists, we often need to study and select the best material for a specific application. In many cases, especially for applications requiring the combination of lightness and resistance, polymeric materials are quite interesting, as well as blends or composites obtained by using them blended with other polymers or with inorganic or organic fillers.

In fact, polymers, with respect to other materials, show a higher versatility due to the possibility of modulating their macromolecular structure by controlling the industrial synthesis in order to achieve specific final properties.

The structural materials selected by nature in plants and animals are based on polymers too. The main structural polymer for plants is cellulose, a polyether, which is the polymer of D-glucose having each repeating unit linked to the following one by a $\beta(1-4)$ -linkage. The main structural polymers for animals are proteins, characterized by a polyamide structure.

In general, polymers can be natural, artificial or synthetic (Table 1). An example of a natural polymer is cellulose, contained in paper or cotton fabric; among

natural polymers are also the polymers produced by microorganisms, such as poly(hydroxyalcanoates) (PHAs). An example of an artificial polymer, obtained by chemical modification of natural polymers, is cellulose acetate, a plastic material, or cellulose xanthate, a fiber for textile applications, or nitro-cellulose, which can be an explosive, but with a low degree of nitration is employed in varnishes and enamels in the cosmetic sector [1].

The natural and artificial polymers show the advantage of being renewable; that is, they are obtained not from petrochemical resources but from natural sources.

Examples of synthetic polymers are given, in the packaging sector, by the so-called commodities, consisting in polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET) or polystyrene (PS).

Currently biosynthetic polymers are distinguished from synthetic polymers because they were industrially produced by traditional polymerization methods, but starting from monomers available from natural sources [2]. Hence they are renewable. Poly(lactic acid) (PLA) is an example of biosynthetic polymer. The advantage of biosynthetic polymers with respect to natural and artificial polymers is the possibility of controlling the primary structure of the polymer and consequently its processability and its properties.

Table 1. Classification of polymers with respect to renewability and biodegradability.

Class	Renewability	Biodegradability
natural	YES	YES ^a
artificial	YES ^b	POSSIBLE
synthetic	NO	NO ^c
bio-synthetic	YES	YES/NO

^a although some evaluations about it were made [3], natural rubber cannot be considered biodegradable; ^b the renewability of the chemicals used for modification should be considered as well; ^c some petrochemical-based polymer are biodegradable.

From the point of view of biodegradability [4,5] usually natural polymers are biodegradable where biodegradability is the capability of resulting in the complete oxidation in the environment giving CH₄, CO₂ and other simple compounds. This is typical of all polymers, but for synthetic polymers very long times—centuries—are required (Figure 1). Artificial polymers can be biodegradable, but usually it depends much on the degree of chemical modification reached. For instance, cellulose acetate, that can have an acetylation degree between 0 and 3, is reported to be biodegradable with an acetylation degree below 2.5 [6]. Biosynthetic polymers are usually both bio-based and biodegradable, such as PLA, but also polymers defined as synthetic, such as PE, traditionally obtained by petrochemicals, can now be produced from natural sources. These polymers are not biodegradable.

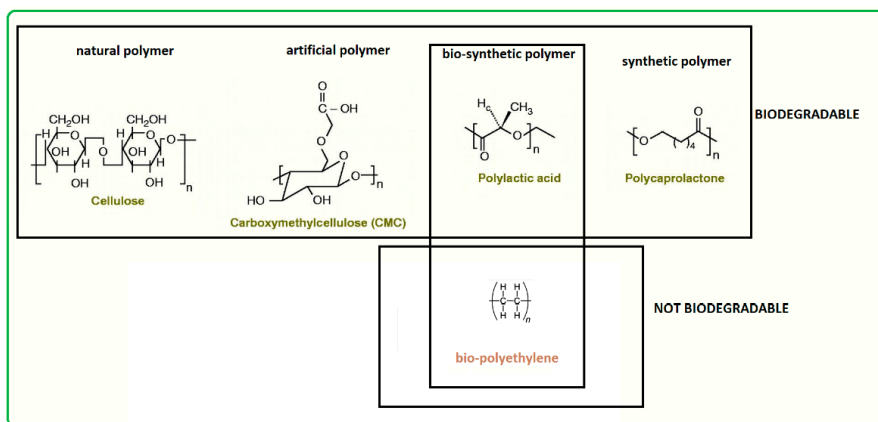


Figure 1. Scheme related to bioplastics with examples of specific polymers.

In addition, in bioplastics also the polymers currently not yet synthesized by biotechnology but from not biobased monomers, such as poly(butylene succinate) (PBS), polycaprolactone (PCL) and poly(butylene adipate-co-terephthalate) (PBAT) et cetera, are included, because they are biodegradable. The bioplastics family thus regroups polymers coming from renewable and/or biodegradable sources [7].

In the field of packaging, the most interesting options for polymers in applications depend much on the end-life option [8,9]. While in durable applications biodegradability is not an interesting property, in the food-packaging sector it could be so, especially if the perspective of composting is selected for the waste packaging.

More important than biodegradability is compostability. The latter is related to the capability of a material to effectively be disintegrated because of microorganism activity in the environment in standard conditions. Biodegradable and compostable products should be certified according to EN 13432/14995 standards [10,11], defining procedures for testing the effective compostability, granting the correct behavior of the material in the composting plants.

The other possible option for packaging management is recycling, which requires the possibility of separating the different polymers, avoiding contamination as well as good durability of the plastic material, especially in re-processing conditions. Thus, it is an option suitable for mono-material packages.

2. Commercially Available Polymeric Materials from Biomass

In considering bioplastics that can be employed in flexible packaging preparation, polymers produced on an industrial scale and yet available in the market and validated in processes commonly used in plastic industry have to be taken mainly into account.

Two different types of basic formulations were developed on a mature technological level: starch-based materials and poly(lactic acid) (PLA)-based materials.

Starch is a natural polymer, consisting of amylose and amylopectin, with the former being linear and water soluble, and the latter branched and water insoluble. The processing of starch was possible some decades ago by controlling the plasticizing effect of water [12], culminating in the thermoplastic processing of starch at approximately its natural water content (about 15%) at a temperature of about 100 °C. Amorphous thermoplastic starch (TPS)-based polymers were thus obtained. An important characteristic of thermoplastic starch formation is the thermal and mechanical (shear-based) destructuring of the starch granules to form a homogeneous melt, the formation being accompanied by swelling. In particular, the gelatinization of starch occurs [13] thanks to the processing, in which the starch granules become swollen and destructured and lose amylose by diffusion. This process, having a typical temperature dependent on the water content, results in the destruction of amylopectin crystallites and molecular order in the granules. The gelatinization represents an undesired state. Hence the range of temperature for processing is superiorly limited by the gelatinization point. From a rheological point of view TPSs show the possibility of being processed only in a restricted screw speed range, but in that range the behavior is shear thinning, similar to the one of low density polyethylene, with apparent viscosity decreasing with the increase of screw speed [14]. Destructured starch behaves as a thermoplastic polymer and can be processed as a traditional plastic; when alone, however, its sensitivity to humidity makes it unsuitable for most of the applications. The main use of destructured starch alone is in soluble compostable foams such as loose-fillers, and other expanded items as a replacement for polystyrene.

The attaining of processable starch-based formulations suitable for flexible film production was possible by blending starch with thermoplastic hydrophilic synthetic polymers such as poly(caprolactone) [15] and poly(ethylene-vinyl alcohol) [16]. Usually plasticizers such as glycerol [17] or polyethylene glycols [12] are used for optimizing TPS processing. Cassava, also known as manioc or yucca, is a plant producing tuberous roots, typical of South America. Ezechia et al. [18] reported the preparation of cassava starch-based formulations employed for preparing films by blown film extrusion. The films were obtained by adding poly(vinyl alcohol) (PVA), which is the matrix in the system. Ali et al. [19] also reported the preparation of films for packaging containing starch, but these films consisted mainly of polyethylene. However, in general it is not possible to employ starch for packaging films without blending it with plasticizers and polymers. The granules available on the market and widely employed for soft packaging, especially for pouches, were developed by considering this approach. NOVAMONT, which is the main producer of MATER-BI material, also follows this approach, but using renewable

and biodegradable self-produced additives. These intermediates are produced by vegetable oils and are defined polymeric complexing agents [20]. In fact, they interact with the starch, incorporating it. Hence the processing and mechanical properties were easily modulated and the starch is protected by environmental humidity by the barrier properties of the host polymers/additives.

