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Developments and Properties of Plastic Mimicking Biopolymers for Food Packaging Application

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ABSTRACT

Sustainability takes an ever increasing importance in the food industry. Here not only the selection of raw materials plays a role, but also packaging materials. Nowadays there is an increasing number of biodegradable and bio-compostable packaging materials available.

However, these materials are still not able to replace mineral oil based packaging materials completely, nevertheless they are becoming increasingly important, since there must be solutions to problems such as pollution of the oceans by plastic waste, growing piles of rubbish from growing population, etc.

The following literature review shows briefly recent developments on plastic mimicking biopolymers, as these materials guarantee great potential in itself and a future wider application in the food industry. The presented biopolymers were systematically classified according to their origin (plant, animal, microbial), and special emphasis have been placed on packaging properties.

Finally, a forecast for the most promising materials and trends will be presented.

KEY WORDS: *Biopolymer, Packaging, Food, Bio, Polymer, Plastic, Film, Environment, Functional Packaging*

1. INTRODUCTION

First of all, must be clarified what a biopolymer is. The term is often used in connection with bio-plastic, bio-compostable plastic and bio-degradable plastic.

The word biopolymer itself is made up of three words. Each from the Greek bio(s) (life), poly (many) and méros (part). So, the name can be deduced as, biopolymers are chemical macromolecules of a natural and living origin. Currently, there is no officially accepted definition, but a general definition can be found from Bhatt and Jaffe in Biopolymers in Medical Implants. It says: "Biopolymers are polymers synthesized by living organisms and are found in nature."[1].

Building on this definition therefore it is possible to determine three categories of biopolymers: biopolymers of plant origin, biopolymers of animal origin, biopolymers microbiological origin.

In accordance to the American Society for Testing and Materials ASTM bio-degradable materials are described as "capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials (e.g. cellulose) and leaves no toxic residue." [2].

2. BIOPOLYMER MATERIALS

2.1 Biopolymers of Plant Origin

2.1.2 Starch & Starch derivate

Starch and cellulose are the two main carbohydrates in plants (algae included). Conventionally, starch is formed in a concentric arrangement around the hilum and consists of two components, namely amylose (linear) and amylopectin (hyper-branched). The formation of the starch takes place in the in the chloroplasts and their storage in the amyloplasts [3]. Starch and starch derivatives are leading when it comes to biopolymers. Strengths are the availability of a large scale (in 2014: 10.5M tonnes) and inexpensive, rapidly renewable raw materials. This makes starch competitive with mineral oil. In addition, the European Starch Industry Association AAP predicts for the chemical sector, an increase in the production of polymers based on starch of nearly 50% in 2025 (in reference to 2010) expected [4].

Starch and its derivatives have a wide application range. Edible films and biologically completely degradable films can be produced. These films can also be combined with functional additives, such as antimicrobial, antioxidant, essential oils, phenols and active nanoparticles. Thus, these films may be adjusted depending on the application [5]. To produce starch films a combination of heat, pressure, time and plasticiser are required. For the production of plain films extrusion is common praxis and the extruded good may be in a film or foam (or subsequently processed by for example microwaves into a foam). Press-moulding is applied if certain geometric shapes are desired [6]. These products are used in the form as a packaging material for fruits and vegetables (foam cups/trays) [7] and are nearly the only application of these products due to their high sensitivity to humidity.

This is called thermoplastic starch, there needs to be brought together for the extrusion/the press-moulding starch with a plasticiser. Over time, significant improvements in strength were achieved on starch films. To show the influence of plasticisers that it is thus possible reduce the brittleness of starch films [8]. The plasticiser also takes direct influence on the moisture content of the film, the permeability and solubility [9]. In particular glycerol and sorbitol are broadly used and promise stabile film [10]–[12]. However, the incorporation of antimicrobial proteins increases the brittleness [13]. Rheology/stretching properties and crystal structure of the films are strong influenced by the amylose:amylopectin ratio [14]. Interesting results provide also recently published studies about the influence of senegalia catechu as colourants in starch films. It turned out here that senegalia catechu improves the tensile strength at a level up to a maximum of 0.2% [15].

Due to the high oxygen permeability, high production costs/ economic insufficiency, or sensitivity to moisture often blends are used [16].

