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BIODEGRADABLE MATERIALS FOR FOOD PACKAGING APPLICATIONS

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Abstract. The request for biodegradable materials is a big challenge of nowadays because of the big amount of plastic trash which is released daily from the anthropic activities. Manufacturing of biobased materials requires knowledge of the processing and material properties of the polymers. If the properties of native polymer are not identical to the required one, or if the polymer by nature is not thermoplastic, a certain modification of the polymer must take place. It should be expected that following requisite processing and product developments of biobased materials resulting properties should equal or better those of the conventional alternatives. Biobased plastic applications are currently targeted towards single-use, disposable, short-life packaging materials, service ware items, disposable non-woven and coating for paper and paperboard applications. In general, the same shapes and types of food packaging can be made from synthetic and biobased resources. Notably, developments are currently focusing towards the biobased materials which must be able to mimic the water vapour barriers of the conventional materials known today. In this paper a review of the available literature was done and the sources of materials production as well as food applications possibility of these packaging materials have been identified.

Keywords: food packaging, biodegradable materials, biopolymers.

AIMS AND BACKGROUND

The purpose of food packaging is to preserve the quality and safety of the food it contains from the time of manufacture to the time it is used by the consumer. An equally important function of packaging is to protect the product from physical, chemical, or biological damage[1]. The most well-known packaging materials that meet these criteria are polyethylene or co-polymer based materials, which have been in use by the food industry for over 50 years. These materials are not only safe, inexpensive, versatile, but also flexible[2]. Plastics are widely used in many applications such as in packaging, building materials and commodities as well as in hygiene products. However, the problem of environmental pollution caused by the indiscriminate dumping of plastic waste has assumed a global proportion.

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However, one of the limitations with plastic food packaging materials is that it is meant to be discarded, with very little being recycled.

These conventional plastics that are synthetically derived from petroleum are not readily biodegradable and are considered as environmentally harmful waste. Most polymers are extremely durable and present a serious environmental problem, especially in urban centers. One option for the management of plastic waste is the use of biodegradable products. New biodegradable polymer blends have been developed to enhance the degradation of the final product. The use of biopolymers is based on renewable resources and contributes to material cycling that is analogous to the natural biogeochemical cycles in nature[3].

In addition to the above environmental issues, food packaging has been impacted by notable changes in food distribution, including globalisation of the food supply, consumer trends for more fresh and convenient foods, as well a desire for safer and better quality foods. Given these and previously mentioned issues, consumers are demanding that food packaging materials be more natural, disposable, potentially biodegradable, as well as recyclable[4].

EXPERIMENTAL

Depending on the production process and on the source, biopolymers can have properties similar to traditional ones. A general scheme of bio-based materials is represented in Fig. 1.

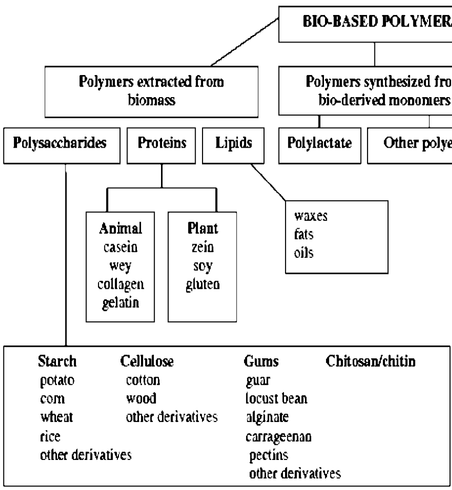

Fig. 1. Different categories of bio-based materials[5]

They are generally divided into three groups: polyesters; starch-based polymer; and others. These materials can be:

(i) Polymers directly extracted from biomass like proteins, lipids, polysaccharides, etc.;

(ii) Polymeric materials synthesised by a classical polymerisation procedure such as aliphatic aromatic copolymers, aliphatic polyesters, polylactide aliphatic copolymer (CPLA), using renewable bio-based monomers such as poly(lactic acid) and oil-based monomers like polycaprolactones;

(iii) Polymeric materials produced by microorganisms and bacteria like polyhydroxyalkanoates.

Aliphatic polyesters. These materials have properties similar to PE and PP polymers, they are biodegradable but with lack of thermal and mechanical properties. These materials come from polycondensation reaction of glycol and aliphatic dicarboxylic acid, both obtained from renewable resources. They are odourless and can be used for beverage bottles and they biodegrade in soil and in water giving carbon dioxide and water, in a period of 2 months (e.g. for a 0.04 mm thick film)[6].

A commercially available aliphatic copolyester is produced by Procter and Gamble Co. (P&G, Cincinnati, OH) with the trade name of Nodax and it can degrade in aerobic and anaerobic environmental conditions. The other one is the Eastar bIo, produced from the Eastam Chemical Company (Hartlepool, UK).

