Research Paper

Bioderadable Polymers in Food Packaging

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Abstract: In recent years, there has been a marked increase in the interest in use of biodegradable materials in packaging. The principal function of packaging is protection and preservation of food from external contamination. This function involves retardation of deterioration, extension of shelf life, and maintenance of quality and safety of packaged food. Biodegradable polymers are the one which fulfill all these functions without causing any threat to the environment. The belief is that biodegradable polymer materials will reduce the need for synthetic polymer production (thus reducing pollution) at a low cost, thereby producing a positive effect both environmentally and economically.

Keywords: Biodegradable · Deterioration · Shelf life · Synthetic polymer

I. INTRODUCTION

As well known, synthetic polymer materials have been widely used in every field of human activity during the last decades. These artificial macromolecular substances are usually originating from petroleum and most of the conventional ones are regarded as non-degradable. However, the petroleum resources are limited and the blooming use of non-biodegradable polymers has caused serious environmental problems. In addition, the non-biodegradable polymers are not suitable for temporary use such as sutures. Thus, the polymer materials which are degradable and/or biodegradable have been paid more and more attention since 1970s. Food is the necessity of our day to day life. Now a day’s most of the food items are packed. In everyday life, packaging is an important area where biodegradable polymers can be used. The primary factors driving development of the biodegradable packaging market include the increase in crude oil prices, which has narrowed the price differential; consumer demand; the proliferation of convenience packaging; development of new applications for bioplastics; increased economic viability as production ramps up and unit costs decrease, and development of the composting infrastructure for optimal disposal of bioplastic products. Even so, consumer demand for products that are environmentally friendly, safer and nontoxic, as well as, a currently favorable economic scenario leads to the conclusion that biodegradable packaging products will become increasingly popular.

In order to reduce the volume of waste, biodegradable polymers are often used. Besides their biodegradability, biopolymers have other characteristics as air permeability, low temperature sealability, availability and low price. Several biopolymers such as starch, cellulose, chitosan, PLA, PCL, PHB etc. are used for packaging purposes. The current trend in food packaging is the use of blends of different biopolymers like starch-PLA blends, starch-PCL blends etc. Bottles, jars, vials; drums, pails, cans, barrels, buckets; caps, closures, aerosol parts, packaging films, food containers, disposable cups; coating for all types of packaging, packaging bags, household and institutional refuse bags and film; boxes and baskets etc. are being manufactured by using biodegradable polymers. Many companies like Novamont, BASF, Biomer, National starch, DuPont etc. are producing biopolymers.

What are Polymers?

Polymer materials are solid, non-metallic compounds of high molecular weights (Callister 1999). They are comprised of repeating macromolecules, and have varying characteristics depending upon their composition. Each macromolecule that comprises a polymeric material is known as a mer. A single mer is called a monomer, while repeating mer units are known as polymers. A variety of materials (both renewable and non-renewable) are employed as feedstock sources for modern plastic materials. Plastics that are formed from non-renewable feedstocks are generally petroleum based, and reinforced by glass or carbon fibers (Williams et al.
2000). Renewable resource feedstocks include microbial-grown polymers and those extracted from starch. It is possible to reinforce such materials with natural fibers, from plants such as flax, jute, hemp, and other cellulose sources (Bismarck et al. 2002).

**What are Biopolymers?**

Biopolymers are long chain compounds made up of long chain molecule subunits. A biopolymer is any organic polymer. Biopolymers have been around for billions of years longer than synthetic polymers like plastics. Well known biopolymers include starch, proteins and peptides, DNA, and RNA. Together these make up much of our bodies and the majority of the biosphere. These are biodegradable, ecofriendly and are obtained from natural sources.

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable, and not toxic to produce. They can be produced by biological systems (i.e. micro-organisms, plants and animals), or chemically synthesized from biological starting materials (e.g. sugars, starch, natural fats or oils, etc.). Biopolymers are an alternative to petroleum-based polymers (traditional plastics).

**Origin and description of biobased polymers**

Biobased polymers may be divided into three main categories based on their origin and production:

**Category 1:** Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose and proteins like casein and gluten.

**Category 2:** Polymers produced by classical chemical synthesis using renewable biobased monomers. A good example is polylactic acid, a biopolyester polymerized from lactic acid monomers. The monomers themselves may be produced via fermentation of carbohydrate feedstock.

