POLYMERS FROM RENEWABLE RESOURCES FOR FOOD PACKAGING

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Abstract: Bio-based food packaging materials (FPMs) are packaging materials obtained from renewable agricultural resources. There are some aspects of great importance that are to be considered in connection with bio-based FPMs, namely: degradation rate under specific conditions, mechanical properties variation during storage, microbial growth, release of toxic by-products, etc. This paper reviews these issues in order to estimate the suitability of polymers from renewable resources as FPMs.

Keywords: foog packaging, bio-based polymers, renewable resources.

1. Introduction

Published statistic data indicate that food packaging accounts for almost two-thirds of total packaging waste by volume and approximately 50% (by weight) of total packaging sales [1]. Disposal of food packaging materials (FPMs) is already an environmental problem, not only in terms of efficiency, but also in terms of by-products toxicity (as result of composting, combustion, landfilling) (Fig. 1).

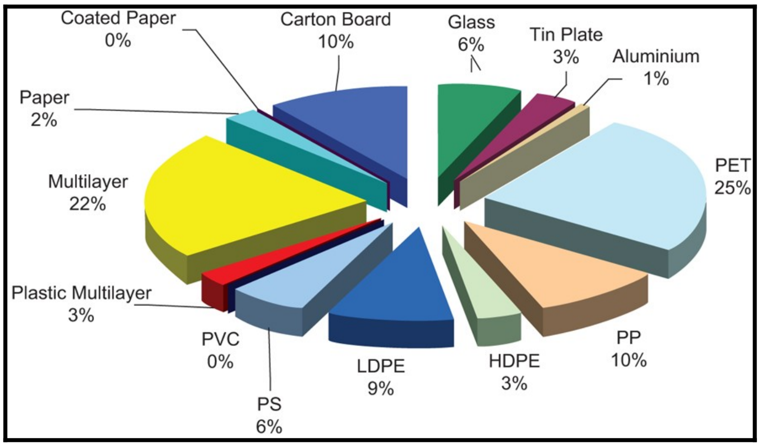
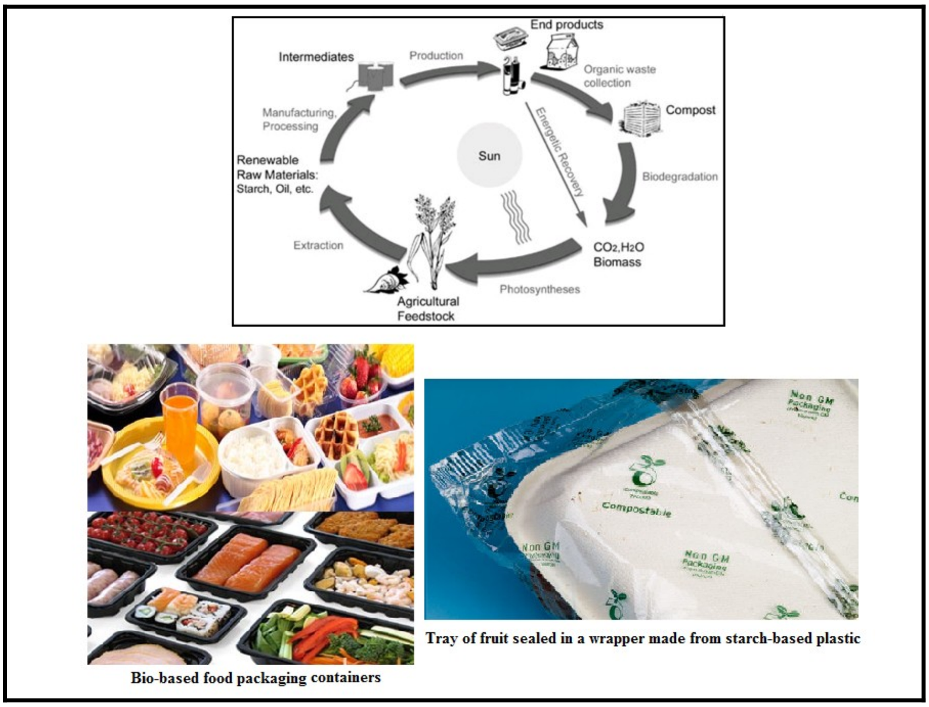