Poly-β-hydroxyalkanoates (PHA) have been attracting much attention in recent years as biocompatible and biodegradable thermoplastics with potential applications. Poly(3-hydroxybutyrate) (PHB) (Fig. 2) is one of the well-known biodegradable poly(hydroxy alkanoates) (PHA).

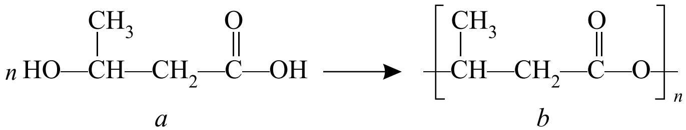

Fig. 2. Chemical structure of: 3-hydroxybutyrate-acid (*a*); poly(3-hydroxybutyrate) (PHB)[3] (*b*)

PHB is a natural thermoplastic polyester and has many mechanical properties comparable to synthetically produced degradable polyesters such as the poly-L-lactides[3]. Polyhydroxybutyrate (PHB) is a naturally occurring β-hydroxyacid (a linear polyester). The homopolymer, poly(hydroxybutyrate) PHB, and its copolymer with hydroxyvalerate (PHBV) are biodegradable engineering thermoplastic polymers with important trade properties that make them suitable in many applications for which petroleum-based synthetic polymers are currently used. PHB polymers are already being used in small disposable products and in packaging materials[7].

Since 1925 PHB has been produced by bacterial fermentation, which takes place in the presence of a wide variety of bacteria, as intracellular reserve material. At least 75 different genera of bacteria have been known to accumulate PHB as intracellular granules. This polymer is synthesised under limited culture conditions and its production has most commonly been studied with microorganisms belonging to the genera Alcaligenes, Azobacter, Bacillus and Pseudomonas. Under limited nitrogen and in the presence of an abundant source of carbon, some bacteria can accumulate up to 60–80% of their weight in PHB. *Alcaligenes eutrophus* is the most widely used organism for the production of PHB because it is easy to grow, it accumulates large amounts of PHB (up to 80% of dry cell weight) in a simple medium, and its physiology and biochemistry leading to PHB synthesis are well understood[8].

Polylactide aliphatic copolymer (*CPLA*). This material is a mixture between renewable resources as lactide and aliphatic polyesters like dicarboxylic acid or glycol, with hard (like PS) and soft flexible (like PP) properties, depending on the amount of aliphatic polyester present in the mixture. It is easy to process and thermally stable up to 200°C. The heating value and the quantity of carbon dioxide generated during combustion are about the half of that generated from commercial polymer like PE and PP, and incineration does not produce toxic substances. In natural environment it starts to degrade in 5 to 6 months, with a complete decomposition after 12 months. If composted with food garbage, it begins to decompose after 2 weeks.

Polycaprolactone (*PCL*). It is a fully biodegradable polymer coming from the polymerisation of not renewable raw material, like crude oil. It is a thermoplastic polymer with good chemical resistance to water, oil, solvent and chlorine, with a melting point of 58 to 60°C, low viscosity, easy to process and with a very short degradation time. It is not used for food application, but if mixed with starch it is possible to obtain a good biodegradable material at a low price, used for trash bags.

Poly(*lactic acid*) (*PLA*). One of the most promising biopolymer is the poly (lactic acid) (PLA) obtained from the controlled depolymerisation of the lactic acid monomer obtained from the fermentation of sugar feedstock, corn, etc., which are renewable resources readily biodegradable[9]. It is a versatile polymer, recyclable and compostable, with high transparency, high molecular weight, good processability and water solubility resistance. In general commercial PLA is a copolymer between poly(L-lactic acid) and poly(D-lactic acid). Depending on the L lactide/D lactide enantiomers ratio, the PLA properties can vary considerably from semicrystalline to amorphous ones. Researches carried out to improve the performance quality of this material are made on PLA with D-lactide content less than 6%, which is the semicrystalline polymer. However, the amorphous one, containing 12% of D-lactide enantiomer, is easy to process by thermoforming, which is the actual technology in the food packaging sector, and it shows properties like polystyrene. This material is commercialised by different companies with different commercial names. Currently it is used in food packaging application only for short shelf-life products.

Polyurethane foams. With the development of the polymer industry, polyurethane has been widely used in the fields of fibers, foams, elastomers, and protective coatings for its steady quality and excellent performance. The ability of microorganism growing on the polyurethane presents a human health problem during the usage and storage of PU. In an effort to address this problem, antibacterial agents have been applied into the polymers.

In general, two major methods have been used to produce antimicrobial polymers: the antimicrobial materials are mixed with the polymer or laid on the surface of polymer. Those methods have disadvantages of a short useful life and undesirable washability. Therefore, it has become very important to find a natural antimicrobial material that can be incorporated into the formulation of PU and retain its bacteriostatic ability.