**Category 3:** Polymers produced by microorganisms or genetically modified bacteria. To date, this group of biobased polymers consists mainly of the polyhydroxyalkanoates, but developments with bacterial cellulose are in progress.

The three categories are presented in schematic form in Figure.1 below:

![Categories of biopolymers](Figure.1)
Starch

Starch is a well-known hydrocolloid biopolymer. It is a low cost polysaccharide, abundantly available and one of the cheapest biodegradable polymers.

(Figure 2: Molecular structure of starch)

Starch is produced by agricultural plants in the form of granules, which are hydrophilic. Starch is mainly extracted from potatoes, corn, wheat and rice. It is composed of amylose (poly-α-1, 4-D-glucopyranoside), a linear and crystalline polymer and amylpectin (poly-α-1, 4-Dglucopyranoside and α-1, 6-D-glucopyranoside), a branched and amorphous polymer. Starch has different proportions of amylose and amylpectin ranging from about 10–20% amylase and 80–90% amylpectin depending on the source. Amylose is soluble in water and forms a helical structure. The relative amounts and molar masses of amylose and amylpectin vary with the starch source, yielding to materials of different mechanical properties and biodegradability (Fredrikson et al. 1998, Ratnayeke et al. 2001). As the amylose content of starch increases, the elongation and strength increase too. The stability of starch under stress is not high. The glucoside links start to break at 150 °C and above 250 °C the granules collapse. Retrogradation, i.e. reorganization of hydrogen bonds, is observed at low temperatures, during cooling. In its applications starch can be mixed, kept intact, and used in various resins as a filler or melt for blending compounds. In the former form, fillers are starch whiskers used with polymer resins.

Starch is usually used as a thermoplastic. It is plasticized through destrucution in presence of specific amounts of water or plasticizers and heat and then it is extruded. Thermoplastic starch (TPS) has a high sensitivity to humidity. Thermal properties of TPS have been shown to be more influenced by the content of water than the starch molecular weight. TPS thus obtained is almost amorphous. Biodegradation of starch is achieved via hydrolysis at the acetal link by enzymes (Chandra and Rustgi 1998, Claus 2000). The α-1, 4 link is attacked by amylases while glucosidases attack the α-1, 6 link. The degradation products are non toxic.

Polyactic acid

PLA is usually obtained from polycondensation of D- or L-lactic acid or from ring opening polymerization of lactide, a cyclic dimer of lactic acid. Two optical forms exist: D-lactide and L-lactide. The natural isomer is L-lactide and the synthetic blend is DL-lactide. Other different synthetic methods have been studied too. PLA is a hydrophobic polymer due to the presence of –CH3 side groups. It is more resistant to hydrolysis than PGA because of the steric shielding effect of the methyl side groups. The typical glass transition temperature for representative commercial PLA is 63.8 °C, the elongation at break is 30.7% and the tensile strength is 32.22 MPa (Briassoulis 2004). Regulation of the physical properties and biodegradability of PLA can be achieved by employing a hydroxy acids co monomer component or by racemization of D- and L- isomers (Sodegard and Stolt 2002). A semi-crystalline polymer (PLLA) (crystallinity about 37%) is obtained from L-lactide whereas poly (DL-lactide) (PDLLA) is an amorphous polymer (Vert 2002). Their mechanical properties are different as are their degradation times (Auras et al. 2004). PLLA is a hard, transparent polymer with an elongation at break of 85%-105% and a tensile strength of 45-70 MPa. It has a melting point of 170-180 °C and
a glass transition temperature of 53 °C (Mochizuki and Hirami 1997). PDLLA has no melting point and a Tg around 55 °C. It shows much lower tensile strength (Rutot and Dubois 2004).

PLA has disadvantages of brittleness and poor thermal stability. PLA can be plasticized to improve the chain mobility and to favor its crystallization. Plasticization is realized with oligomeric acid, citrate ester or low molecular polyethylene glycol (Jacobsen and Fritz 1999). High molecular weight PLAs are obtained through ring opening polymerization. This route allows also the control of the final properties of PLA by adjusting the proportions of the two enantiomers (Okada 2002). Other routes are melt/solid state polymerization (Maharana et al. 2009), solution polymerization or chain extension reaction (Zeng et al. 2009). High molecular weight PLA has better mechanical properties (Perego et al. 1977).