Another promising material for packaging application, because of its cost, which is now not much higher than the one of PS (at about 2 €/kg in Europe [21]), is poly(lactic acid) (PLA), which is renewable and biodegradable. Because of its rigidity it is not suitable alone for flexible packaging applications. However, commercial granules suitable for flexible packaging applications are available. In fact, in the last decade, many studies were carried out about PLA blends with other biodegradable polyesters or plasticizers. Plasticized and nano-filled films were prepared by flat die extrusion by Scatto et al. [22]. The rheological measurements carried out by capillary viscometer suggested that the processability of plasticized and nano-filled PLA is suitable for the industrial production of cast films. Plasticization reduces the glass transition temperature of the plastic material, making it ductile at room temperature. A good miscibility of the plasticizer is important, to avoid demixing and loss in transparency of films. Moreover, the plasticizer should not migrate out of the film. The production of film based on PLA, biodegradable plasticizers and nano clays was investigated in the running EC project DIBBIOPACK "Development of injection and extrusion blow molded biodegradable and multifunctional packages by nanotechnologies" [23].

Blending with other commercial polymers is also another possibility for increasing PLA flexibility. Blends of PLA and poly(butylene adipate-co-terephthalate) (PBAT) show a good flexibility and ductility in a proper composition range [24,25]. The addition of a plasticizer to PLA/PBAT blends can also provide a further alternative for properties modulation [26].

The use of chain extenders [27] or peroxides [28] can be also important for modulating rheological properties introducing an increase in melt viscosity, some branching and hence a shear thinning behavior.

Blends of PLA and PBS were also studied [29,30] for application in flexible film preparation, thanks to the good compatibility between these polyesters.

Many companies are developing new PLA-based formulations of granules suitable for flexible packaging applications and many different granules can be found in the market. The formulations are often very complex, as they contain fillers, such as calcium carbonate or talc, or nucleating agents, to control crystallization of PLA during processing by increasing resistance without compromising the transparency of films. Our research unit has recently developed novel copolymers consisting of PLA, organic plasticizers with epoxy functions and biodegradable elastomeric polyesters, which allows the production of transparent PLA-based

films, maintaining compostability [24,31] and activities for exploiting this know-how producing commercial granules are ongoing.

3. Production of Flexible Packaging by Using Biobased Polymers

The production of flexible packaging is based on the preparation of films. Plastic films and multilayer systems can be manufactured using different converting processes such as blown film extrusion, flat die extrusion, extrusion coating, extrusion laminating and co-extrusion. These processes have advantages and disadvantages depending on the material type in use, the width and thickness of film and the required film properties. The use of starch or biopolyester in such processes introduced some modification with respect to the use of polyolefins (high density poly(ethylene)—HDPE and low density poly(ethylene)—LDPE) and PET. Biopolyesters showed a processability similar to traditional plastics. The control of humidity of biopolyesters is significant for limiting the increase of melt fluidity due to chain scission, hence industrial plants must be equipped with proper drying sections. In this equipment usually biopolyester pellets are heated in presence of a dried air flow, with a low dew point, maintaining them stirred [32] to avoid undesired agglomeration, before extrusion.

One of the most commonly employed methods for preparing plastic film is blown film extrusion [30,33]. The produced film is tubular, hence this process is usually employed for the production of pouches, industrial bags or packaging films for shrink wrapping. The necessary industrial equipment consists of an extruder equipped with an annular die. The blown film process involves the biaxial stretching of annular extrudate to make a suitable bubble according to the product requirements. During this film-blowing process, the molten polymer from the annular die is pulling upward applying the take-up force; air is introduced at the bottom of the die to inflate the bubble and an air ring is used to cool the extrudate. The nip rolls are used to provide the axial tension needed to pull and flatten the film into the winder (Figure 2). The speed of the nip rolls and the air pressure inside the bubble are adjusted to maintain the process and product requirements. At a certain height from the die exit, molten polymer is solidified due to the effect of cooling followed by crystallization, and a freeze line height (FLH) can be observed. Above this point the bubble diameter is assumed to be constant.

Bubble size is maintained by controlling the air through a hole in the die face. Addition of air inside the bubble will expand it to a larger diameter and vice versa. This inflation process will stretch the bubble in the circumferential direction (CD). The ratio of this expanded bubble diameter and the die diameter is defined as blow-up ratio (BUR). To pull the extrudate in the upward direction, an axial force is applied by means of nip rollers and hence another stretching in the axial or machine direction (MD) occurs. Draw-down ratio (DDR), which is another important process variable

is defined as the ratio of the linear speed of the film at the nip rolls and the average melt velocity at the die exit. Melt rheological properties are important in the blown film extrusion to determine the processability, shape and stability of the film bubble and the onset of surface roughness.

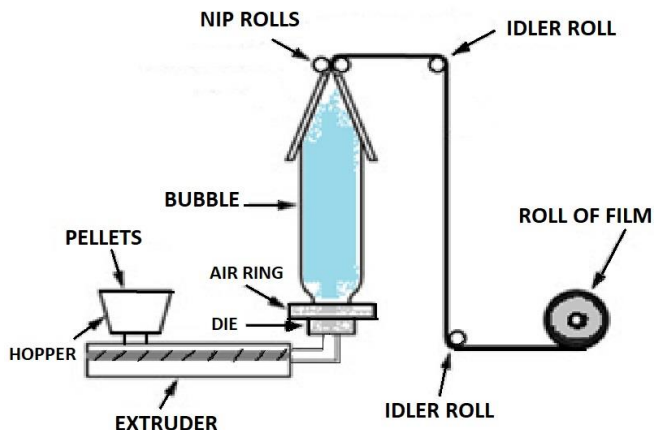


Figure 2. Schematic diagram of the blown film process.

Usually the polymer employed in this process for film production is low-density polyethylene (LDPE) or linear low-density polyethylene (LLDPE). The degree of branching and the length of the branching are particularly important for the success of the process. Generally, a high short chain branching of LDPE influences much the capability of crystallizing of the polymer, much influencing the mechanical and optical properties of the film. A polymer having a more irregular structure is thus more transparent. Long chain branching (LCB) is usually necessary because, considering the rheological behavior, it is correlated to shear thinning (viscosity decreasing by increasing shear rate in a stationary flow) and tension thickening (viscosity increasing by increasing the extensional flow) [34].

PLA-based materials show generally a melt fluidity too high to be processed in these plants. Usually chain extenders are used to improve the viscosity of the melt and the melt strength to allow the production of films, and commercial ones are available on the market [35]. Lazzeri et al. developed a patent to produce transparent PLA-based blends containing an epoxidized molecule acting both as plasticizer, compatibilizer and fluidity regulator [24], thus allowing a good control of processability and final properties. With respect to traditional polyolefins, the tearing strength of these blends should be improved. Recently it was evidenced that by using the epoxidized molecule in combination with a nucleating agent it was possible to improve the tearing strength of the blends [36] reaching values comparable to those of PP.

Flat die extrusion consists of an extrusion through a linear die of adjustable thickness (die gap) usually between 3 and 1.4 mm. This technology allows the production of polymeric sheets and films (with thicknesses ranging from 50 microns to a millimeter) and consists of the extrusion of the molten polymer through a die of rectangular geometry. The geometry generally used for the flat die distribution channel is the coat hanger die. The material comes out from the die in the form of a molten plate that is immediately in contact with a thermostatic roller to allow cooling and solidification. Due to the motion of the roller, the film undergoes elongation with a consequent reduction in thickness. The film then passes through a second roller and to a measuring, cutting and winding station.

The operating parameters to be controlled during flat die extrusion are the extrusion and windup rolls temperatures, distance between die and the first roll and the draw ratio (ratio between windup roll speed and polymer speed at the die exit).

All of these parameters have a big influence on the final product characteristics (morphologically and mechanically). (Figure 3).