Some investigations have indicated that tannin is the efficient antimicrobial agent in the bark. 'Tannin' is a general descriptive name for a group of polymeric phenolic substances, which can be found in almost every plant part: bark, wood, leaves, fruits, and roots. Its molecular weights range from 500 to 3000. The introduction of plant components into PU formulation has been reported. WT can be successfully incorporated into PU foams formulation, which enhances the biodegradability and microorganism resistance. Also, WT is utilised as a polyol component in polyurethane synthesis, because it has both aliphatic and aromatic hydroxyl groups.

FILLERS FOR BIOBASED PACKAGING MATERIALS

*Chitosan***,** a linear β-1,4-D-glucosamine, is a biocompatible, nontoxic compound mainly obtained by deacetylation of chitin, a natural structural component present for instance in crustaceans. Several works exist in literature that demonstrate the inherent biocide properties of this natural carbohydrate polymer against a wide range of microorganisms such as filamentous fungi, yeast and bacteria[10].

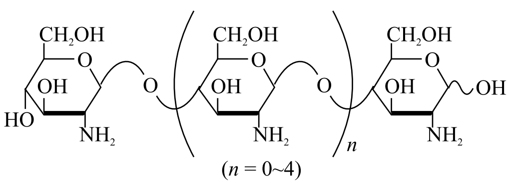

Fig. 3. Chemical structure of chitosan oligosaccharide

Suyatma et al.[11] attempted to combine the water vapour barrier properties of chitosan with the hydrophobic biodegradable properties of PLA. While the study demonstrated that the incorporation of PLA into chitosan improved water barrier properties and decreased water sensitivity of the chitosan films, tensile strength and other mechanical and thermal properties were not improved. In additional experiments, the authors demonstrated that a phase separation occurred, thereby proving the incompatibility of the two materials. Several additional studies have demonstrated the effect of PLA, alone or in combination with other antimicrobials to inhibit microorganisms on fresh or further processed meat products. In Ref. 12 was demonstrated the synergistic effect of 2% low-molecular weight polylactic acid alone or in combination with lactic acid or nisin against *Escherichia coli* O157: H7 on raw beef during irradiation and during refrigerated storage.

While the authors demonstrated inhibition against the pathogen on beef using PLA or lactic acid, as well as combinations of PLA with lactic acid and nisin, the authors concluded that the antimicrobial effect of PLA was not significantly different than that of lactic acid alone. In another study it was examined the effect of PLA for reducing pathogens on raw meat. *E. coli* O157:H7, *Listeria monocytogenes*, *S. typhimurium*, or *Yersinia enterocolitica* associated with lean beef surfaces treated with PLA, lactic acid, or sterile water. PLA treatments at pH of 3.0 resulted in significant reductions of *E. coli* O157:H7; however, *E. coli* O157: H7 was not inhibited when PLA was applied at pH 5.0, 6.0, and 7.0. When applied to ground beef, ground pork or breakfast sausage inoculated with *E. coli* O157:H7 and subjected to long-term refrigerated storage, PLA treatments did result in up to a 1.7 log10 reduction of the pathogen. In Ref. 13 was demonstrated that low-dose PLA, in combination with low-dose irradiation (2.0 kGy), followed by long-term refrigerated storage could effectively reduce populations of *E. coli* O157:H7 and *S. typhimurium* up to 5 log10 CFU/cm^2 (99.999%) on beef surfaces. Subsequent experiments on PLA also demonstrated that irradiation did not affect the tensile strength of the packaging materials[14].

Cellulose fibre. Sanchez-Garcia et al.[15] studied the morphology, thermal and transport properties of solvent cast biocomposites of poly(lactic acid) (PLA), polyhydroxybutyrate-co-valerate (PHBV) and polycaprolactones (PCL) containing purified alfa micro-cellulose fibres as a function of filler content. The scanning electron microscopy (SEM), optical microscopy and the Raman imaging results indicate that a good dispersion of the fibres in the matrix was achieved for the three biopolymers. However, detrimental fibre agglomeration was clearly observed to take place for samples with fibre contents in excess of 5 wt.%. The heat of fusion (related to crystallinity) of the semicrystalline PCL and PHBV biopolymers was seen to decrease, particularly in low fibre content biocomposites, but it seemed to increase slightly in the highly amorphous PLA biocomposites. The supplied material was a melt-processable semicrystalline thermoplastic PHBV (polyhydroxybutyrate with 12 mol% of valerate) copolymer made by biological fermentation from renewable carbohydrate feedstocks. The semicrystalline PLA used was a film extrusion grade (with a D-isomer content of approximately 2%).

A purified cellulose fibre grade having an average fibre length of 60 μm and an average fibre width of 20 μm was used. According to manufacturer specifications, these fibres had an alfa-cellulose content of >99.5% and an aspect ratio of ca. 3.

