Abstract: The huge amount of plastic used in packaging application and the related problems of disposal of the packaging after its use have gained research and industrial interest in both bio-based polymers that are not biodegradable but produced by renewable resources and bio-based compostable polymers, to be used for production of packaging. The production of bio-polymers is more costly than that of conventional fossil fuel-based polymers. Moreover, the range of applications of polymers derived from natural sources was limited due to difficulties in processing natural materials, moisture sensitivity, incompatibility at the interface between natural fillers and polymeric matrices, possible toxicity related to natural material degradation, poor mechanical properties, etc. Mass transfer properties are very important for packaging application, and at present, bio-based packaging generally lacks in maintaining barrier properties compared to traditional petro-derived polymers. The combination of traditional polymers and biodegradable ones in multilayer systems allowed obtaining a good balance of mass transfer properties, but the presence of the non-biodegradable layer negatively affects, and in some cases compromises, the composting of the final packaging. Recent advances in technology are reducing the cost of manufacturing bio-based plastics and are producing materials with an expanded range of properties that has made them suitable for low cost and high demanding applications such as packaging. Chemical modifications of the bio-based polymers, as well as blending with biodegradable additives or polymers are the preferred solutions to improve and control the properties of these materials. In this work, several materials derived from biomasses such as polyesters (poly lactic acid, poly hydroxyl alkanoates), polysaccharides (starch), vegetal and animal proteins, etc., which can be used in hard packaging applications are reviewed. Modification and processing of bio-based products with additives, polymers and natural fibers (cellulose, wood fibers, etc.) are discussed as well. The suitability of these materials for the industrial processing required for the production of hard food packaging is reported critically in order to evidence the challenges and perspectives for polymers derived from renewable resources to be applied in this sector.
1. Introduction

Plastic materials applied in packaging can match almost all requirements, perfectly meeting customers’ demands, offering important advantages such as low weight, protection of the packaged good (and consequent reduction of food waste), suitable mass transfer properties and low cost. Hard packaging comprises containers, bottles, canisters, jars, cups, buckets, trays, clamshells, blisters and the like.

In 2012 in the European Union, the post-consumer plastic waste ending up in the waste upstream was 25.2 million tons; 62% of this waste was recovered through energy recovery and recycling processes, while 38% still was sent to landfill [1].

The recent European Commission (EC) regulation promotes the bio-recycling of plastic waste through composting or anaerobic digestion, as well as the utilization of renewable resources for the production of plastics. Most recently, the development of environmental-friendly bio-based and or biodegradable polymeric materials from renewable sources has attracted extensive interest. This is due to the waste accumulation, but also to the limitation of crude oil or gas supply. Crude oil is the starting point of any conventional plastic, and it will only last for a few more decades, since it is used mainly to serve the energy demand of the population on a worldwide scale. An early conversion to renewable sources is thus important for the plastics industry.

Although only 4% of the global oil consumption is used to produce plastics (and a further 4% is used to produce the energy for the production of plastics), the new technologies required to process renewable sources thus preparing for the “post-oil era” require a sufficient time to be developed. About 46 million tons of plastics were used in the European Union in 2012 [1], about 40% for packaging production, and ca. 12 million tons of this plastic were used for rigid packaging.

In a recent fact sheet [2], European Bioplastic reports that the bioplastic producers are engaged to life cycle thinking and further improving their products, increasing the yield of their processes, thus producing more with less and ensuring sustainable resource supply to decrease the impact on the environment. Various life cycle analyses are in agreement with the better performance of bio-based rigid packaging, in particular in the impact categories of global warming potential (often referred to as a carbon footprint) and in the category of the consumption of fossil resources.

Some bio-based plastics are commercialized or are announced to be ready for the market such as polylactic acid (PLA), polybutylene succinate (PBS), polyhydroxy alkanoates (PHA), polyethylene furanoate (PEF) and also bio-based commodity plastics such as polyethylene (PE), polyethylene terephthalate (PET) or, in the very near future, polypropylene (PP). These polymers can be used for the production of rigid packaging.
The traditional market of rigid containers for food and beverages consists essentially of two different categories: the first one, usually defined as mono-material packaging, is based on unique plastic materials; the second is based on two or more materials (multi-material).