(Figure.3: Schematic view of the ring-opening polymerization reaction of polylactide from lactide, a dimer of lactic acid.)

The rate of degradation of PLA depends on the degree of crystallinity. The degradation rate of PLLA is very low compared to PGA; therefore, some copolymers of lactide and glycoside have been investigated as bioreabsorbable implant materials (Miller et al. 1977). The biodegradability of PLA can also be enhanced by grafting. The graft copolymerization of L-lactide onto chitosan was carried out by ring opening polymerization using a tin catalyst. The melting transition temperature and thermal stability of graft polymers increase with increasing grafting percentages. As the lactide content increases, the degradation of the graft polymer decreases (Luckachan and Pillai 2006).

**Poly (hydroxyalkanoates) (PHAs)**

PHAs, of which poly (hydroxybutyrate) (PHB) is the most common, are accumulated by a large number of bacteria as energy and carbon reserves. Due to their biodegradability and biocompatibility these biopolymers may easily find numerous applications. The properties of PHAs are dependent on their monomer composition, and it is, therefore, of great interest that recent research has revealed that, in addition to PHB, a large variety of PHAs can be synthesized by microbial fermentation. The monomer composition of PHAs depends on the nature of the carbon source and microorganisms used. PHB is a typical highly crystalline thermoplastic whereas the medium chain lengths PHAs are elastomers with low melting points and a relatively lower degree of crystallinity. A very interesting property of PHAs with respect to food packaging applications is their low water vapor permeability which is close to that of LDPE (Claus 2000).

Since 1925, PHB is produced biotechnologically and was attentively studied as biodegradable polyester (Zhang et al. 1997). The R alkyl substituent group is methyl. PHB is highly crystalline with crystallinity above 50%. Its melting temperature is 180 °C. The pure homopolymer is a brittle material. Its glass transition temperature is approximately of 55 °C. It has some mechanical properties comparable to synthetic degradable polyesters, as PLA (Savenkova et al. 2000). During storage time at room temperature a secondary crystallization of the amorphous phase occurs. As a result, stress and elongation modulus increase (E = 1.7 GPa) while the polymer becomes more brittle and hard. Elongation at break is then much lower (10%) (El.Hadi et al. 2002). Compared to conventional plastics, it suffers from a narrow processability window (Barham and Keller 1986). PHB is susceptible to thermal degradation at temperatures in the region of the melting point (Grassie et al. 1984). To make the process easier, PHB can be plasticized, with citrate ester.

PHB resembles isotactic polypropylene (iPP) in relation to melting temperature (175-180°C) and mechanical behavior. PHBs Tg is around 9°C and the elongation to break of the ultimate PHB (3-8%), which is markedly lower than that of iPP (400%). Incorporation of 3HV or 4HB co-monomers produces remarkable
changes in the mechanical properties: the stiffness and tensile strength decrease while the toughness increases with increasing fraction of the respective co-monomer (Claus 2000). PHB is degraded by numerous microorganisms (bacteria, fungi and algae) in various environments (Kim et al. 2000). The hydrolytic degradation yields to the formation of 3-hydroxy butyric acid, a normal constituent of blood, nevertheless with a relatively low rate. Different monomers have been grafted onto PHB to prepare biodegradable polymers to be used for wastewater treatments. The grafted monomers were either hydrophilic as acrylic acid or sodium-p-styrene sulfonate, or hydrophobic as styrene or methyl acrylate (Hsieh et al. 2009). The degree of grafting was different according to the monomers, increasing with the following order styrene, sodium-p-styrene sulfonate, methyl acrylate and acrylic acid.

Multicomponent polymeric systems containing PHB have been obtained by two ways. The first is a radical polymerization of an acrylic polymer in the presence of PHB. The second consists in melt mixing PCL with PHB. Peroxide is used in both processes to form intergrafted species responsible for compatibilization (Avella et al. 1996). These methods have been considered as reactive blending. It should be noted that apart from the bacterial synthetic way, other chemical ways have been developed for the production of PHB. The ring opening polymerization of β-butyrolactone yields to PHB too (Sheldon et al. 1971, Hori et al. 1996, Juzwa and Jedlinski 2006). Different structures are obtained according to the synthesis route. An isotactic polymer with random stereo sequences is obtained via bacterial process while a polymer with partially stereo regular block is obtained via chemical synthesis. Applications that have been developed from PHB and related materials (e.g. Biopol) can be found in very different areas and cover packaging, hygienic, agricultural, and biomedical products. Recent application developments based on medium chain length PHAs range from high solid alkyd-like paints to pressure sensitive adhesives, biodegradable cheese coatings and biodegradable rubbers. Technically, the prospects for PHAs are very promising. When the price of these materials can be further reduced, application of biopolysterels will also become economically attractive (Claus 2000).