PLA/starch blends are often used as a substitute of polystyrene. It is used for example in the food industry as a disposable package in the form of boxes or trays [17].

PVA/starch blends are mechanically resistant, but have a poor moisture barrier properties and tensile strengths [18]. Currently PVA/starch blends do not have commercial importance due to high production costs compared to mineral oil-based packaging materials [19]. Currently the Fraunhofer Institute in Germany is researching to implement a commercial application for PVA/starch blends. The aim is to develop portion packs for detergents which dissolve after a predetermined time interval in water [20].

ILTPS/PBS-starch blends are promising future trends. These products have significantly improved tensile strength and elongation to break point compared to PBS/TPS blends [21].

PBS blends produced by thermoforming find use as packaging material of preserved baked goods in the form of trays [22].

Polylactic acid (PLA) derived from vegetable starch by metal catalysis or condensation [23]. It has high and increasing economic importance and is one of the most produced biopolymers worldwide [24].

To improve the tensile strength and mechanical properties of starches it is widely used in starch blends, too [25], [26].

If PLA reinforced with bamboo charcoal, so it can be suitable due to the sorption properties of coal also good for the packaging of foodstuffs. PLA can also be added to bio-nanocomposite films to increase their gas barrier properties and thermal stability [27], [28]. PLA can also be processed well to tissues and serves as teabags and higher priced products. Frequently it is also used in cosmetics for the production of jars [29], [30].

2.1.2 Cellulose & Cellulose derivate

Cellulose, which makes up 20 to 40% of the plant's cell walls [31], is a homopolymer of glucose (β-1,4 linkage) [32]. Primarily it is obtained from wood, although there are microorganisms that synthesise cellulose (e.g. Gluconacetobacter) [33]. There is great potential for cellulose for the coming years expected because it is the mostly abundant polymer on our planet [34].

Since cellulose itself is hydrophilic in its structure, insoluble in water and crystalline, no films can be produced from it. In the food industry, there are therefore only two known forms of application, Cellophane and cellulose acetate. Both are commonly used for the packaging of processed meats, baked goods, cheese and confectionery, due to its good barrier properties [35].

Usually Cellophane is provided with a coating of PVDC or nitrocellulose wax. These coatings aim to improve the moisture barrier properties [36], [37]. A further limitation is also given by the fact that both materials are not hot-sealable [38].

Recent research deal with microbiological cellulose biopolymers. Here, it is investigated how these polymers can be used in wound healing processes, as a substitute for synthetic mesh [37]. Also wins the reinforcement of other polymers with cellulose fibre increasing interest for improving oxygen permeability, biodegradability, tensile strength, modulus, etc. [39]–[41].

Other applications are targeted at so-called cellulosic electro active paper. Base is here Cellophane that is prepared in such a way that it can be used as a piezoelectric element [42]. Possible applications may here a completely biodegradable bio sensor which can be integrated on packaging.

Esterification of cellulose (single OH-groups) leading to thermoplastic properties. Here citrate and blends of citrates/derivatised oils are used (further used as substitute for environmentally harmful phthalates) as plasticiser [43]. Cellulose and cellulose/acrylic acid copolymer coatings have very good barrier properties against grease and are showing similar effectiveness to mineral oil-based films [44].

2.1.3 Proteins

Wheat (Triticum L.), rice (Oryza L.), corn (Zea mays L.) and soybeans (Glycine max (L.) Merrill) are the four of the most important vegetable protein suppliers worldwide [45]. This makes these raw materials interesting for use as biopolymers, due to high availability and low cost compared to other crops.

Wheat gluten is a mixture of protein (90%), fat (8%) and carbohydrates (2%) - mainly pentosans. The interaction of water-insoluble pentosans (can bind water) and fats, which form a lipoprotein complex with the gluten is relevant for viscoelastic properties [46]. This leads to the fact that these proteins are suitable for the production of films.

Gluten-based films have a low carbon dioxide and oxygen and a high water vapour permeability compared to mineral oil-based plastic films. The thickness of the film is in linear relationship to permeability of gases [47].

Studies by Barron et al. have shown that gluten biopolymer films are very suitable for the packaging of mushrooms and achieved better results than commercial hydrophilic polyether polyamide copolymer packaging films [48].