In the first category, the most used polymers are poly(ethylene terephthalate) (PET), high density poly(ethylene) (HDPE), poly(propylene) (PP) and polystyrene (PS). PET and HDPE are employed for the production of bottles, as they can be processed by blow molding, whereas PP and PS are much employed in the production of rigid food trays or jar as they can be extruded in sheets and thermoformed. At room temperature, all plastic materials are rigid, but HDPE and PP are above their glass transition temperature. Hence, the rigidity is provided by the presence of the crystalline phase domains, embedded in the main amorphous matrix. As many molecular motions are possible above the glass transition, this peculiar morphology can explain the performance impact properties of these polymers.

Multilayer rigid packaging can consist of thermoplastic polymers or of different materials, such as a multilayer system consisting of plastic, board and aluminum, with board representing the most abundant material. The former is processed usually by thermoforming starting from extruded sheets, whereas the latter is processed by properly creasing and sealing the board-based multilayer sheet.

On the market, rigid packaging based on bio-based and biodegradable polymers is already present, and some examples are reported in Figure 1.

![Figure 1](image-url)  
**Figure 1.** Examples of rigid packaging produced with bio-based polymers.
In all cases, as the market of products is huge, the containers, which are designed purposely for preserving the specific properties of food or beverages, can consist of many different polymeric materials. The polymers cited above are the most employed, because of their wide-scale production and low price. However, many other polymers with specific properties can be addressed to allow the achievement of the desired requirement, and some examples are reported in Table 1.

Table 1. Main application of bio-based polymers in hard packaging.

<table>
<thead>
<tr>
<th>Hard Packaging</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PLA</td>
</tr>
<tr>
<td>Bottles</td>
<td>x</td>
</tr>
<tr>
<td>Trays</td>
<td>x</td>
</tr>
<tr>
<td>Containers</td>
<td>x</td>
</tr>
<tr>
<td>Caps</td>
<td>x</td>
</tr>
<tr>
<td>Blisters</td>
<td>x</td>
</tr>
<tr>
<td>Foamed</td>
<td>x</td>
</tr>
<tr>
<td>Packaging</td>
<td>x</td>
</tr>
<tr>
<td>Cutlery</td>
<td>x</td>
</tr>
</tbody>
</table>

PLA = poly lactic acid, PHA = poly hydroxyl alkanoate, PE = poly ethylene, PET = poly ethylene terephthalate. x = used and present on the market, - = not commonly used.

The applications of these packaging have still a huge potential to increase, and at present, most of the rigid packaging from renewable resources is represented by cardboard and its laminates. This is due to difficulties in processing of bio-based biodegradable polymers for the production of hard packaging and the cost being higher than that of petro-derived polymers.

Thus, an overview of processing technologies for the production of hard packaging is reported below with particular focus on issues related to processing of bio-based-biodegradable polymers.

2. Processing for Production of Hard Packaging

2.1. Injection Molding

The production of plastic rigid containers is carried out by different processes. Among those, injection molding is a processing method applied for polymeric thermoplastic materials. In this process, the polymer is melted in a heated barrel and injected in a mold to produce pieces with a defined shape. The automation of the process allows for series production. This method can be employed for example for producing caps, thick jars for cosmetics, cutlery and coffee capsules. The process consists of three main phases: the injection, in which the partial filling of the mold with the molten polymer is achieved; the holding pressure and plastification, in which
the mold is completely filled by the molten polymer and kept in the mold at a defined pressure and temperature; and the ejection, in which the solid piece is extracted from the mold (Figure 2).

![Figure 2. Three main steps of the injection molding process.](image)

Figure 2. Three main steps of the injection molding process.

The selection and control of the temperature is fundamental in the first step of the process, since, when processing polymers with this technique, a very low viscosity at a high shear rate is required in order to grant a rapid and perfect filling of the mold. The knowledge and control of the rheological behavior of the molten polymer is thus very important to allow a good processing. In particular, melt flow index (MFI) determination at the same temperature of injection molding can be useful, and generally, thermoplastic polymers having MFI above about 10 g/min are suitable for injection molding. In some cases, the dimensions of the filling channel in the mold should be well dimensioned as a function of the melt rheology of the thermoplastic material employed.

In the second step, the temperature of the mold, the holding pressure and the holding time are the parameters that are important to be controlled. Some polymers can crystallize during the holding step; hence, the temperature of the mold and the holding time are quite important to allow the material to reach the desired crystalline morphology, as the amount and distribution of crystals in the material influence its final properties. This is particularly the case for bio-polyesters such as PLA and PHAs.