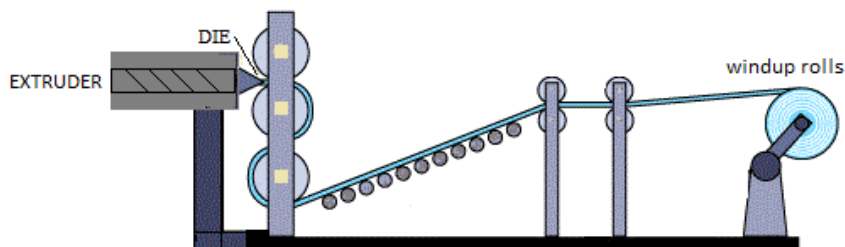


Figure 3. Schematic diagram of the flat die extrusion.

In flat die extrusion, as well as in blown extrusion, the necessity of increasing the melt viscosity of PLA-based blends is often an issue, but usually melt fluidity values higher than those adopted in the blown extrusion are suitable for this processing technique.

Films produced through this technique (Figure 3) can be used in flexible packaging and they can be used also in multilayer systems. Diaper top-sheets are generally made by using polyolefins with a specific patterning of holes on the surface allowing the controlled passage of liquids through the film. Currently the ongoing POLYBIOSKIN European project [37] is active in developing a diaper top-sheet based on biobased formulations to replace traditional ones. The final objective is developing diapers completely compostable and with improved compatibility with skin. Hence PLA-based granules are selected and processed by flat die extrusion to obtain flexible films (Figures 3 and 4).



Figure 4. Flat die extrusion of PLA (**left**) and flat die extruded films based on PLA/PBAT blends (**right**).

Extrusion coating consists of the extrusion of a film of plastic onto a preformed film made of plastic, cellulose or aluminum, hence it is a technique suitable for multilayer packages. The current process of extrusion coating involves extruding resin from a slot at temperatures up to 300 °C directly onto the moving substrate. The control of velocity at which the substrate runs allows to control the coating thickness. High extensional flows are encountered at non-isothermal conditions, especially in industrial conditions requiring higher and higher output speeds. Currently it is very difficult for biopolyester-based materials to have the suitable processing properties in terms of fluidity and melts strength typical of polyolefins to perform extrusion coating in industrial plant currently used for producing PE/aluminum bilayer typical of the most employed multilayer packages such as TETRAPACK [38].

Coating of plastic films with water-based solution containing whey was studied in the framework of the WHEYLAYER European project [39]. The project results showed that the layer made of whey, coming from the waste cheese industry, a protein in between other polymeric films (for instance PET and PE films), allowed separation of different materials in a water bath containing enzymatic detergents [40]. Hence a multilayer package allowing the full recovery and recycling of all the polymeric components was developed in the framework of this project. Moreover, the whey layer shows interesting barrier properties towards oxygen.

Another technique for producing multilayer packaging is extrusion laminating. It is similar to the extrusion coating process except that the extruded melt polymer acts as the adhesive to a second film of material (Figure 5). Specific scientific papers about this technique could not be found. In any case, in this sector, the development of biodegradable glues is an interesting topic of current research [41].

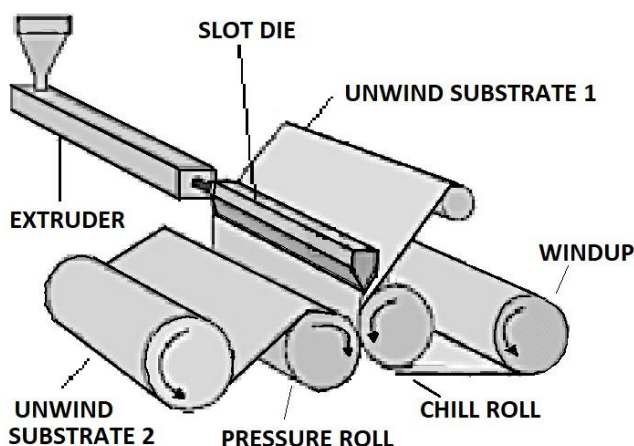


Figure 5. Schematic diagram of extrusion laminating.

Co-extrusion is a similar process to extrusion coating but with two or more extruders coupled to a single die head in which the individually extruded melts are brought together and finally extruded as a multi-layer film. In this case, the viscosity differences between the different layers are of critical importance to avoid distortions of the produced multilayer system. Regarding this process applied to bioplastics, only a patent reported the co-extrusion of PLA with poly(ethylene-co-vinyl acetate) (EVA), a not biodegradable polymer, to obtain multilayer films [42]. Certainly the study of processes allowing to obtain completely biodegradable systems would be useful.

In general, for the processing of biobased polymers, structural and rheological properties of extruded polymers are fundamental for optimizing industrial processes. In general, as stated above, usually for extrusion coating, less viscous polymer melts are required than for blown film extrusion, but a polymer having proper shear thinning and tension thickening behavior must be selected to avoid instabilities and defects thus avoiding the breakage of the film, leading to the undesired interruption of the industrial production [43].

Regarding the processing of starch-based materials, the method based on blown film extrusion is quite common. In fact, the commercial starch-based materials are used for producing pouches and shopping bags. The use of these bags to replace polyolefin ones is supported by EU regulation [44]. Regarding the processing of PLA, films are produced by flat die extrusion [37] or blown film extrusion [36].

4. Innovative Plastic Formulations for Flexible Packaging

Innovative biopolymer-based materials are developed by academics and companies all over the world. Many studies are focused on improving the

properties of starch or PLA-based formulations, but also in fostering the use of other biopolymers by making easier their preparation and finding new applications or also by trying to develop new materials employing natural abundant polymers such as polysaccharides (cellulose or chitin) or proteins. In both cases the studies are focused onto waste coming from agricultural or food industries as starting materials.

Innovative materials based on starch are currently developed by preparing blends with other biodegradable polymers to improve processability and mechanical properties. Recently Hwang et al. [45] prepared PLA/starch blends by melt blending by using maleic anhydride in the presence of a peroxide in order to obtain in one processing step both functionalization of PLA and reactive compatibilization between starch and PLA. Although some improvements in compatibility were observed, the tensile properties were very similar to the one of pure PLA. Reasonably, the combination of increased compatibility with biopolyesters and a better knowledge about the effect of plasticizers coming from renewable sources, as more and more of them will be obtained by new biorefineries [46], will lead towards the formulation of materials with improved properties.

PLA-based materials for flexible packaging applications will be improved by deepening the knowledge about nano-composite preparation and properties and selecting suitable and performing plasticizers. PLA nano-composites are promising because the presence of nano-fillers can improve some functional properties (barrier properties, thermo-mechanical properties, anti-microbial properties, etc.) without affecting the density of material, because generally only a few percent of nano-fillers is needed to improve physical-chemical and mechanical properties. These properties are in fact very important for flexible packaging applications. The addition to PLA of layered nano-filler was widely studied [47] as these kinds of fillers affect barrier properties and so are very interesting in the attempt to develop packaging films. The barrier properties of PLA to O₂, CO₂ and water vapor are reported by Auras et al. [48] and summarized on Table 2. It can be noticed that in general the permeability properties are slightly lower than the ones of PET, with the exception of water vapor permeability, where the PLA is slightly better.

Table 2. Barrier properties of PET and PLA on the basis of Auras paper [48].

	CO ₂ Permeability	Oxygen Permeability	Water Vapor Permeability Coefficient (WVPC)
PLA	$1.99^a - 2.77^b \times 10^{-14}$ g·m/(m ² ·s·Pa) at 0% RH from 25 °C	$1.39^a - 1.21^b \times 10^{-15}$ g·m/(m ² ·s·Pa) at 25 °C and 70% RH	$1.61^a - 1.65^b \times 10^{-11}$ g·m/(m ² ·s·Pa) at 30 °C in the 40% to 90% RH range
PET	1.73×10^{-15} g·m/(m ² ·s·Pa) at 0% RH from 25 °C	1.88×10^{-16} g·m/(m ² ·s·Pa) measured at 25 °C and 70% RH	1.1×10^{-12} g·m/(m ² ·s·Pa) at 25 °C in the 40% to 90% RH range

^a PLA 4040-D commercial product; ^b PLA 4030-D commercial product.

On the basis of these data, PET and PLA are both hydrophobic films that absorb very low amounts of water and show similar barrier property behavior. Hence the replacement of PET in flexible packaging applications would be possible.