Polycaprolactone (PCL):
Poly-ε-caprolactone is a relatively cheap cyclic monomer. A semi-crystalline linear polymer is obtained from ring-opening polymerization of ε-caprolactone in presence of tin octoate catalyst (Mochizuki and Hirami 1997). PCL is soluble in a wide range of solvents. Its glass transition temperature is low, around -60 °C, and its melting point is 60 – 65 °C. PCL is a semi-rigid material at room temperature, has a modulus in the range of low-density polyethylene and high-density polyethylene, a low tensile strength of 23 MPa and a high elongation to break (more than 700%). Thanks to its low Tg, PCL is often used as a compatibilizer or as a soft block in polyurethane formulations. Enzymes and fungi easily biodegrade PCL (Chandra and Rustgi 1998, Tokiwa 1977). To improve the degradation rate, several copolymers with lactide or glycoside have been prepared (Nair and Laurencin 2007). PCL is commercially available under the trade names CAPA® (from Solvay, Belgium), Tone® (from Union Carbide, USA) or Celgreen® (from Daicel, Japan) and many others. Possible applications in packaging have been investigated.

Cellulose and derivatives

Cellulose is the most abundantly occurring natural polymer on earth and is an almost linear polymer of anhydroglucose. It is a linear polymer with very long macromolecular chains of one repeating unit, cellobiose. Cellulose is crystalline, infusible and insoluble in all organic solvents (Chandra and Rustgi
Because of its regular structure and array of hydroxyl groups, it tends to form strongly hydrogen bonded crystalline micro fibrils and fibers and is most familiar in the form of paper or cardboard in the packaging context. Waxxed or polyethylene coated paper is used in some areas of primary food packaging; however the bulk of paper is used for secondary packaging.

Cellulose is a cheap raw material, but difficult to use because of its hydrophilic nature, insolubility and crystalline structure. The cellophane produced is very hydrophilic and, therefore, moisture sensitive, but it has good mechanical properties. It is, however, not thermoplastic owing to the fact that the theoretical melt temperature is above the degradation temperature, and therefore cannot be heat-sealed.

Cellophane is often coated with nitrocellulose wax or PVdC (Poly Vinylidene Chloride) to improve barrier properties and in such form it is used for packaging of baked goods, processed meat, cheese and candies. A number of cellulose derivatives are produced commercially, most commonly carboxy-methyl cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and cellulose acetate. Of these derivatives only cellulose acetate (CA) is widely used in food packaging’s (baked goods and fresh produce). CA possesses relatively low gas and moisture barrier properties and has to be plasticized for film production (Claus 2000). Many cellulose derivatives possess excellent film-forming properties, but they are simply too expensive for bulk use. This is a direct consequence of the crystalline structure of cellulose making the initial steps of derivatization difficult and costly. Research is required to develop efficient processing technologies for the production of cellulose derivatives if this situation is to change. Tenite® (Eastman, USA), Bioceta® (Mazzucchelli, Italy), Fasal® (IFA, Austria) and Natureflex® (UCB, Germany) are some of the trade names of cellulose-based polymers.

II. BLENDS

Starch-polyvinyl alcohol: TPS and PVOH have excellent compatibility and their blends are of particular interest. TPS and starch can be blended at various ratios to tailor the mechanical properties of the final material. Compared to pure TPS materials, blends present improved tensile strength, elongation and processability (Mao and Imam 2000, Fishman and Coffin 2006). Their biodegradability has been recently investigated (Russo et al. 1998). The PVOH content has an important impact on the rate of starch degradation increasing the amount of PVOH will decrease this rate.