A specific selection of parameters is necessary also for the further steps. In fact, the ejection step should be done when the piece is solid and resistant enough, in order to avoid the breakage of the piece inside the open mold. The thermal properties such as the glass transition temperature of the material and/or its crystallization kinetics can greatly influence this step. Hence, the determination of the heat deflection temperature (HDT) usually allows one to know the maximum temperature of the mold suitable to allow the ejection without deformation of the prepared item.
This point is critical as the deformation or breakage of the item would require interrupting the processing cycle, thus wasting time, material and energy, but at the same time, in the least time possible, to avoid the waste of time and energy as well.

2.2. Injection Stretch Blow Molding Process

The injection stretch blow molding process, which is the most advanced method for producing bottles, consists of the preliminary injection molding of a pre-form, having the shape of a test tube with a threaded neck. Then, this piece is transferred to a mold where it is blown with an air jet in order to obtain a container having the shape of the mold. The container wall is thus bi-oriented, that is stretched both in the direction of air-flow and in the radial direction. By using this method, bottles of many different shapes and dimensions can be obtained. Transparent bottles available for water or fizzy beverages are made of PET, whereas the opaque ones, used for milk or liquid detergents, are made of HDPE. PLA is also suitable for this process, and most recently, bottles produced from PLA have been proposed; one example on the market is reported in Figure 3 [3–5].

![Figure 3. Plastic bottle based on PLA.](image)

2.3. Thermoforming

Arrays, plastic cups, blisters and jars are produced by another important processing method, thermoforming. Whereas in the injection molding or injection stretch blow molding, granules are fed into the equipment, in this case, the polymeric material must be fed in sheets having a thickness in the range of 50–300 microns for packaging production. The process can be applied also to thicker sheets, but in this case, the applications are in the automotive or electric and electronic fields, for the production of bodies or shells. Hence, a preliminary flat die extrusion step
is necessary for producing suitable sheets for thermoforming. In the packaging field, PS or PP is usually employed, but positive results and interesting products were produced also with PLA and PLA filled with natural fibers. In Figure 4 are reported examples of rigid packaging trays and egg containers produced by thermoforming of sheets based on PLA and wood fibers, produced by the authors in the activity of the EC project FORBIOPLAST “Forest Resource Sustainability through Bio-Based-Composite Development”. GA 212239 [6].

![Figure 4](image)

**Figure 4.** Trays and egg containers based on PLA and wood fibers.

The method consists of heating the material above its glass transition temperature, but below its melting point, thus obtaining a softened sheet usually by using infrared heaters. Then, a mold is inserted (or a vacuum is applied), which gives the softened sheet the desired shape (Figure 5).

![Figure 5](image)

**Figure 5.** Thermoforming process.

### 2.4. Multi-Material Packaging

The methods listed up to now are suitable for packages consisting of one single material. However, usually, fresh food requires packaging with enhanced barrier properties, and for these reasons, packaging consisting of two or more layers is necessary. An interesting example is the packaging consisting of one layer of PET and one layer of poly(ethylene) (PE). These bi-layer sheets can be obtained by lamination
of PE and PET or also by co-extrusion, usually employing compatibilizers consisting of ethylene copolymers, such as poly(ethylene-co-vinyl acetate) (EVA) in between the two layers to enhance adhesion and barrier properties. The multi-layer sheets can be thus thermoformed to obtain arrays or blisters, especially employed to pack fresh foods in supermarkets because of their structural, barrier and optical properties (high transparency).

The production of rigid packaging for liquids can be made also by using board-based materials. The usual rigid multilayer system consists of different layers (Figure 6) of different thicknesses, with a layer of PE in contact with the food. In dependence of the perishability of the liquid, a total barrier layer of aluminum may be necessary. This is the case of rigid containers for milk. However, also in the most complex multilayer sheet, the content of cellulose is at least 70% by weight, as the board is the main structural material of the packaging.

![Figure 6. Structure of typical board-based multilayer packaging.](image)

The sheets can be obtained by extrusion coating of PE on Al foil and co-extrusion of PE and board. To obtain the final packaging, the sheets must be properly creased and folded (Figure 7) [7].