As stated above, many researchers tried to improve the barrier properties of PLA by preparing nano-composites. The dispersion of phyllosilicates into polymers or blends at the nanometer scale [49] allowed improvement of the properties of the polymer matrix such as thermal stability. PLA nano-composites that contain phyllosilicates are considered superior for providing improved gas barrier properties, due mainly to the strong effect of confinement as the result of a high surface:volume ratio (i.e., reducing chain mobility and permeability [49]), as well as to the enhancement of tortuosity [50] of the path required for small molecules to permeate through a polymer film due to the presence of silicate lamellae.

New synthetic and processing routes were investigated by Castiello et al. for the production of PLA-based nano-composites containing a modified clay [51]. The direct synthesis of PLA by ring opening polymerization in the clays was compared in terms of structure and property features of nano-composites with a method based on melt processing in a laboratory batch mixer adding clay or modified clay to PLA. Although the in situ polymerization could be promising, the latter method showed evident advantages in terms of time and cost. Successively, the processing was successfully scaled up in a semi-industrial extruder in order to prepare extruded films for flexible packaging [22,23]. However, since the addition of plasticizer was necessary for attaining the suitable flexibility, the barrier property improvements due to the clay addition was counterbalanced by its reduction due to plasticization, making the material in the amorphous state at room temperature and so more suitable for gases and vapors diffusion.

Nano-cellulose, which represents the crystalline part of cellulose fibers, is also very interesting as a filler to be dispersed in PLA in an attempt to improve the barrier properties of PLA to oxygen, as evidenced by several authors [52,53].

Chitin is another interesting source, as it is very abundant because it represents a waste of the food industry being present in the exoskeletons of crabs, krills, lobsters and shrimps [54]. From chitin it is possible to obtain on an industrial scale chitin nano-fibrils [55] up to now employed in the sector of cosmesis and biotextiles [56]. The addition of chitin nano-fibrils to PLA is very innovative and plasticized, and nano-filled PLA showed composition-dependent tensile properties [57] suitable for flexible packaging. As an antimicrobial and antifungal behavior was reported for chitin [58] and chitin nano-fibrils [59], the possibility of exploiting this approach for producing nano-reinforced antimicrobial films is quite interesting. This represented one of the objectives of the European project N-CHITOPACK [60]. One of the aims of the project was to develop a biodegradable nanostructured film containing chitin nano-fibrils. The observed transparency of the films was in agreement with

a nano-scaled dispersion of chitin nano-fibrils inside the material (Figure 6). This result was achieved by studying a suitable method for adding chitin nano-fibrils to polymers during extrusion avoiding nano-fibril agglomeration. These films were biodegradable, as evidenced by Cinelli et al. [61].



Figure 6. Commercial compostable biobased films (**left**) based on BioComp® BF 3051; films (**Right**) obtained with the same material but with addition of chitin nano-fibrils.

In the field of polyesters, polyhydroxyalcanoates (PHAs) should also be considered [62], as they are produced by microorganisms. Since the biotechnology for obtaining them is not yet at a mature level, the price of these polymers is quite high (4–5 €/kg [63]). Several researchers are targeting optimization of production and extraction process and the use of waste material-based substrates for the growth of microorganism producing PHAs, as developed in the EC project Oli-PHA “A novel and efficient method for the production of PHA polymer-based packaging from olive oil waste water” under the scientific coordination of our research unit [64]. Their processability changes as a function of the molecular weight and also primary structure of the PHAs. However, in general these materials are brittle and very viscous when melted. Hence the use of a proper plasticizer is fundamental for processing. The necessity of controlling the migration of plasticizer from PHAs to avoid stickiness of the material and loss of ductility was evidenced by Farris et al. [65].

The other important class of biomaterials is represented by proteins, widely available as by-products or waste of the agricultural and horticultural industries and the industry of food or leather.

Hence different kinds of proteins are also studied as potential plastic materials for producing films. As a result, proteins from plants (wheat gluten, soy, sunflower, and corn) and animals (gelatin, keratin, casein, and whey) were employed in plastic formulation [66–68].

However many studies have been carried out using casting and compression molding techniques. In fact, the processing of proteins is still difficult to control with a conventional extrusion machine, as evidenced by Verbeek et al. [69].

In particular the employment of flat die extrusion and calendering is quite difficult. In this case, a successful production of protein-based laminates was reported by blending with non-biodegradable polymers such as poly(ethylene-co-vinyl acetate) (EVA) [70]. Moreover, new fully biodegradable composites based on whey/PBS blends were developed in the framework of the BIOBOARD European project [38,70] but it was possible to prepare films with a higher thickness than conventional films used in packaging. On the other hand, to exploit the barrier properties of whey, the application of layer coating made of protein onto a polymeric seemed easier, as evidenced by Cinelli et al. [36]. If techniques based on casting from water solutions are considered, also chitosan, the polymer obtained industrially by the deacetylation of chitin, can be a very interesting material for the production of coatings [71,72].

Chitosan is a biodegradable polymer that may be used to elaborate edible films or coatings to enhance shelf life of foods. Its water vapor permeability is about 20 times higher with respect to PS, so it is too high with respect to conventional packaging. However, it was demonstrated to have an anti-microbial activity that can be interesting for the production of biopolymer-based biodegradable packaging materials with additional bioactive functions [60].

The necessity of improving the chitosan barrier properties was evidenced by Morreno-Osorio et al. [73], who added to chitosan a natural compound acting as cross-linker, thus improving both mechanical and barrier properties. More frequently nano-fillers were used to improve chitosan barrier properties. Azeredo et al. [74] demonstrated that cellulose nano-fibers (CNF) can improve the mechanical and water vapor barrier properties of chitosan films. A nano-composite film with 15% CNF and plasticized with 18% glycerol was comparable to some synthetic polymers in terms of strength and stiffness, but with poorer elongation and water vapor barrier, indicating that they can be used for applications that do not require high flexibility and/or water vapor barrier. The more important advantage of such films when compared to synthetic polymer films is their environmentally friendly properties.

However up to now, despite of the production of cast films based on chitosan being successfully set-up [75], there are not yet suitable continuous machines for preparing chitosan-based films. In addition, the packaging of wet food cannot be done, as the material can dissolve in water and has a too much high water permeability. However anti-microbial properties are reported for chitosan films and biotextiles [76]. Hence the preparation of multilayer systems including one layer of chitosan should be very interesting.

5. Multi-Layer Systems: The Most Environmental Friendly Application in Food Packaging

The production of multilayer packaging films is very important in the field of packaging because it offers the opportunity of protecting the content of packaging from the interaction with different gases. As an example, the case of traditional multilayer sheets based on poly(ethylene terephthalate) (PET) and poly(ethylene) (PE) can be reported.

The recycling of these multilayer packages is not easy because the different polymeric, cellulosic or metal-based materials must be separated. Natural polymers are much used in flexible packaging, since cellulose is employed in paper-based packaging. Usually this kind of packaging consists of two layers for dried food, as the paper does not have the suitable barrier properties to water (but it has good barrier properties towards oxygen). Hence, the paper is present in a multilayer system in which also a polyethylene layer, granting the suitable water barrier properties, is present. For non-dried food, creams or liquids, also an aluminum foil layer is present to grant a total barrier effect for the packaging. For cellulose-based materials the option of recycling is possible also by considering multilayer systems. The recycling of cellulose is actually carried out in paper plants, by repulping the grinded recovered packaging material. A residual fraction (about the 30% by weight of the material) consists of aluminum and polyethylene, which can be employed in the injection-molding sector. The recycling process should be optimized, for example by separating the aluminum from the PE or replacing the PE with a biodegradable polymer and recovering Al after composting. These possible options for multilayer paper-based packaging are the object of the BIOBOARD European project [38] research activities. In the perspective of having a composting option for future packaging, the possible future scenario can be the one described in Figure 7. The monolayer plastic-based, the multilayer plastic-based and the multilayer paper-based flexible packaging systems need to be modified by replacing the layer with compostable ones. Overall, the packaging must grant the same properties in terms of content protection as the synthetic polymer-based options.