Starch-PLA: The mechanical properties of blends of starch with PLA using conventional processes are poor due to incompatibility. An elongation increase can be achieved by using plasticizers or reacting agents during the extrusion process. Coupling agents like isocyanates have been used. The hydroxyl groups of starch could react with the isocyanate group resulting in urethane linkages and compatibilization of these systems. The effect of gelatinization of starch was also investigated. It has been shown that in PLA/gelatinized starch blends, starch could be considered as a nucleating agent, resulting in an improvement of crystallinity in PLA blends and a greater superiority of mechanical properties. Another way to improve compatibilization is to use a compatibilizer. Maleic anhydride can be used for this purpose (Zhang 2004). An initiator was used to create free radicals on PLA and improved the reaction between maleic acid and PLA. The anhydride group on maleic acid could react with the hydroxyl groups present in starch. Interfacial adhesion between starch and PLA was then significantly improved. The mechanical properties obtained for PLA/starch blends compatibilized with maleic acid are higher than those obtained for virgin PLA/starch blends. A biodegradable PLA-grafted amylose copolymer has been synthesized, to be used as compatibilizer agent in starch/PLA blends (Ouhib et al. 2009).

Starch – PCL: To prepare films by using the film blowing technique, TPS was blended with PCL to adjust the rheological properties of the melt before the process (Matzinos et al. 2002). Novamont (Italy) produces a class of starch blend with different synthetic components. Its trade name is Mater-Bi®. Four grades are available; one of them consists of PCL (Mater-Bi® Z). The highest amount of starch allows the acceleration of the degradation of PCL. The behavior of some PCL-modified starch blends has been studied (Yavuz 2003). The addition of modified starch leads to an increase of the Young’s modulus of PCL and a decrease in tensile strength and elongation at break values. The blend becomes less ductile (Shin et al. 2004). Some synthetic polymers with lower biodegradability are used to control the rate of biodegradation according to the applications. The modulus of blends of high-amylose corn starch (25% wt.) and PCL was 50% higher than that of PCL and the tensile strength 15% lower. To increase the mechanical properties of PCL/starch, blends with LDPE were prepared. The biodegradation rate of PCL, which is very low, can be significantly increased by the presence of starch (Bastioli et al. 1995).

PCL/Chitin-chitosan blends: PCL blends with chitin were prepared as biodegradable composites by melt blending (Yang et al. 2001). Increasing the amount of chitin has no effect on the melting or crystallization
temperature. This was attributed to a non miscible blend. Another blending route is solvent casting (Senda et al. 2001). The degree of crystallinity of PCL decreases upon blending with chitin. Same results are obtained with PCL/chitosan blends. These blends are expected to have good mechanical properties.

III. MATERIAL PROPERTIES

1. Gas barrier properties

Many foods require specific atmospheric conditions to sustain their freshness and overall quality during storage. Hence, increasing amounts of our foods are being packed in protective atmosphere with a specific mixture of gases ensuring optimum quality and safety of the food product in question. To ensure a constant gas composition inside the package, the packaging material needs to have certain gas barriers. In most packaging applications the gas mixture inside the package consists of carbon dioxide, oxygen and nitrogen or combinations hereof. The objective of this section is to describe the gas barriers of biobased materials using mineral oil based polymer materials as benchmarks. In Figure.5, different biobased materials are compared to conventional mineral-oil-based polymer materials. The figure is based on information from literature and on measurements of commercially available materials performed by ATO (Wageningen, NL) (Claus 2000).

(Figure.5: Comparison of oxygen permeability of biobased materials compared to conventional mineral-oil-based materials. Permeability of materials marked with * was measured by ATO, Wageningen, NL (23°C, 50% RH), information on other materials are based on literature (Rindlav-Westling et al., 1998; Butler et al., 1996).)

Alternatives to presently available gas barrier materials like EVOH and PA6 and an equivalent biobased laminate would be an outer-layer of plasticized chitosan, a protein or starch-derived film combined with PLA or PHA. Notably, the gas barrier properties of PA6 and EVOH are sensitive towards moisture and the LDPE creates a very effective water vapor barrier ensuring that the moisture from the foodstuff does not interfere with the properties of PA6 or EVOH. In the same fashion, PLA and PHA will protect the moisture-sensitive gas-barrier made of polysaccharide and protein (Claus 2000).