Usually, the multilayer sheet is produced by worldwide producers, then adapted to the final users by the conversion plant, where also the printing is realized, whereas the folding is usually carried out in the packaging plant.
In Table 2, a summary of the different processes used for the different types of rigid packaging is reported.

### Table 2. Examples of processes used for the production of rigid packaging.

<table>
<thead>
<tr>
<th>Rigid Packages or Products</th>
<th>Process</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caps, coffee capsules, jars, etc.</td>
<td>Injection molding</td>
<td>HDPE, PP, PLA, PHA</td>
</tr>
<tr>
<td>Bottles</td>
<td>Injection stretch blow molding</td>
<td>PET, HDPE, PLA</td>
</tr>
<tr>
<td>Arrays, cups, jar, trays, blisters, etc.</td>
<td>Thermoforming</td>
<td>PS, PP, PET, PET/PE, PLA</td>
</tr>
<tr>
<td>Bricks for beverages or cups, etc.</td>
<td>Extrusion coating/laminating, creasing, folding</td>
<td>Cellulose/PE(/Al)</td>
</tr>
</tbody>
</table>

### 3. Adapting Biobased Polymers to Process for Rigid Packaging

#### 3.1. Poly Lactic Acid

PLA is an aliphatic, thermoplastic polyester derived from renewable resources such as starch and appears as one of the best sustainable alternatives to petrochemical-derived products for applications in packaging [8].

PLA has been found to have good stiffness and strength, and it can be processed with conventional plastic processing machinery (extrusion, extrusion blow molding, injection molding, vacuum forming) and is being used in several applications for hard packaging such as boxes, jars, trays, water and milk bottles.

Products made from PLA degrade in the environment, fragmenting into small molecules, and can be compostable, as, depending on their thickness, they can fully disappear in less than 30 days in ideal conditions [9,10].

Lim et al. [11] explained that the processing of PLA requires a preliminary drying step in order to reduce the detrimental effect of water on the PLA properties [12]. Thus, during the processing in the melt, water can result in the chain scission of PLA macromolecules because of hydrolysis. The hydrolysis is due to the nucleophilic attack of the water molecules on the carbonyl ester groups of PLA. All the authors that processed PLA for producing blends [13,14] adopted this strategy or took into account
the effect of hydrolysis on the final properties of their material. Lim [11] evidenced that commercial-grade PLA pellets are usually crystallized. This permits drying at higher temperatures to reduce the required drying time. In fact, if amorphous pellets are available, they must be dried below the Tg (≈60 °C) to avoid pellets sticking together. In this case, drying under vacuum is suggested.

Industrial desiccators are available to control the water content before processing. Drying of PLA is usually attained using a closed-loop dual-bed regenerative desiccant-type dryer, where the dew point of the drying air should be at least −40 °C or lower.

The extrusion of PLA is the processing step allowing granules to be obtained. To ensure the melting of all the crystalline phases and to achieve an optimized melt viscosity for processing, the heater set point is usually set at 200–210 °C. Commercial-grade PLA can be processed in a conventional extruder equipped with a general purpose screw of an l/d ratio in the range of 24–30. Screws for extruding PET, which are low-shear to grant mild mixing (to minimize chain scission and acetaldehyde generation), are also suitable for processing PLA [10]. The compression ratio (the ratio of the flight depth in the feed section to the flight depth in the metering section) for PLA extrusion is in the range of 2–3 [15].

In injection molding, the cycle time is an important parameter, which is often minimized to maximize the production throughput. The filling, holding and cooling events that occur during injection molding have an important implication on the shrinkage of the injection molded articles, which must be controlled to avoid undesired piece deformation. In general, injection molded PLA pieces are relatively brittle, and this brittleness is attributed to the rapid physical aging of the polymer, as the ambient temperature is only about 25 °C below the glass transition temperature. Cai et al. [16] showed that endothermic enthalpy relaxation measured in the glass transition region by DSC increased with increasing aging time. Moreover, it was observed that when molded specimens were aged at room temperature for 3–8 h, they became very brittle [17]. This occurrence was attributed to the reduction of the free volume of the polymer due to rapid relaxation to the equilibrium amorphous state.