Extensive research has been devoted to the set-up of new synthetic routes for compostable polymer synthesis [77,78], and to the recovery process of materials from biomass in order to make them available for employment in materials production [79–81]. Many papers have been devoted to the blending of currently available polymers with processing aids in order to allow them to have the same properties of commodities [82,83] and others (less numerous) have been trying to find out new industrial technologies suitable for biomass derived materials [84]. All this research work can contribute to the aim of replacing flexible packaging with compostable and renewable ones in the future, but it should be stressed that the last point is fundamental. In fact, often the new materials cannot be processed

exactly as commodities. Given that the plastic industrial sector mainly consists of numerous and small enterprises, plastics converters requiring new biobased plastics that have the same characteristics and processability of conventional plastic-based counterparts, as the conversion of industrial lines to new ones, could require huge investments for them.

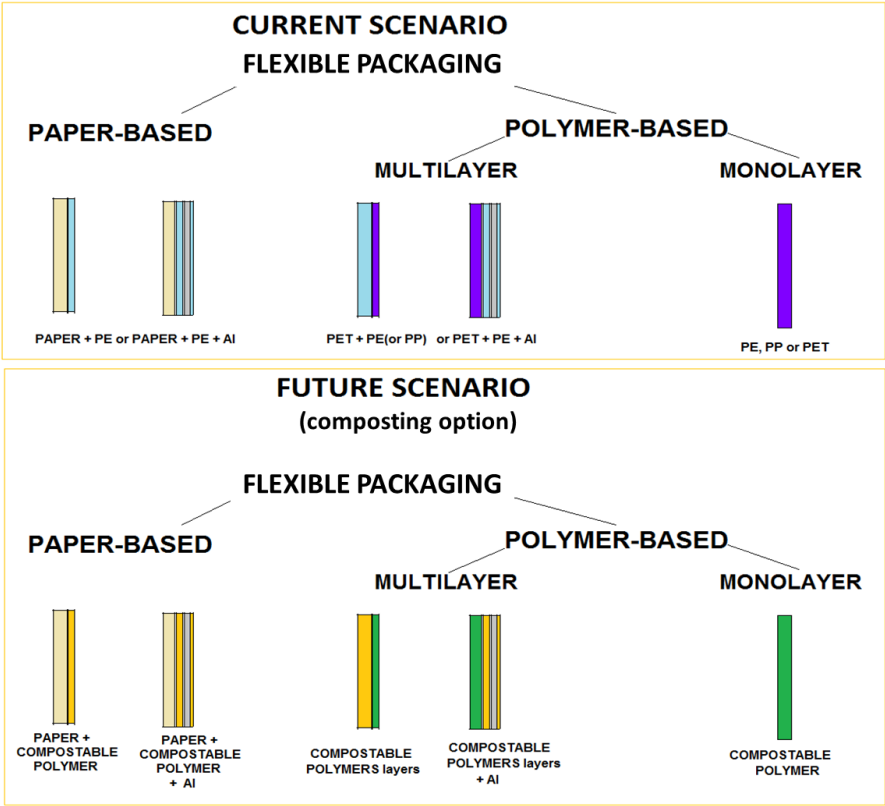


Figure 7. Polymeric materials currently employed in packaging and future perspectives in the hypothesis of composting option for flexible packaging.

The preparation of nano-composites can be effective in reducing gas permeability, hence a system in which the different layers are nanostructured can allow an optimized set of properties for a specific packaging.

Multilayer systems should be prepared preferentially by co-extrusion or lamination. Hence the material employed for making the different layers must be processable by these techniques. It is fundamental for controlling the structure of the polymers and especially their rheological behavior. However recently some researchers published a work about a new technique for preparing a peculiar

multilayer system by using a wet method [85]. A PLA film was immersed in a aqueous solution (Figure 8) of chitosan and successively in a aqueous suspension of sodium montmorillonite (MMT).

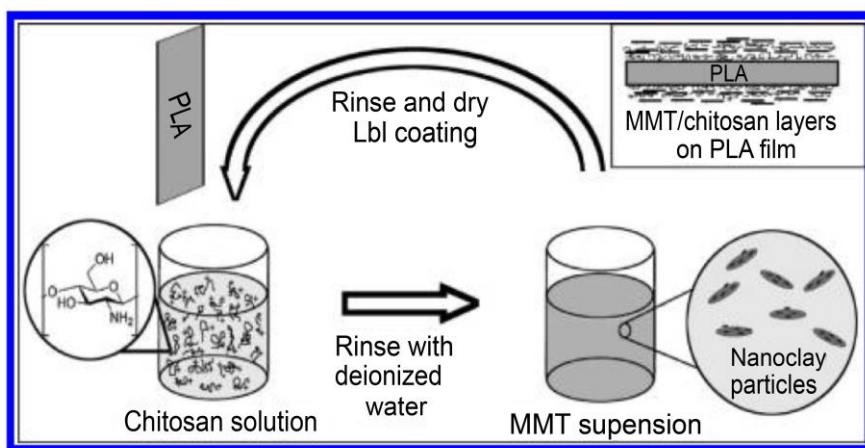


Figure 8. Illustration about LBL technique for depositing a chitosan/montmorillonite nano-structured coating on the surface of a PLA film. Reprinted with permission from [80], Copyright 2012, American Chemical Society.

By making 40 successive immersion steps, 40 alternate layers of chitosan (having a positive charge) and MMT platelets (having a negative charge) were deposited on the PLA films, thus producing a nanostructured coating. The peculiar technique was called LBL (layer by layer). Successively Laufer et al. [86] employed again the technique for preparing multilayer nano-coatings made with three food contact-approved components (chitosan (CH), poly(acrylic acid) (PAA), and montmorillonite (MMT) clay). They deposited the layers onto PET and polylactic acid (PLA) substrates. At 38 °C and 90% relative humidity (RH), the oxygen transmission rate (OTR) of 500 μm PLA was reduced from 50 to 4.6 cc/(m² day atm), which is lower than 179 μm PET film under the same conditions. This good gas barrier is believed to be due to the nano-brick wall structure present in this thin film, where clay platelets act as bricks held together by polymeric mortar. These assembled thin films are also very transparent, which combined with ambient processing and the use of renewable and food contact approved ingredients, makes this a promising foil replacement technology. This technology is quite interesting even if it is not easy to apply it on an industrial scale.

The coating of polymeric films made with biodegradable polymers with a film made with chitosan or another hydro-suspendable biopolymer-based formulation can be obtained by continuously spraying a film at the end of a flat die extrusion

plant. In this way a bilayer system can be obtained continuously without introducing enormous changes in the plant.

These papers evidence that the preparation of a multilayer containing biopolyesters and chitosan, also with the presence of nano-filler, is a quite interesting scientific and technological challenge.

The preparation of multilayer packaging containing paper layers and biobased polymers can be very interesting for producing fully biodegradable soft packaging with optimal barrier properties. Coltelli et al. reviewed the use of proteins from many natural sources in paper and paperboard coatings, making an extensive comparison in mechanical and barrier properties between proteins from several sources and having different primary structures [87].

In multilayer systems the formulation of biodegradable glues for lamination or biodegradable hot melt for extrusion coating is an interesting topic for current research [41]. For binding, protein or starch-based adhesives can be used, whereas for hot melt glues, PLA or PCL can be used. Sodergard et al. [88,89] studied blends of lactic acid-based hot melt adhesives with oxidized potato starch and poly(ethylene glycol). Thanks to this approach the authors increased the disintegration rate of the glue, making it suitable for the production of compostable multilayer packaging.

6. Challenges and Perspectives

The use of biobased plastics in flexible packaging is possible by employing different products. The main commercial products are based on starch or PLA. In both cases biopolymers, plasticizers, chain extenders and fillers are added to the material to modulate their properties. Some commercial products are available on the market, but research is in progress to better understand the correlation between formulation (new biobased additives are continuously introduced in the market especially thanks to the ongoing developments of biorefineries [46]), processability and final properties of such bioplastic materials.

In the field of starch-based materials, systematic research aimed at developing a knowledge about the integrated effect of biopolyesters, plasticizers and fillers in the starch-based material could be useful. PLA-based nanostructured composites, containing nano-fillers (such as phyllosilicates or cellulose or chitin nano-fibrils) can be promising to improve the barrier properties of biodegradable films without modifying their optical properties (transparency).