Fig. 1. Materials consumption for food packaging as estimated by the European Food Safety Authority (EFSA, available at http://www.efsa.europa.eu/)

Therefore, biodegradability must be one of the most important characteristics of new food packaging materials in order to provide alimentary industry with environmentally friendly FPMs able to ensure food quality preservation, as well as effective non-toxic disposal (by-products as carbon dioxide, water, good quality compost). This goal can be achieved in different ways. During the last decade, due to joint efforts made by R&D community along with packaging and food industries, a real progress was recorded, mainly in the field of bio-based food packaging materials (Fig. 2).



Bio-based food packaging containers

Tray of fruit sealed in a wrapper made from starch-based plastic

Fig. 2. Food packaging materials from renewable agricultural feedstock

The roles of food packaging are to protect food products from outside influences and damage, to contain the food and to provide consumers with ingredient and nutritional information. Traceability, convenience and tamper indication are secondary functions of increasing importance. But the main goal of food packaging is to contain food in a cost-effective way that satisfies industry requirements and consumer desires, to maintain food safety and minimize the environmental impact after disposal. A wide variety of materials are used for food packaging: glass, metals (aluminum, tin), plastics (polyolefins: polyethylene and polypropylene; polyesters: PET, polycarbonates, etc; polyvinyl chloride; polystyrene, polyamides), paper and paperboard. Regulations on solid waste management indicated that source reduction, recycling, composting, combustion and landfilling are agreed as methods for an integrated approach.

Disposal of FPMs is already an environmental problem, not only in terms of efficiency, but also in terms of by-products toxicity (as result of composting, combustion, landfilling). Therefore, biodegradability must be one of the most important characteristics of new food packaging materials in order to provide alimentary industry with environmentally friendly FPMs able to ensure food quality preservation, as well as effective non-toxic disposal (by-products as carbon dioxide, water, good quality compost). Bio-based biodegradable packaging has commanded great attention and numerous research projects are under way in this field. One important reason for this attention is the marketing of environmentally friendly packaging materials. Furthermore, use of biodegradable packaging materials has the greatest potential in countries where landfill is the main waste management tool. Bio-based FPMs are materials obtained from renewable agricultural resources and include both edible films and edible coatings, along with primary and secondary packaging materials [2]. Such FPMs can be used for almost all types of food: fresh and cured meat, sea food, eggs, dairy products, fruits and vegetables, butter, fats and oils, as well as dry products (such as: bakery products, cakes and cookies, pastas, chocolate), beverages and frozen food.

2. Bio-based food packaging materials (FPMs)

Bio-based FPMs are the present and future generation of FPMs due to the fact that they are derived from renewable resources and are biodegradable (although, some natural polymeric materials vary in their rate of degradation in the environment and some proteins, for example, cannot presently be classified as biodegradable). Polymers derived from renewable resources are broadly classified according to method of production, which yields in the following three main groups:

1. polymers obtained directly from natural materials (mainly plants): polysaccharides (such as: starch, cellulose) and proteins (casein, wheat gluten);
2. polymers produced by classic chemical synthesis from bio-derived monomers obtained from renewable raw materials: polylactate, a biopolyester from lactic acid monomers produced by fermentation of carbohydrate feedstock [3];
3. polymers produced by microorganisms or genetically transformed bacteria: polyhydroxyalkanoates, mainly polyhydroxybutyrates and copolymers of hydroxybutyrate (HB) and hydroxyvalerate (HV) [4].

FPMs made of or based on polymers from all these categories are either already used for packaging or have considerable potential in this field. However, the food packaging is still dominated by oil-derived polymers, despite global concerns about the environment, indicating that problems remain associated with the use of these renewable materials. A notable exception is cellulose and cellulose-based FPMs, which in the form of paper and cardboards/cartons enjoy wide usage as exterior packaging. Although highly biodegradable, paper is fibrous and opaque, with a poor barrier and moisture resistance properties, therefore, its role will remain limited to exterior packaging of foods, except in very specific cases (dry products).