Increasing the crystallinity of the polymer can reduce the aging effect [18]. Several authors investigated and are still investigating the effect of nucleating agents on PLA [19–21] in order to make compatible effective crystallization, mechanical stability during time and short injection molding cycles enabling series production. In fact, the formed crystallites act like physical crosslinks to retard the polymer chain mobility. In the framework of the DIBBIOPACK European project “Development of Injection and Extrusion Blow Moulded Biodegradable and Multifunctional Packages by Nanotechnologies” GA 280676 [22], some nucleating agents were studied in combination with a plasticizer, to control the evolution of crystallinity in injection
molded specimens [23]. To reduce the brittleness, the plasticization [24–26] and the blending with biodegradable elastomeric polymers [27,28] was also investigated and successfully applied, in some cases following reactive blending [29] or reactive extrusion [30,31] approaches.

Interestingly, by considering the injection stretch blow molding process, it was observed that the molecular orientation induced by this process limits the effect of aging by stabilizing the polymer free volume [17]. Aging is also reduced by the crystallites produced during strain-induced crystallization acting as physical crosslinks to stabilize the amorphous fraction, thus reducing the brittleness. Similarly to PET, PLA exhibits strain-hardening when stretched to high strain. This is desirable for blow molding of pre-forms to minimize wall thickness variation. As strain-hardening occurs only when the PLA is highly stretched, the pre-form must be designed as a function of mold dimension such that optimal stretch ratios are achieved during blow molding. It was noticed that the crystallinity after stretching decreases by decreasing the stereo isomeric fraction of the polymer [22]. Thus, the optimal stretch ratios depend on the grade of employed PLA.

The thermoforming of PLA can be generally made with aluminum molds in the range of 80–110 °C. Molds, trim tools and ovens designed for thermoforming PET and PS can be used for forming PLA containers. On the other hand, molds for thermoforming of PP cannot be used likewise for PLA, since PP shrinks significantly more than PLA during cooling [11]. Many processing methods are thus available to obtain rigid packages from PLA, especially if its properties are modulated by using proper additives, such as other polymers, fillers or low molecular weight additives such as stabilizers and chain extenders.

3.2. Poly Hydroxy Alkanoate

PHAs are gaining attention among biodegradable polymers to be used for packaging production due to their characteristic properties (such as high biodegradability in different environments such as soil and marine water, not just in composting plants) coupled with high barrier properties to oxygen and moisture and relatively high thermal stability [32–35]. These properties differentiate PHAs from PLA and are particularly interesting because of addressing the issue of plastic waste accumulation in the oceans.

The brittleness of polyhydroxy Butyrate (PHB) and polyhydroxy butyrate-co-valerate (PHB/V) is due to the secondary crystallization of the amorphous phase that occurs during storage at room temperature; in fact, the glass transition temperature (Tg) of PHB is close to room temperature. The crystallization kinetics of PHB usually starts from homogeneous nuclei, unless specific nucleating agents are added, since this polymer is free of heterogeneities. In fact, PHB does
not contain catalyst residues or other impurities that can act as heterogeneous nuclei [36–40]. To achieve high elongation at break and a higher flexibility for modified/formulated PHB, the glass transition temperature must reach a lower value than the testing temperature. By adding plasticizers, the molecular mobility is improved and the glass transition temperature is lowered, as well as the melting temperature. For processing, it must be considered also that PHB thermally decomposes at temperatures just above its melting point. Short exposure of PHB to temperatures near 180°C could induce severe degradation. The main reaction consists of a random chain scission that involves a cis-elimination reaction of β-CH and a six-member ring transition, which results in a rapid decrease in molecular weight accompanied by production of the degraded products of olefinic and carboxylic acid compounds, such as crotonic acid and various oligomers [41–44].