In accordance with the morphology data, water and D-limonene direct permeability were seen to decrease to a significant extent in the biocomposites with low fibre contents. The permeability reduction was mostly related to a decrease in diffusivity but solubility was also found to be favourable. The main conclusion from this work is that purified cellulose fibres can also be used to enhance the barrier properties of thermoplastic biopolyesters of interest in, for instance, packaging and membrane applications[15].

Wood fibre. Glenn et al.[16] have studied the functional properties needed for commercial food containers made of a composite of potato starch, water, wood fibre, $CaCO_3$, release agents, and thickeners with a moisture resistant coating. A fundamental understanding of the physical and mechanical properties that is important in the functionality of hinged food containers. The hinged food containers are attractive, completely degrade in composting conditions and are a viable replacement for hinged containers made of extruded polystyrene (EPS) and coated paperboard (PB).

Unmodified wheat starch, unmodified dent corn and tapioca starches, bleached softwood fibre, magnesium stearate calcium carbonate were used as materials.

The objective of Glenn et al. study[16] was to establish a functional range in density and various flexural and tensile properties based on tests conducted on commercial EPS and PB food containers and to determine the effect of starch, fibre, moisture coating, $CaCO_3$ and composites of all these components on the functional properties of baked foams.

The data characterising the properties of paperboard (PB) and extruded polystyrene (EPS) provided a functional range in the properties that could be used as a benchmark for properties needed in commercial containers. Both materials were lightweight (<0.20 g/cm^3), especially the EPS foam that was approximately one third the density of PB.

Flexural stress/strain curves for PB and EPS samples revealed two distinct patterns (Fig. 4). The stress of the EPS sample gradually dropped with increasing strain beyond the maximum stress point whereas stress in the PB sample fell sharply as strain increased beyond the maximum stress point. Both samples had only a small decrease in stress with additional strain even beyond 5% strain until a crease or fold formed.

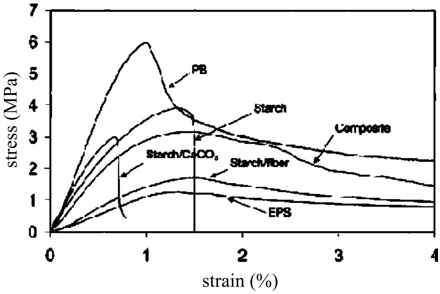

Fig. 4. Graph of flexural stress/strain curves for foam samples including extruded polystyrene (EPS), paperboard (PB) and baked foams made of formulations containing starch, starch and fibre (starch/fibre), starch and $CaCO_3$ (starch/$CaCO_3$) or composites of starch, fibre and $CaCO_3$ (composite)[16]

The starch-based, baked foam containers had some of the functional properties found in commercial EPS or PB containers. The starch component provided the foaming properties for the baking process, but it also rendered the foam product susceptible to changes in MC that, in turn, changed the mechanical properties. Moisture resistant coatings are required to make starch-based foam containers functional for commercial applications. A study of moisture resistant coatings would be valuable in determining their effectiveness on moisture resistance and also their effect on mechanical properties. The potential of baked foam technology for commercial applications appears promising in spite of some limitations. An important limitation is that the baking process is much slower compared to the process for making EPS. This is aggravated because foams have a very low MC the moment they are removed from the molds, and are relatively weak and brittle and more prone to breakage during handling.

TECHNICAL REQUIREMENTS

To produce food containers, for instance egg containers, density is important because it relates to the weight of each container and determines, in part, the amount of feedstock needed to produce each article. The amount of feedstock waste in the manufacturing process also contributes to the total amount of feedstock used to produce a single part. Containers made of relatively expensive materials such as EPS are cost-competitive with PB containers because of their low density and the small percentage of waste generated in the manufacturing process[17]. Some technical requirements regarding a 6-egg unit refers to pack dimensions, opening force, clamp force as well as the pressure withstand by the package itself. Another particularity beside biodegradability of the egg package container is that it should be manufactured in compliance with the safety food requirements.

A given egg seat may be adapted to hold one or more eggs. The body may be opaque or may comprise transparent sections, such as a see-through front cover, top cover, or side windows. Manufacturing of the various components of the egg container may be by any known method such as injection molding, ultrasonic welding, casting, machine tooling, stamping, die cutting, thermoforming, rapid prototyping, laser curing, etc.

CONCLUSIONS

Food industry is one of the greatest packaging disposal producers and realising biodegradable packages for food stuffs is an important requirement of nowadays environmental problems.

Due to the fact that functional/organic eggs (e.g. omega 3 eggs) are preferred by educated consumers, which are aware of the higher costs of this product, they are also willing to pay more for the biodegradable package of the product.

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ABBREVIATIONS

PE – polyethylene
PP – polypropylene
PS – polystyrene
WT – wood tannins.

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