On average soybeans consist of 40 to 45% protein and have an average lipid content of 18 to 20%. Carbohydrates are representing about 35% (fibres included) [49].

Since plasticised soy protein is very brittle, plasticisers are used to tackle this problem. Most common is the use of glycerol [50].

It has been found that water vapour permeability can be significantly improved by using a mixture of 40% glycerol to 6% soy protein isolate. Reason for this is that the formation of organised protein networks is reduced at low protein concentrations [51].

Similar to thermoplastics from wheat protein, thermoplastics of soy protein also show good grease resistance [52]. The hydrophobicity of soy protein isolates can descend when they are associated with glutaraldehyde (cross-linkage) [53].

Using thermal compaction technique stable and inexpensive films in scale-up can be produced, which has however only been studied on a laboratory scale [54].

Furthermore, attempts have been made to apply soy biopolymer coating on paperboard. A $CaCl_2$ post-treatment showed an improvement of the water barrier properties for these coated products. However, this is accompanied by a reduction in tensile strength. Agricultural products and foods with high moisture content (e.g. fruits) would be potential applications [55].

Rice Proteins consist of 4 protein fractions: albumin, globulin, prolamin and glutenin. These together account for 41-42% of the rice grain, at a moisture content of 10.6% [56].

Research of rice bran films have shown that the pH influences the strength, oxygen permeability, water solubility and colour of the film largely, due to the solubility of proteins. However, the pH takes no effect on the water vapour permeability [57]. Alkaline conditions lead to stronger films, as well as a share of 2% glycerol as a plasticiser [58]. The practical application of rice bran film showed that the shelf life of strawberries can be extended by 2 days (in combination with UV-C and ClO_2) [59].

New approaches to the use of rice bran as a biopolymer as a replacement for PS uses the company Valueform Ltd in the UK. It does not aim to produce from films from rice bran, but moulded articles. A current research project together with the University of Reading examines the utility of such a moulded part for food intended packaging use (pizza) [60], [61]. A ratio of 25% to 75% rice starch glutenin exhibit acceptable film strength without great influence on the water vapour permeability. The higher the concentration of rice proteins is, the thicker film layers can be produced which, although increases the elongation at break point, but also reduces the tensile strength [62], [63].

Glycerol at a concentration of 30% leads to an optimum in reducing the brittleness of rice starch films for injection-moulding procedure [64]. However, the addition of glycerol and sorbitol as plasticiser leads to an increase in the water vapour permeability [65]. With phenols enriched films are effected on their tensile strength and opacity [66].

Zein are a group of proteins (prolamins) from corn, that occur as storage proteins in maize kernels (endosperms) [67].

Films made of zein are comparable with partially etherified cellulose in their sorption and water barrier properties and have for protein films typical excellent barrier properties for greases [68].

The higher the aw value in the film, the lower is the transition from glass-like state to rubber-like state (glass transition) [69].

The addition of glycerol and sorbitol lowers the water vapour permeability, the addition of mannitol increases the "critical surface tension of wetting" [70] and the addition of sorbitol, manitol, and glycerol increases the surface tension [71].

Recent research by Ozcalik and Tihminlioglu (2013) showed that a PP/zein blends can be used as "flexible antimicrobial and antioxidant films with controlled release properties by using zein" for food packaging applications [72]. Active packaging also can also be produced from zein-wax composites and zein-fatty acid blends [73].

2.1.3 Saccharides

Pectin is found in plants and is incorporated especially in the primary cell walls [74]. The most important pectin supplier hereby are citrus plants, followed by apples [75]. In recent years, increasingly research has been successfully performed, to produce active packaging films from pectin [76]–[78]. As plasticiser for pectin films glycerol can be used [79].

2.2 Biopolymers of Animal Origin

2.2.1 (Poly)saccharides

Chitin and chitosan are in a number of organisms present (e.g. exoskeleton of insects, fungi (no animal), crustacean) [80]. In industrial production mainly by-products of shellfish processing are used for the production of chitin/chitosan, like cancer armor, crab shell, lobster shells [81]. Increasingly, fungi or microorganisms are used [82], [83]. However, in the last year an increasing interest occurred in the production of biopolymers out of chitin/chitosan [84]. Several studies have shown that chitin/chitosan films have antimicrobial and antifungal effects [85], [86] and is therefore well suited for the packaging of food and agricultural products. In addition, it is an ideal material for the development of active packaging solutions and coatings, for example through the use of Lycium barbarum fruit extract in the biopolymer matrix [87] or as a coating for tomatoes after harvesting [88]. It is thus superior to mineral oil-based plastics in many ways.