Several blends among PHB and other biodegradable polymers and several types of plasticizers have been investigated [45,46]. Materials of relatively low cost, biodegradable and possibly produced by renewable resources are preferred as plasticizers. Examples are: oxypropylated glycerin (or laprol), glycerol, glycerol triacetate, 4-nonylphenol, 4,40-dihydroxydiphenylmethane, acetyl tributyl citrate, salicylic ester, acetylsalicylic acid ester, soybean oil, epoxidized soybean oil, dibutyl phthalate, triethyl citrate, dioctyl phthalate, dioctyl sebacate, acetyl tributyl citrate, di-2-ethylhexylphthalate, tri(ethylene glycol)-bis(2-ethylhexanoate), triacetin, fatty alcohols with or without glycerol fatty esters, polyethylene glycol (PEG), as well as low molecular weight polyhydroxybutyrate since PHAs with a medium chain length are elastomers with a low melting point and a relatively lower degree of crystallinity [47,48]. In our research unit, we have recently investigated the performances of different degrees of polyethylene glycol (PEG) as plasticizers for PHB-based blends compared to tributyl citrate and the effect of the kinetic of crystallization by the use of these plasticizers [49]. PEG400 and tributyl citrate are very efficient plasticizers for PHB, and PEG400 resulted in being an efficient lubricating agent for the production of composite based on PHB and wood fibers, allowing better processing of the viscous melt containing up to 30% by weight of wood fibers [50]. Blends based on either PHB or PHA and PEG400 have been used for the production of hard packaging jars intended for cosmetic applications, in the research activity of the EC project Oli-PHA [51], as reported in Figure 8.

Although plasticization was the object of many studies, it must be noticed that the improvement in mechanical properties is often limited. For instance, for PHBV, Martino et al. [52], in the framework of the ECObiocap project “Ecoefficient Biodegradable Composite Advanced Packaging” GA No. 265669 [53], obtained an improvement of the elongation at break of 6% starting from 2% from the pure PHBV. Hence, the improvement in properties of PHA polymers is still an open issue in current bioplastics research.
3.3. Starch

Polysaccharides such as starch are considered for the production of rigid packaging due to relatively low cost and high degradability, in compost, soil and marine water. Thus, as previously addressed, the long-term impact of plastic waste in the marine environment is a primary issue since birds, mammals and fish may become entangled in plastic films or ingest plastic particles [54].

Non-durable plastic hard packaging includes plates, bowls and cups, as well as peanuts used for packaging fragile materials. Polystyrene (PS) is the plastic mostly used in plastic food service items (79%), and a low recycling rate is reported for the packaging waste made of PS also due to difficulties in collection and cleaning of the packaging after use [55]. Polymers such as PS are especially persistent and difficult to degrade in the environment, and for foamed items, their light weight promotes the dispersion in the environment by wind or storm drains [56]. Native starch is not a thermoplastic material, and it thermally degrades before its glass transition temperature (Tg) when its melting temperature (230–240 °C) is reached [57,58].

However, as evidenced in the previous section, when starch is heated in the presence of plasticizers such as water or polyols, the semi-crystalline structure of the starch granule is disrupted. Then, the glass transition temperature decreases below the thermal degradation temperature, and the starch actually behaves as a thermoplastic, it is then denominated thermoplastic starch (TPS) [56]. In extrusion processing, the TPS melts at much lower moisture content (10–20%) than that used for conventional cooking methods [59,60].

Several companies have introduced starch-based products on the market, Novamont (Novara, Italy), Cereplast (Seymour, IN, USA), BASF (Suffolk, VA, USA), Biotec GmbH (Gütersloh, Germany), Plantic (Altona, VIC, Australia) and Biolice.
(Ennezat, France), among others. Some images of starch-based hard packaging (peanuts and clams shell) are reported in Figure 9.

![Figure 9. Image of hard packaging made by starch.](image)

An alternative procedure to produce foamed starch-based packaging is based on a baking technology that was firstly developed for the food industry and was successively adapted for making starch-based foam food service products with a process similar to that used to produce waffles [61–64]. A starch dough is first prepared containing gelatinized or pre-gelatinized starch, native starch, water, fiber, fillers and other additives and then mixed for about 10 min. A predetermined amount of aqueous starch dough is placed into a preheated (150–200 °C) mold cavity. The dough rapidly heats, and the starch component is gelatinized, forming a melt that fills the mold cavity. A skin forms on the upper and lower surfaces where the dough contacts the mold surfaces. The steam formed during the process acts as a blowing agent and allows the formation of a foam structure in the core region of the product. Steam is then allowed to vent from the mold, and within about 45–60 s, the product dries and solidifies into the desired shape. The starch-based products are very similar to PS foam and are marketed by Biopack (Graz, Austria), Apack-IBEK Verpackungshandel GmbH (Markt Erlbach, Germany), Earthshell (Santa Barbara, CA, USA) and Biosphere Industries (Carpinteria, CA, USA).

Packages based on starch are sensitive to water; hence, some researchers studied the possible cross-linking of starch to decrease its solubility in water [65,66] with the aim of using starch for application as paper coating.