A bioplastic material for flexible packaging applications should have rheological and mechanical behavior similar to polyolefins. In particular, these conditions are difficult to respect for materials based on natural polymers, such as polysaccharides or proteins. In this case, the application to flexible packaging requires further efforts. In the case of PLA the melt viscosity is low, and usually for developing the blown film extrusion or flat die extrusion a chain extension approach, also leading to branching,

can be followed. On the other hand, in the case of proteins, their tendency to give extensive crosslinking by heating during processing can be counterbalanced by the addition of plasticizers or reactive molecules, which results in the decrease in melt viscosity.

In addition, the preparation of multilayer systems by employing biopolymer sheets can be a promising technique for flexible packaging. The replacement of current multilayers packaging with fully biodegradable ones, by keeping into account the scheme of Figure 7, will require a good adhesion between the different polymers and paper sheets. In the case of starch-based materials the good adhesion is granted by the high chemical affinity between starch and cellulose. In some cases the necessity of improving the adhesion by the use of proper biodegradable glues, by the application of surficial treatments (mechanical, plasma or corona) or by peculiar thermal and mechanical treatments to films could be useful to better design multilayer packages taking into account their end-life management.

Acknowledgments: EU is gratefully acknowledged for supporting the authors research activities thanks to the funding of several projects, all cited in the present chapter: Nano-chitopack (GA 315233), Dibbiopack (GA 280676), WheyLayer (218340), OliPHA (GA 280604), Bioboard (GA 315313) and the ongoing H2020 BBI project PolyBioSkin (GA 745839).

Author Contributions: Maria-Beatrice Coltelli made the outline and mainly wrote the chapter; Vito Gigante contributed to describing the processing of biopolymers; Patrizia Cinelli wrote the parts related to starch and PHB and revised thoroughly the chapter; Andrea Lazzeri revised the chapter.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fernandez de la Ossa, M.A.; Torre, M.; Garcia-Ruiz, C. Nitrocellulose in propellants: Characteristics and thermal properties. In *Advances in Materials Science Research*; Wythers, M.C., Ed.; Nova Science Publishers: Hauppauge, NY, USA, 2012; Volume 7, pp. 201–220.
2. Harmsen, P.F.H.; Hackmann, M.M.; Bos, H.L. Green building blocks for bio-based plastics. *Biofuels Bioprod. Bioref.* **2014**, *8*, 306–324. [CrossRef]
3. Linos, A.; Steinbüchel, A. Biodegradation of Natural and Synthetic Rubbers. In *Biopolymers Online*; Steinbüchel, A., Ed.; Wiley: Hoboken, NJ, USA, 2005; Volume 2, pp. 321–335.
4. Babu, R.P.; O'Connor, K.; Seeram, R. Current progress on bio-based polymers and their future trends. *Prog. Biomater.* **2013**, *2*, 81–116. [CrossRef]
5. Tokiwa, Y.; Calabia, B.P.; Ugwu, C.U.; Aiba, S. Biodegradability of Plastics. *Int. J. Mol. Sci.* **2009**, *68*, 3722–3742. [CrossRef] [PubMed]
6. Cantor, P.A.; Mechals, B.J. Biological degradation of cellulose acetate reverse-osmosis membranes. *J. Polym. Sci. Polym. Symp.* **1969**, *28*, 225–241. [CrossRef]

7. What are Bioplastics? European Bioplastics Fact Sheet. Available online: http://docs.european-bioplastics.org/2016/publications/fs/EUBP_fs_what_are_bioplastics.pdf (accessed on 25 November 2017).
8. Raschka, A.; Carus, M.; Piotrowski, S. Renewable raw materials and feedstock for bioplastics. In *Bio-Based Plastics: Materials and Applications*; Kabasci, S., Ed.; Wiley: Hoboken, NJ, USA, 2013; pp. 331–334.
9. Malinconico, M.; Cerruti, P.; Santagata, G.; Immirzi, B. Natural Polymers and Additives in Commodity and Specialty Applications: A Challenge for the Chemistry of Future. *Macromol. Symp.* **2014**, *337*, 124–133. [CrossRef]
10. EN13432: Packaging. Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging. 2000.
11. EN14995: Plastics—Evaluation of compostability—Test Scheme and Specifications, 2006.
12. Stepto, R.F.T. Development and Processing of Thermoplastic Starch Materials. In *Modification and Blending of Synthetic and Natural Macromolecules*; NATO Science Series; Ciardelli, F., Penczek, L., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2004; pp. 219–240.
13. Pereira, A.G.B.; Gouveia, R.F.; de Carvalho, G.M.; Rubira, A.F.; Muniz, E.C. Polymer blends based on PEO and starch: Miscibility and spherulite growth rate evaluated through DSC and optical microscopy. *Mater. Sci. Eng. C* **2009**, *29*, 499–504. [CrossRef]
14. Willet, J.L.; Jasberg, B.K.; Swanson, C.L. *Polymers from Agricultural Coproducts*; ACS Symposium Series 575; Fishman, M.L., Friedman, R.B., Haag, S.J., Eds.; American Chemical Society: Washington, DC, USA, 1994; pp. 51–68.
15. Kalambur, S.; Rizvi, S.S.H. Biodegradable and Functionally Superior Starch–Polyester Nanocomposites from Reactive Extrusion. *J. Appl. Polym. Sci.* **2005**, *96*, 1072–1082. [CrossRef]
16. Contat-Rodrigo, L.; Ribes-Greus, A. Thermal and viscoelastic properties of some commercial starch products. *J. Appl. Polym. Sci.* **2003**, *88*, 1242–1251. [CrossRef]
17. Rahman, W.A.W.A.; Sin, L.T.; Rahmat, A.R.; Samad, A.A. Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends. *Carbohydr. Polym.* **2010**, *81*, 805–810. [CrossRef]
18. Ezeoha, S.L.; Ezenwanne, J.N. Production of Biodegradable Plastic Packaging Film from Cassava Starch. *IOSR J. Eng.* **2013**, *3*, 14–20. [CrossRef]
19. Ali, R.R.; Rahman, W.A.W.A.; Kasmani, R.M.; Ibrahim, N. Starch Based Biofilms for Green Packaging. In *Developments in Sustainable Chemical and Bioprocess Technology*; Pogaku, R., Ed.; Springer: New York, NY, USA, 2013; pp. 347–354.
20. Bastioli, C. Properties and applications of Mater-Bi starch-based materials. *Polym. Degrad. Stab.* **1998**, *59*, 263–272. [CrossRef]
21. Platt, D. Polymer Demand Picks up as Holiday Season Comes on, *Plastics News Europe*. Available online: <http://www.plasticsnewseurope.com/article/20171011/PNE/171019982/polymer-demand-picks-up-as-holiday-season-comes-to-end> (accessed on 11 October 2017).