Gas barriers and humidity

As many of these biobased materials are hydrophilic, their gas barrier properties are very much dependent on the humidity conditions for the measurements and the gas permeability of hydrophilic biobased materials may increase manifold when humidity increases. Notably, this is a phenomenon also seen with conventional polymers. The gas permeability of high gas barrier materials, such as nylon and ethyl vinyl alcohol, is likewise affected by increasing humidity. Gas barriers based on PLA and PHA is not expected to be dependent on humidity (Claus 2000).
Water vapor transmittance

A major challenge for the material manufacturer is the by nature hydrophilic behavior of many biobased polymers as a lot of food applications demand materials that are resistant to moist conditions. However, when comparing the water vapor transmittance of various biobased materials to materials based on mineral oil (see Figure 6); it becomes clear that it is possible to produce biobased materials with water vapor transmittance rates comparable to the ones provided by some conventional plastics. However, if a high water vapor barrier material is required, very few biobased materials apply. Notably, developments are currently focusing on this problem and future biobased materials must also be able to mimic the water vapor barriers of the conventional materials known today (Claus 2000).

(Figure 6: Water vapor transmittance of biobased materials compared to conventional packaging materials based on mineral oil. Water vapor transmittance of materials marked with * was measured by ATO (Wageningen, NL) at 23°C, 50% RH. Transmittance of other materials are based on literature and measured at same conditions (Rindlav-Westling et al., 1998; Butler et al., 1996).)

Thermal and mechanical properties

Next to the barrier properties of the final packaging, the thermal and mechanical properties of the materials are both important for processing and also during the use of the products derived from these materials. Most biobased polymer materials perform in a similar fashion to conventional polymers. This indicates that polystyrene-like polymers (relatively stiff materials with intermediate service temperatures), polyethylene-like polymers (relatively flexible polymers with intermediate service temperatures) and PET-like materials (relatively stiff materials with higher service temperatures) can be found among the available biobased polymers. The mechanical properties in terms of modulus and stiffness are not very different compared to conventional polymers. In figure 7 a comparison of the thermal properties of biobased polymers with existing polymers is made. The modulus of biobased materials ranges from 2500-3000 MPa and lowers for stiff polymers like thermoplastic starches to 50 MPa and lower for rubbery materials like medium chain polyhydroxyalkanoates (Claus 2000).

Furthermore, the modulus of most biobased and petroleum derived polymers can be tailored to meet the required mechanical properties by means of plasticizing, blending with other polymers or fillers, cross linking or by the addition of fibers. A polymer like bacterial cellulose could for instance be used in materials which require special mechanical properties. In theory, biobased materials can be made having similar strength to the ones we use today (Iguchi et al., 2000).
Figure 7: Comparison of the thermal properties of biobased polymers with conventional polymers. (All data is from company information.)

IV. COMPOSTABILITY

Compostability is another important property required for biopolymers used in food packaging. Figure 8 compares the compostability of various biobased materials. Notably, the “composting time” depicted in the figure represents the approximate period of time required for an acceptable level of disintegration of the material to occur. This means that the original material should not be recognizable anymore in the final compost (fraction < 10 mm) nor in the overflow (fraction > 10 mm). The composting time does not reflect the time required for the biodegradation of the materials to be fully completed. The process could subsequently be completed during the use of the compost. The level of technology applied in the composting process highly affects the composting time needed for complete disintegration. Hence, it takes much longer to obtain a mature compost using low technology composting (e.g. passive windrow composting) than using high technology as in an intensively controlled tunnel composting process. The durations presented in figure 2.6 are based on an intermediate level of technology as observed in actively aerated and mechanically turned hall composting. Furthermore, the composting time needed for complete disintegration is also affected by the particle size of the material. For example, wood is rapidly composted in the form of sawdust and small chips. A wooden log,
however, takes more than one year to be completely disintegrated. The durations presented in this figure are based on dimensions regularly used for packaging applications (Claus 2000).

(Figure 8: Indication of the time required for composting of various biobased and synthetic polymeric materials. Measurements of composting times were performed at ATO. The durations presented in this figure are based on an intermediate level of technology as observed in actively aerated and mechanically turned hall composting.)

The compostability of the materials are highly dependent on the other properties of the materials, e.g. the first step of the composting is often a hydrolysis or wetting of the material. The rate of this step is very much related to the water vapor transmittance and the water resistance of the material. Hence, the composting rate of a material will be dependent on its other properties (Claus 2000).