3.4. Proteins

Proteins (casein, collagen, gelatine, corn, soy, wheat, etc.), can be obtained from a variety of agricultural commodities and/or wastes and food products. Proteins can be processed by casting or by melt extrusion in the presence of plasticizers or other polymers [67–79]. The mechanical and barrier properties offered by protein-based films are generally superior to those offered by polysaccharide-based
films due to, and contrary to polysaccharides, which are mainly homopolymers, the specific structure (based on 20 different monomers), which confers functional properties and high intermolecular binding. High molecular weight proteins are insoluble, or only partially soluble, in water and, thus, present themselves as very interesting film-forming molecules for the formation of water-resistant films, particularly after crosslinking [80]. As proteins are hydrophilic, they adhere very well to polar surfaces such as paper, thus acting as barriers to oxygen and carbon dioxide. Materials with protein coatings are expected to show good barrier properties offering an alternative to nonrenewable polymers such as ethylene vinyl alcohol (EVOH) or silica-based coating. Achievements in this application were gained by the EC project WHEY-LAYER “Whey Protein-Coated Plastic Films to Replace Expensive Polymers and Increase Recyclability” and the following demo action WHEY-LAYER2 “Barrier Properties for Sustainable Packaging” [81]. An image of the WHEY-LAYER approach and of the products are reported in Figure 10.

![Figure 10. (a) WHEY-LAYER approach and products; (b) EVOH, ethylene vinyl alcohol.](image)

In the WHEY-LAYER-based packaging, a whey-based coating is applied on a plastic film substrate, such as PET, and the coated film is used for the production of multi-layer packaging.

It is possible to achieve a separation of the different layers of the packaging by removing the whey protein layer by washing with water containing a protease enzymatic detergent [82,83]. This procedure promotes the recyclability of the material that constitutes the packaging. When WHEY-LAYER is applied on a compostable substrate such as PLA, it is possible to produce a completely biodegradable multi-layer material with improved barrier properties [84].

Furthermore, in rigid paperboard packages, the main innovation can be the introduction of a new bio-based layer that can replace, at least partially, polyethylene, thus increasing the bio-content of the packaging and allowing a better management of the package end life.

More research activity is running on this very promising approach of the application of protein in packaging. The most recent project BIOBOARD [85] aims
at developing a food waste-based protein-based film by flat die extrusion. In this project, both whey protein from the dairy industry and potato pulp from the starch industry are used [86,87].

The project LEGUVAL “Valorisation of Legumes Co-Products and by-Products for Package Application and Energy Production from Biomass” GA No. 15241 [88] aims at the use and valorization of co-products and by-products of processed grain legumes thanks to the extraction of their proteinaceous fraction, which can be used as a raw material in packaging.

4. Conclusions

This overview of processing technologies for the production of hard packaging from bio-based polymers and the strategies for maximum valorization of bio-based polymer in this application outlines the potentiality and the growing attention not just of researcher, but also of producers and consumers towards bio-based materials. The renewable origin, as well as the biodegradability and compostibility of several products based on bio-based and biodegradable polymers represent a benefit for the environment and human life.

The research will continue to improve the properties of packaging based on these materials, as well as optimize their processing, with also the aim to lower the cost of bio-based products, which at present represents the main limit to the wide spreading of their applications. With the growing awareness of the need for environment and resource preservation, the market for bio-based products applied in single use applications is forced to increase. Thus, we expect more and more achievements and innovative bio-based products suitable for use in the production of hard packaging.

Author Contributions: Conceptualization, P.C. and M.B.C.; Writing – Original Draft Preparation, P.C. and M.B.C.; Writing – Review & Editing, P.C. and A.L.; Supervision, A.L.

Acknowledgments: The authors acknowledge the financial support from the European Community’s Seventh Framework Programme under: Grant agreement (GA) No. 280604 Oli-PHA, GA No. 280676 DIBBIOPACK, GA No. 315313 BIOBOARD, N-Chitopack GA 315233, WHEYLAYER GA No. 218340-2, LEGUVAL GA No. 315241.

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

References


25. Kulinski, Z.; Piorkowska, E. Crystallization, structure and properties of plasticized poly(L-lactide). *Polymer* 2005, 46, 10290–10300. [CrossRef]