22. Scatto, M.; Salmini, E.; Castiello, S.; Coltelli, M.B.; Conzatti, L.; Stagnaro, P.; Andreotti, L.; Bronco, S. Plasticized and Nanofilled Poly(lactic acid)-Based Cast Films: Effect of Plasticizer and Organoclay on Processability and Final Properties. *J. Appl. Polym. Sci.* **2013**, *127*, 4947–4956. [CrossRef]
23. DIBBIOPACK. *Development of Injection and Extrusion blow Moulded Biodegradable and Multifunctional Packages by Nanotechnologies*; GA 280676; European Commission: Brussels, Belgium, 2012.
24. Lazzeri, A.; Thanh Phuong, V.; Cinelli, P. Copolymers Based on Reactive Polyesters and Plasticisers for the Manufacture of Transparent, Biodegradable Packaging Film. WO2013164743, 7 November 2013.
25. Coltelli, M.B.; Toncelli, C.; Ciardelli, F.; Bronco, S. Compatible blends of biorelated polyesters through catalytic transesterification in the melt. *Polym. Degrad. Stab.* **2011**, *96*, 982–990. [CrossRef]
26. Coltelli, M.B.; Della Maggiore, I.; Bertoldo, M.; Bronco, S.; Signori, F.; Ciardelli, F. Poly(lactic acid) (PLA) properties as a consequence of poly(butylene adipate-co-terephthalate) (PBAT) blending and acetyl tributyl citrate (ATBC) plasticization. *J. Appl. Polym. Sci.* **2008**, *110*, 1250–1262. [CrossRef]
27. Dong, W.; Zou, B.; Yan, Y.; Ma, P.; Chen, M. Effect of Chain-Extenders on the Properties and Hydrolytic Degradation Behavior of the Poly(lactide)/Poly(butylene adipate-co-terephthalate) Blends. *Int. J. Mol. Sci.* **2013**, *14*, 20189–20203. [CrossRef] [PubMed]
28. Coltelli, M.B.; Bronco, S.; Chinea, C. The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends. *Polym. Degrad. Stab.* **2010**, *95*, 332–341. [CrossRef]
29. Park, J.W.; Soon Im, S. Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *J. Appl. Polym. Sci.* **2002**, *86*, 647–655. [CrossRef]
30. Pucci, A.; Ruggeri, G.; Bronco, S.; Signori, F.; Donati, F.; Bernabò, M.; Ciardelli, F. Colour responsive smart polymers and biopolymers films through nanodispersion of organic chromophores and metal particles. *Prog. Org. Coat.* **2011**, *72*, 21–25. [CrossRef]
31. Fehri, S.M.K.; Cinelli, P.; Coltelli, M.B.; Anguillesi, I.; Lazzeri, A. Thermal Properties of Plasticized Poly (Lactic Acid)(PLA) Containing Nucleating Agent. *Int. J. Chem. Eng. Appl.* **2016**, *7*, 85.
32. Mujumdar, A.S. classification and selection of industrial dryers. In *Handbook of Industrial Drying*; Mujumdar, A.S., Ed.; CRC Press: Boca Raton, FL, USA, 2006.
33. Majumbder, K.K. Blown Film Extrusion: Experimental, Modelling and Numerical Study. Ph.D. Thesis, School of Civil, Environmental and Chemical Engineering Science, Engineering and Technology Portfolio, RMIT University, Melbourne, VIC, Australia, 2008.
34. Dartora, P.C.; Campomanes Santana, R.M.; Fontes Moreira, A.C. The influence of long chain branches of LLDPE on processability and physical properties. *Polímeros* **2015**, *25*, 531–539. [CrossRef]

35. Al-Itry, R.; Lamnawar, K.; Maazouz, A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym. Degrad. Stab.* **2012**, *97*, 1898–1914. [CrossRef]
36. Mallegni, N.; Phuong, T.V.; Coltelli, M.B.; Cinelli, P.; Lazzeri, A. Poly(lactic acid) (PLA) based tear resistant and biodegradable flexible films by blown film extrusion. *Materials* **2018**, in press.
37. POLYBIOSKIN. *High Performance Functional Bio-Based Polymers for Skin-Contact Products in Biomedical, Cosmetic and Sanitary Industry*; GA 745839; European Commission: Brussels, Belgium, 2017.
38. BIOBOARD. *Development of Sustainable Protein-Based Paper and Paperboard Coating Systems to Increase the Recyclability of Food and Beverage Packaging Materials*; GA 315313; European Commission: Brussels, Belgium, 2012.
39. WHEYLAYER. *Whey Protein-Coated Plastic Films to Replace Expensive Polymers and Increase Recyclability*; GA 218340; European Commission: Brussels, Belgium, 2011.
40. Cinelli, P.; Schmid, M.; Bugnicourt, E.; Coltelli, M.B.; Lazzeri, A. Recyclability of PET/WPI/PE Multilayer Films by Removal of Whey Protein Isolate-Based Coatings with Enzymatic Detergents. *Materials* **2016**, *9*, 473. [CrossRef] [PubMed]
41. Jennyangel, S.; Dhandapani, R. Eco-friendly biopolymers as adhesives—An overview. *Int. J. Pharm. Bio Sci.* **2013**, *4*, 524–533.
42. Gullick, G.; Isonhood, S.; Sanders, E. Coextruded Film with Polylactic Acid (PLA) and Ethylene Vinyl Acetate (EVA). U.S. 20080026171 A1, 31 January 2008.
43. Shi, B.; Topolkaraev, V.; Wang, J. Biopolymers, Processing, and Biodegradation. In *Renewable and Sustainable Polymers*; Chapter 8; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2011; Volume 1063, pp. 117–132.
44. Directive (EU) 2015/720 of the European Parliament and of the Council of 29 April 2015 Amending Directive 94/62/EC as Regards Reducing the Consumption of Lightweight Plastic Carrier Bags. Available online: <https://publications.europa.eu/en/publication-detail/-/publication/58d93aee-f3bc-11e4-a3bf-01aa75ed71a1/language-en> (accessed on 25 November 2017).
45. Hwang, S.W.; Shim, J.K.; Selke, S.; Soto-Valdez, H.; Rubino, M.; Auras, R. Effect of Maleic-Anhydride Grafting on the Physical and Mechanical Properties of Poly(L-lactic acid)/Starch Blends. *Macromol. Mater. Eng.* **2013**, *298*, 624–633. [CrossRef]
46. Clark, J.H. Green Chemistry for the second generation biorefinery—Sustainable chemical manufacturing based on biomass. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 603–609. [CrossRef]
47. Coltelli, M.B.; Coiai, S.; Bronco, S.; Passaglia, E. Nanocomposites Based on Phyllosilicates: From Petrochemicals to Renewable Thermoplastic Matrices. In *Advanced Nanomaterials I*; Geckeler, K.E., Nishide, H., Eds.; Wiley: New York, NY, USA, 2010; pp. 403–458.
48. Auras, R.A.; Harte, B.; Selke, S.; Hernandez, R.J. Mechanical, physical and barrier properties of Poly(lactic acid) films. *J. Plast. Film Sheet* **2003**, *19*, 123–135. [CrossRef]
49. Pavlidou, S.; Papaspyrides, C.D. A review on polymer-layered silicate nanocomposites. *Prog. Polym. Sci.* **2008**, *33*, 1190–1198. [CrossRef]

50. Neilsen, L.E. Models for the permeability of filled polymer systems. *J. Macromol. Sci.* **1967**, *1*, 929–942. [CrossRef]
51. Castiello, S.; Coltelli, M.B.; Conzatti, L.; Bronco, S. Comparative Study About Preparation of Poly(lactide)/Organophilic Montmorillonites Nanocomposites Through Melt Blending or Ring Opening Polymerization Methods. *J. Appl. Polym. Sci.* **2012**, *125*, E413–E428. [CrossRef]
52. Beck, S.; Bouchard, J.; Berry, R. Dispersibility in water of dried nanocrystalline cellulose. *Biomacromolecules* **2012**, *13*, 1486–1494. [CrossRef] [PubMed]
53. Espino-Perez, E.; Bras, J.; Ducruet, V.; Guinault, A.; Dufresne, A.; Domenek, S. Influence of chemical surface modification of cellulose nanowhiskers on thermal, mechanical and barrier properties of poly(lactide) based bionanocomposites. *Eur. Polym. J.* **2013**, *49*, 3144–3154. [CrossRef]
54. Mincea, M.; Negrulescu, A.; Ostafe, V. Preparation, modification and application of chitin nano-whiskers: A review. *Rev. Adv. Mater. Sci.* **2012**, *30*, 225–242.
55. Muzzarelli, C.; Morganti, P. Preparation of Chitin and Derivatives Thereof for Cosmetic and Therapeutic Use. U.S. WO2006048829 A2, 11 May 2006.
56. Morganti, P.; Morganti, G.; Morganti, A. Transforming nanostructured chitin from crustacean waste into beneficial health products: A must for our society. *Nanotechnol. Sci. Appl.* **2011**, *4*, 123–129. [CrossRef] [PubMed]
57. Coltelli, M.B.; Cinelli, P.; Anguillesi, I.; Salvadori, S.; Lazzeri, A. Preparation of biopolyester composites containing nano-chitin from sea food waste. In Proceedings of the BIOPOLPACK, Parma, Italy, 29–30 May 2014.
58. Singh, R.; Chacharkar, M.P.; Mathur, A.K. Chitin membrane for wound dressing application—Preparation, characterisation and toxicological evaluation. *Int. Wound J.* **2008**, *5*, 665–673. [CrossRef] [PubMed]
59. Salaberria, A.M.; Fernandes, S.C.M.; Herrera Diaz, R.; Labidi, J. Processing of α -chitin nanofibers by dynamic high pressure homogenization: Characterization and antifungal activity against *A. niger*. *Carbohydr. Polym.* **2015**, *116*, 286–291. [CrossRef] [PubMed]
60. N-CHITOPACK. *Sustainable Technologies for the Production of Biodegradable Materials Based on Natural Chitin-Nanofibrils Derived by Waste of Fish Industry, to Produce Food Grade Packaging*; GA 315233; European Commission: Brussels, Belgium, 2012.
61. Cinelli, P.; Coltelli, M.B.; Mallegni, N.; Morganti, P.; Lazzeri, A. Degradability and sustainability of nanocomposites based on polylactic acid and chitin nanofibrils. *Chem. Eng. Trans.* **2017**, *60*, 115–120.
62. Reddy, C.S.K.; Ghai, R.; Rashmi; Kalia, V.C. Polyhydroxyalkanoates: An overview. *Bioresour. Technol.* **2003**, *87*, 137–146. [CrossRef]
63. Kootstra, M.; Elissen, H.; Huurman, S. *PHA's (Polyhydroxyalkanoates): General Information on Structure and Raw Materials for Their Production*; Report 727; ACRRES: Wageningen, The Netherlands, 2017.
64. Oli-PHA. *A Novel and Efficient Method for the Production of Polyhydroxyalkanoate (PHA) Polymer-Based Packaging from Olive Oil Waste Water*; GA 280604; European Commission: Brussels, Belgium, 1 June 2012.