Problems associated with renewable FPMs are threefold: performance, processing, costs. These issues are interrelated in all cases, but problems due to processing and level of performance are more complicated when it comes to polymers obtained directly from biomass (cellulose, starch, proteins). Polymers from categories 2 and 3, generally behave very well and are easily processed into films by standard plastics techniques, but they are expensive compared with synthetic analogues. Most commonly available natural polymers (category 1) are extracted from agricultural or forest resources (ligno-cellulosic polymers, starch, pectins and vegetal proteins). They form cell wall, plant storage structures or are structural polymers; by nature, they are hydrophilic and crystalline (in various degrees); all these are yielding in processing and performance problems [5].

2.1. Polysaccharides

2.1.1. Cellulose (Fig. 3) is the most abundant natural polymer in nature, is a cheap raw material (0.5-1 euro/kg, prior to derivatization) and, due to its chemical structure, it is highly crystalline, fibrous and insoluble. Hence, for cellophane film production, cellulose is dissolved in an aggressive, toxic mixture of sodium hydroxide and carbon disulphide and then recast into sulphuric acid. It has good mechanical properties, is hydrophilic and, consequently, sensitive to moisture. Cellophane is not thermoplastic and, therefore, not heat-sealable. Because of its poor moisture barrier properties (at relative low humidity, cellophane is a good gas barrier, but barrier properties are reduced at higher humidity), it is often coated with nitrocellulose wax (NC-W) or polyvinylidene chloride (PVDC) to minimize side effects, but this procedure inevitably increases production cost.

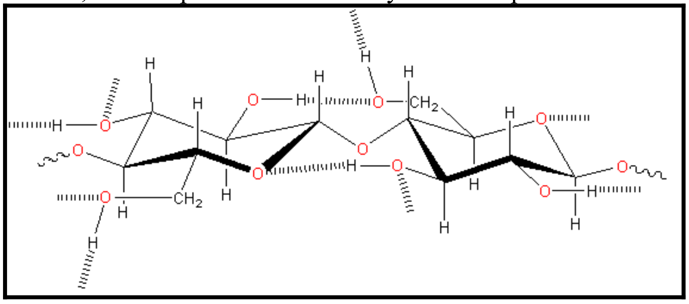
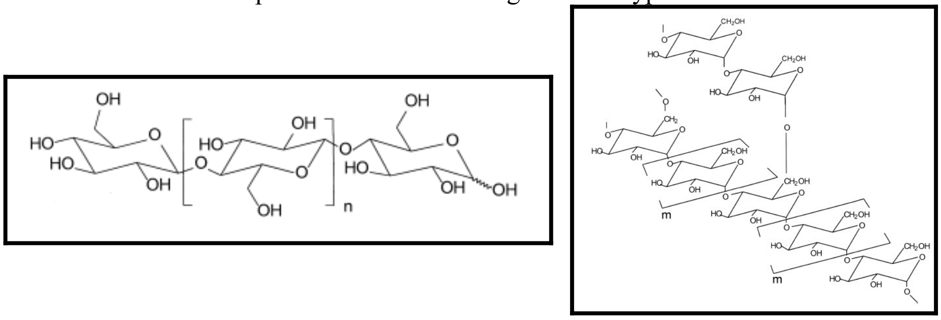


Fig. 3. Cellulose structure: β-glucose units tridimensionally connected by hydrogen bonds

Cellulose may be functionalized from the solvated state, by esterification or etherification of free hydroxyl groups, and derivatives commercially available are cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose. These processes are expensive (the cellulose diacetate is 3-4 euro/kg) and for further thermoplastic processing an addition of up to 25% plasticizer is required. The gas and moisture barrier properties of cellulose acetate are not optimal with respect to food packaging. Some grades of cellulose acetate (degree of substitution < 1.7) are biodegradable, although at a slower rate than cellophane [2].