2.2.2 Proteins

Keratin is a protein which occurs for example in hair, feathers, horns and skin and has a fibrous structure. Generally, a distinction is made between α- and β-keratin [89]. So far relatively little research has been done in terms of keratin, even if it is present cost-effective. The use of glycerol as plasticiser, shows transparent, barrier strong and more than 100% stretchable films [90]. PHA/keratin films show in comparison to pure keratin film improved barrier properties, but also showed a lowered water, limonene and oxygen permeability by 50% [91]. Dialdehyde starch/keratin films have also been made into stable packaging films [92]. Currently, however, there is no commercial use for keratin biopolymers (exception textile and cosmetics industry) but they might have a potential for future applications.

Milk proteins mainly consist of two protein fractions in particular casein (approximate 81%) and whey protein (approximate 19%) [46].

In particular, whey protein, which accumulates a by-product of cheese manufacturing, has a growing interest in the production of biopolymers. The Fraunhofer Institute is currently conducting research on several projects with the industry on the use of biopolymers based on whey as a food packaging material or as a coating [93]. Sorbitol and glycerol can be equally used as a plasticizer, wherein glycerol leads to higher oxygen permeability93. Here can be a trend towards active packaging observed with respect to antimicrobial and antifungal function [94], [95].

2.3 Biopolymers of Microbiological Origin

2.3.1 PHA, PHB, PHBV

There are currently more than 300 known microorganisms producing polyhydroxyalkanoates (PHA) and its derivatives (PHB, PHBV, PLLA etc.). It is used in microorganisms for energy and carbon storage properties [96]. Brittleness and poor thermal and mechanical properties currently prevent commercial use as packaging material [97]. These poor properties can be improved in use for starch blend or in the presence of plasticiser [98].

2.3.2 Microbial Cellulose

Acetobacter xylinum is the predominant microorganism for producing microbial cellulose. In this case the bacterium converts to sugar in cellulose, which is then won biotechnological [99].

Due to high purity it has for food packaging or coatings a good opportunity for future applications [100]. Anyway, this is not currently the case. Recent research, however, are focused on nanocomposites on bacterial cellulose-based, so as to develop active packaging [101], [102].

3. CONCLUSION & FORECAST

The packaging and food industry is undergoing a transformation. More and more the trend towards environmentally friendly products is present. The field of biopolymers offers here a wide scope. Currently, there are only a few industrially widely used solutions, as PLAs, but a lot of research progress is perceivable, such as the use of plasticiser, nanocomposites, blends and reinforcements.

Recent scientific research focuses increasingly in the direction of developing functional coatings and active packaging concepts. Their functionality has already been proved in laboratory scale. In addition, efforts are being made to make the production of biopolymers industrially attractive, by the use of by-products from the food processing industry (e.g. whey proteins, rice bran).

Interesting is also the approach of the company Valueform Ltd, which produces first moulded articles from rice bran. This is a new use and has great potential as a replacement for PS. It would be attractive if these products might be suitable as active packaging materials (reducing spoilage, moisture blocking capability, etc.) by using coatings or new formulations, which is still under investigation.

Such a product would appear also in direct competition with cellulose/lignin, which are still mainly produced from wood fibres, and thus counteract an increasing deforestation.

Cellulose extracted from microorganisms are bidding potential, but are still too expensive and therefore only used in the pharmaceutical industry and other highly specialised industries. However, high-purity products can be produced by microorganism.

Polymers of starch are one of the most studied materials. Starch is readily available and can be obtained from annually harvests. These products are currently most developed and also provide the basis for PLAs. However, these products could be in times of population increase in the criticism, because usable space for food production has to be sacrificed (similar criticism is currently present in the production of bio-ethanol).

Certainly, the market share and the importance of biopolymers will grow, since mineral oil is a limited resource and is also harmful to the environment.

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