65. Farris, G.; Cinelli, P.; Anguillesi, I.; Salvadori, S.; Coltelli, M.B.; Lazzeri, A. Effect of Ageing Time on Mechanical Properties of Plasticized Poly(hydroxybutyrate) (PHB). *AIP Conf. Proc.* **2014**, *1599*, 294–297.
66. Hatti-Kaul, R.; Tornvall, U.; Gustafsson, L.; Borjesson, P. Industrial biotechnology for production of bio-based chemicals—A cradle to grave perspective. *Trends Biotechnol.* **2007**, *25*, 119–124. [CrossRef] [PubMed]
67. Hernandez-Izquierdo, V.M.; Krochta, J.M. Thermoplastic processing of proteins for film formation—A review. *J. Food Sci.* **2008**, *73*, 30–39. [CrossRef] [PubMed]
68. Barone, J.R.; Arikan, O. Composting and biodegradation of thermally processed feather keratin polymer. *Polym. Degrad. Stab.* **2007**, *92*, 859–867. [CrossRef]
69. Verbeek, C.J.R.; Van de Berg, L.E. Extrusion Processing and Properties of Protein-Based Thermoplastics. *Macromol. Mater. Eng.* **2010**, *295*, 10–21. [CrossRef]
70. Schmid, M.; Herbst, C.; Müller, K.; Stäbler, A.; Schlemmer, D.; Coltelli, M.B.; Lazzeri, A. Effect of potato pulp filler on the mechanical properties and water vapor transmission rate of thermoplastic WPI/PBS blends. *Polym. Plast. Technol. Eng.* **2016**, *55*, 510–517. [CrossRef]
71. Elsabee, M.Z.; Abdou, E.S. chitosan based edible films and coating: A review. *Mater. Sci. Eng. C* **2013**, *33*, 1819–1841. [CrossRef] [PubMed]
72. Rhim, J.W.; Hong, S.I.; Park, H.M.; Perry, N.G. Preparation and Characterization of Chitosan-Based Nanocomposite Films with Antimicrobial Activity. *J. Agric. Food Chem.* **2006**, *54*, 5814–5822. [CrossRef] [PubMed]
73. Moreno-Osorio, L.; Garcia, M.; Villalobos-Carvajal, R. Effect of Polygodial on Mechanical, Optical and, Barrier Properties of Chitosan Films. *J. Food Proc. Preserv.* **2010**, *34*, 219–234. [CrossRef]
74. Azeredo, H.M.C.; Mattoso, L.H.C.; Avena-Bustillos, R.J.; Filho, G.C.; Munford, M.L.; Wood, D.; McHugh, T.H. Nanocellulose Reinforced Chitosan Composite Films as Affected by Nanofiller Loading and Plasticizer Content. *J. Food Sci.* **2010**, *75*, N1–N7. [CrossRef] [PubMed]
75. Mikešová, J.; Hašeka, J.; Tishchenko, G.; Morganti, P. Rheological study of chitosan acetate solutions containing chitin nanofibrils. *Carbohydr. Polym.* **2014**, *112*, 753–757. [CrossRef] [PubMed]
76. Naseri, N.; Algan, C.; Jacobs, V.; John, M.; Oksman, K.; Mathew, A.P. Electrospun chitosan-based nanocomposite mats reinforced with chitin nanocrystals for wound dressing. *Carbohydr. Polym.* **2014**, *109*, 7–15. [CrossRef] [PubMed]
77. Alves, M.H.; Sfeir, H.; Tranchant, J.F.; Gombart, E.; Sagorin, G.; Caillol, S.; Billon, L.; Save, M. Terpene and Dextran Renewable Resources for the Synthesis of Amphiphilic Biopolymers. *Biomacromolecules* **2014**, *15*, 242–251. [CrossRef] [PubMed]
78. Oh, J.K. Polylactide (PLA)-based amphiphilic block copolymers: Synthesis, self-assembly, and biomedical applications. *Soft Matter* **2011**, *7*, 5096–5108. [CrossRef]
79. Liu, Z. Preparation of biopolymers from plant oils in green media. *BioEnergy Res.* **2013**, *6*, 1230–1236. [CrossRef]

80. Mozejko, J.; Ciesielski, S. Saponified waste palm oil as an attractive renewable resource for mcl-polyhydroxyalkanoate synthesis. *J. Biosci. Bioeng.* **2013**, *116*, 485–492. [CrossRef] [PubMed]
81. Bernardini, J.; Cinelli, P.; Coltelli, M.B.; Lazzeri, A. Flexible polyurethane foams green production employing lignin or oxypropylated lignin. *Eur. Polym. J.* **2014**, *64*, 147–156. [CrossRef]
82. Gurgel, A.V.M.; Altenhofen da Silva, M.; Oliveira dos Santos, L.; Masumi Beppu, M. Natural-based plasticizers and biopolymer films: A review. *Eur. Polym. J.* **2011**, *47*, 254–263.
83. Fehri, M.K.; Mugoni, C.; Cinelli, P.; Anguillesi, I.; Coltelli, M.B.; Fiori, S.; Montorsi, M.; Lazzeri, A. Composition dependence of the synergistic effect of nucleating agent and plasticizer in poly(lactic acid): A mixture design study. *Express Polym. Lett.* **2016**, *10*, 274–288. [CrossRef]
84. Loppinet-Serani, A.; Aymonier, C.; Cansell, F. Supercritical water for environmental technologies. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 583–589. [CrossRef]
85. Svagan, A.J.; Åkesson, A.; Cárdenas, M.; Bulut, S.; Knudsen, J.C.; Risbo, J.; Plackett, D. Transparent Films Based on PLA and Montmorillonite with Tunable Oxygen Barrier Properties. *Biomacromolecules* **2012**, *13*, 397–405. [CrossRef] [PubMed]
86. Laufer, G.; Priolo, M.A.; Kirkland, C.; Grunlan, J.C. High oxygen barrier, clay and chitosan-based multilayer thin films: An environmentally friendly foil replacement. *Green Mater.* **2013**, *1*, 4–10. [CrossRef]
87. Coltelli, M.B.; Wild, F.; Bugnicourt, E.; Cinelli, P.; Lindner, M.; Schmid, M.; Weckel, V.; Müller, K.; Rodriguez, P.; Staebler, A.; et al. State of the Art in the Development and Properties of Protein-Based Films and Coatings and Their Applicability to Cellulose Based Products: An Extensive Review. *Coatings* **2016**, *6*, 1. [CrossRef]
88. Viljanmaa, M.; Södergård, A.; Törmälä, P. The use of lactic acid-based hot melt adhesive in the industrial lamination process. *Int. J. Adhes. Adhes.* **2003**, *23*, 151–154. [CrossRef]
89. Inkinen, S.; Stolt, M.; Södergård, A. Stability studies on blends of a lactic acid-based hot melt adhesive and starch. *J. Appl. Polym. Sci.* **2008**, *110*, 2467–2474. [CrossRef]