2.1.2. Starch is another widely abundant polysaccharide obtained as granules from corn, cereal grain, rice and potatoes; basically, it is a mixture of amylose (a linear polymer made of α-glucose molecules bound in position 1-4) and amylopectin (a highly branched polymer made of α-glucose units linearly linked by 1-4 glycosidic bonds, while branching takes place through 1-6 bonds occurring every 24-30 glucose units, resulting in a soluble molecule that can be quickly degraded as it has many ends for enzymes to attach onto) (Fig. 4). The ratio of the two components varies according to starch types used.



a) amylose b) amylopectin

Fig. 4. Structure of starch components: a) amylose; b) amylopectin

Starch is widely used in several non-food sectors, most notably in sizing and coating paper, as adhesive, a thickener and as additive to simple composite materials such as briquettes [6]. As FPM, starch has received great attention only recently [7]. It is highly biodegradable, partially crystalline and quite inexpensive (0.5-1.5 euro/kg), but is also very hydrophilic, therefore poor moisture barrier, and shows moderate gas barrier properties. Films based on starch have moderate mechanical properties, generally inferior to synthetic polymers. When a plasticizer is added, such as water, starches exhibit thermoplastic behaviour [2].

Due to all these factors, starch requires substantial processing in order to obtain stable films for FPMs. This goal is achieved either by destructuration and plasticization in an extruder, or by chemical modification. Blending with various amounts of synthetic polymers (as polyvinyl alcohol, PVA, or poly-ε-caprolactone, PCL) is also used to produce transparent films [8]. The starch component of the film is biodegradable, while the others degrade during composting. Starch-PVA materials are very sensitive to moisture, therefore improving hydrophobic characteristics will result in higher costs.

An alternate way is starch direct chemical modification. Industry already produces modified starch for a various applications, but these are surface-modified starch granules (i. e., cationic starches for paper treatment) [9]. Only few chemically modified starches are now available on the market because this method is expensive, despite the fact that starch is more chemically accessible and has lower crystallinity than cellulose. In addition, starch is more sensitive to degradation during chemical treatment than cellulose, so mild conditions are required in order to prevent extensive depolymerization and loss of properties.

Intensive research is still needed in this field for using starches as FPMs to their full potential. Despite all issues above mentioned, starch remains the one of the most promising of the bio-based available polysaccharides for food packaging, as it is easier to process than cellulose, at low cost, and highly biodegradable. The challenge is, now, to design strategies to improve the moisture stability of starch films without losing beneficial characteristics.

2.2. Proteins

Proteins from renewable resources (as casein, whey, soy, corn, zein, collagen, wheat gluten, keratin, egg albumen) have attracted renewed attention as biodegradable polymers for FPMs. They are used in adhesives, as edible and non-edible films and coatings, and have considerable potential as slowly degrading packaging. Proteins possess multiple chemical functionalities and molecules with a wide range of properties are available in nature (i.e., extrusion applications are possible with respect to plant proteins such as wheat glutens and seed proteins). Crosslinked protein films are often more stable than their polysaccharide-based counterparts and have a longer lifetime. Animal proteins (casein, keratin, collagen) are also available, although proteins derived from animal tissue, like collagen, are not so attractive from the consumer point of view, due to the adverse publicity on the BSE (bovine spongiform encephalopathy) syndrome.

Technically, protein films have good gas barrier properties and many of them are water resistant, though not entirely hydrophobic [2]. A drawback to the mass production of plant proteins as FPMs is the lack of some specific knowledge concerning tertiary and quaternary structures of complex materials (such as gluten, a protein composite made of a gliadin and a glutelin, found in foods processed from wheat and related grain species). Protein-based FPMs are not expensive (1-10 euro/kg), but their mechanical properties still need improvement. Nanotechnology is a viable route to improve both tensile and barrier properties (i.e., addition of montmorillonite nanoplarticles led to increased tensile strength and elastic modulus [10]). Nanoparticles and variations at the nanometer scale affect electronic and atomic interactions without changing the chemistry.

2.3. Polyesters

2.3.1. Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a family of polyhydroxyesters (Fig. 5) and, as attractive biopolymers with a wide range of applications, have been extensively studied.

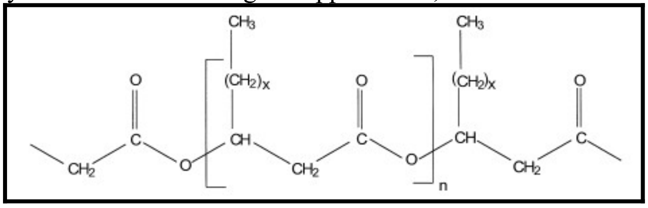


Fig. 5. PHAs structure

Besides studies on bacterial species and transgenic plants [11], many new strategies have been employed to effectively and economically produce PHAs, including the use of renewable materials or industrial waste. PHB and PHBV are representative members of PHAs that are produced at commercial scale. Although PHAs have properties close to classic plastics (polyethylene, PE, polypropylene, PP, or polyethylene terephthalate, PET), are biodegradable in soil and water resistant, can be readily processed using typical plastics technologies, they are much more expensive, mostly due to the separation from the microbiological medium. Properties of the PHBV copolymer films, i. e., may be adjusted by changing the ratio between hydroxyvalerate (HV) and hydroxybutyrate (HB), which can be achieved by manipulation of the growth media. A high content of polyhydroxybutyrate (PHB) gives a strong and stiff material, whereas polyhydroxyvalerate (PHV) improves flexibility and toughness. The PHAs are more hydrophobic than the polysaccharide-based materials, resulting in FPMs with good moisture barrier properties, at satisfactory prices (10-12 euro/kg). Under these circumstances, the potential of these PHAs as FPMs is excellent.

2.3.2. Polylactides (PLAs)

A more immediate option is polylactides (PLAs) (Fig. 6) – a class of thermoplastic aliphatic polyesters based on lactic acid from renewable resources, such as corn starch (in the USA), tapioca products (roots, chips or starch mostly in Asia) or sugarcanes (in the rest of world).

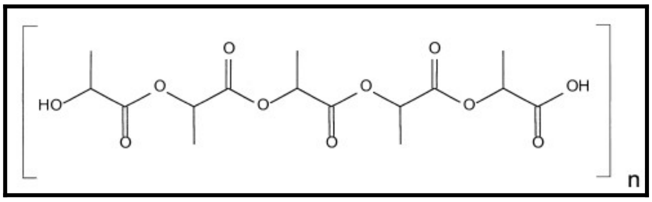


Fig. 6. PLA structure

PLAs display good mechanical properties compared with standard thermoplastics and the moisture barrier is higher than for the starch-based materials, as the production of flexible, water-resistant PLA films has demonstrated. The final polymer cost strongly depends on the efficiency of the initial fermentation process to produce the lactic acid monomer.

The bio-based FPMs may contain further natural extracts as components, i. e. lignin and waxes which act as preservatives stalling the initial stage of food degradation processes. This still needs thorough testing, as well as the use of natural antioxidants, plasticizers, etc.

3. Economic and technologic considerations

A comparison between properties of bio-based FPMs and two other classic plastics (LDPE and PS) was made [5] and its conclusions are presented herein (Table 1.)

Table 1. Basic properties of some bio-based FPMs and classic plastics

Polymer	**Moisture permeability**	**Oxygen permeability**	**Mechanical properties**
Cellulose/Cellophane	High – medium (low if coated)	High	Good
Cellulose acetate	Moderate	High	Moderate (plasticizers needed)
Starch-PVA	High	Low	Good
Proteins	High - medium	Low	Moderate
PHAs	Low	Low	Good
PLA	Moderate	High - moderate	Good
LDPE	Low	High	Moderate - good
PS	High	High	Good - moderate

In general, thermoplastics commonly used FPMs, such as PE, PS, PET, are made in high volume at large scale production plants and are relatively inexpensive due to their low cost per unit (PE costs 0.7-1 euro/kg, PS costs twice as much). Because of the high amount, continuous production, product quality and performance it is easy to control and adapt parameters such as moisture and gas barrier.

On the other hand, many of the bio-based polymers (cellulose esters and ethers, starch derivatives, etc.) are still produced in batch reactors and are more expensive and subject to quality variations, despite the relatively low cost of the starting materials. A key factor in the spreading of bio-derived polymers in food packaging is, therefore, the development of analogous continuous processes to produce biopolymer films at reduced costs and with designed characteristics.

Another key factor is the production of polymer resins that can be readily processed into films using existing machines, with eventual minor modification. In this respect, PLAs and the PHAs are the polymers with the best prospects for commercial production, if initial fermentation or bio-production costs can be reduced.

In addition, the starch based FPMs which can be continuously extruded are also promising, provided factors such as moisture resistance and moisture barrier can be improved.

One of the challenges facing the bio-based FPMs is to match the durability of the packaging with product shelf-life: they must remain stable without changes of their mechanical and/or barrier properties and must function properly during storage until disposal. Subsequently, the FPMs should be biodegradable. Environmental conditions that favours the biodegration must be avoided during storage and the most important parameters for controlling stability of the biologically based FPMs are humidity, pH, nutrients, oxygen, storage time and temperature.

Prior to their use, bio-based FPMs must be tested in terms of interactions with food. For many years, coated cellophane (bakery products, fresh products, processed meat, cheese, candy) and cellulose acetate (bakery products, fresh products) have been used for food packaging. The moisture and gas barrier properties of cellulose acetate are not optimal for food packaging. Still, the film is excellent for high-moisture products as it allows respiration and reduces fogging [12].

Recently, a biodegradable laminate of chitosan-cellulose and polycaprolactone film was developed in order to investigate the possibility to use the laminate for modified atmosphere packaging [5] for fresh vegetables, such as head lettuce, cut broccoli, whole broccoli, tomatoes, sweet corn. The results were promising. The same in the case of a PE film containing 6% corn starch [13]. The type of packaging film seemingly did not affect the evaluated quality parameters, i.e. bread staling, broccoli colour, lipid oxidation of ground beef. However, a significant loss of elongation occurred in corn starch-containing film, which could be due to interactions between the film and free radicals developed during lipid oxidation in ground beef during frozen storage. Therefore, corn starch based PE films are recommended to be used only for packaging of wet and dry low-lipid foods. However, their use for high fat content foods was discouraged due to possible interactions with free radicals derived from lipid oxidation.

Studies on lean beef and bologna established that the microbiological quality of the foods was not affected by the presence of corn starch in PE films [5]; this leads to the conclusion that these FPMs have true potential as primary food containers for selected products.

In Belgium, packaging containing starch is used commercially for fast-food packaging of French fries. Other applications include disposable food service items and paper coatings [2].

Research on polylactate and polyalkanoate FPMs have been intensified during the last decades, so packaging materials are now readily available in dairy products industry (i.e., polylactate based cups for yoghurt). Other potential commercial applications include disposable food service items and bags (as for bakery products). With respect to polyalkanoates, suggested use as FPMs includes beverage bottles, coated paperboard milk cartons, cups, fast food packaging, as well as films [14].

More recently, it was demonstrated that the use of gluten films may actually be advantageous for storage of respiring fresh products [15] because it has suitable O_2 barrier properties, while remaining sufficiently permeable to carbon dioxide. Thus, a modified atmosphere containing 2-3% O_2 and 2-3% CO_2 was developed, which seems to be favourable to the overall quality of mushrooms.

4. Conclusion

Taking into consideration the presented data, it may be assumed that most of the present problems will be solved due to fundamental and applied research efforts. Legislative and consumer pressure are the driving force able to attract more attention on this sensitive field and the rate of development will parallel this enhanced commercial awareness.

Great possibilities exists for bio-based FPMs, aside from the most known products which are high price and niche products (i.e., organic products). However, further research within different areas of bio-based packaging (legislation, processing technology, food-packaging compatibility studies) must be achieved before bio-based FPMs can be used at large scale for primary food packaging.

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