Manufacturing of biobased food packaging

Engineering of a biobased package or packaging material requires knowledge of the processing and material properties of the polymers. If the properties of the native biopolymer 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. For very specific requirements (very low gas permeability or high water resistance) it is unlikely that one polymer will be able to provide all required properties even after modifications. Hence, it is necessary to use multiple materials in a composite, a laminate or co-extruded material (Claus 2000).

(Figure 9: Designing and manufacturing of biobased packages and packaging materials require a multistep approach)
Possible products produced of biobased materials

The fundamental repeating chemical units of the biobased materials described so far are identical to those of a significant body of the conventional plastics. Thus, in the broadest sense, poly-saccharides possessing repeating acetal functionality can be regarded as the naturally occurring analogues of the synthetic polyacetals; proteins (repeating peptide functionality) can be compared to the synthetic polyamides while polylactic acid is merely an example of the diverse group of polyesters.

<table>
<thead>
<tr>
<th>Processing route</th>
<th>Product examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Co-)Extruded film</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Cast film</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Thermoformed sheets</td>
<td>Trays, cups</td>
</tr>
<tr>
<td>Blown films</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Injection (blow-)moulding</td>
<td>Salad pots, cutlery, drinking breakers, cups, plates, drinks bottles, trays</td>
</tr>
<tr>
<td>Fibres and non-wovens</td>
<td>Agricultural products, diapers, feminine hygiene products, certain medical plastics, clothing</td>
</tr>
<tr>
<td>Extrusion coating</td>
<td>Laminated paper or films</td>
</tr>
</tbody>
</table>

(Figure 10: The major processing routes to potential biobased products.)

Clearly, however, the gross physical and chemical properties of native biobased materials and their synthetic counterparts are quite different and this is a feature of additional chemical functionality inherent in biobased materials. It should be expected that following requisite processing and product development of biobased materials resulting properties should equal or better those of the conventional alternatives. However, such processing and product development is not always trivial and is unlikely to be cost effective in all cases. It is not surprising, therefore, that the current applications of biobased materials seek not to emulate the properties of conventional plastics, but to capitalize on inherent biodegradability and on other unique properties of these polymers. Biobased plastic applications are currently targeted towards single-use, disposable, short-life packaging materials, service ware items, disposable non-woven's and coatings for paper and paperboard applications. In general, the same shapes and types of food packaging can be made from synthetic and biobased resources. The question is whether the same performance can be achieved by using the biobased materials as with the synthetic ones (Claus 2000).

Blown (barrier) films

Blown films comprise one of the first product categories to be developed based on mineral oil derived biodegradable polyesters. They have successfully been applied as garbage bags and related applications. Film blowing grades of renewable polymers have been developed based on PLA. Blown films based on these biopolymers exhibit excellent transparency and cellophane-like mechanical properties. The sealability depends on the degree of crystallinity and good printability can also be achieved. The possibilities of film blowing PHB/V materials are at this time limited due to their slow crystallization and low melt strength. In many food packaging applications, water vapor barriers as well as gas barriers are required. No single biobased polymer can fulfill both these demands. In this case, the use of co-extrusion can lead to laminates which meet the objectives. Paragon (Avebe, NL) materials which are based on thermoplastic starch can be film blown in a co-extrusion set-up with polymers like PLA and PHB/V as coating materials, resulting in a barrier coating which, for example, proved to be successful in the packaging of cheese (Tuil et al., 2000). The use of Paragon tie-layers provides the adhesion between the coating and the base layer. In this way, starch-based materials could provide cheap alternatives to presently available gas barrier materials like EVOH and PA6 (Claus 2000).

Thermoformed containers

A next class of products is thermoformed containers for food packaging. In order to be able to thermoform a polymer it should be possible to process this material from the melt (extrusion) into sheets and consequently thermoforming these sheets just above the Tg or Tm of the material. Thermoformed products can be found based on PLA and PHB/V. Again, it is possible to produce thermoformed articles from laminates based on Paragon as well as other thermoplastically processable biopolymers (Claus 2000).
Foamed products

Starch-based foams for loose fill applications (Novamont, (I), National Starch (USA) a.o.) have been commercially introduced with success some years ago and the market for these products is still growing. Foamed products like trays and clamshells based on starch for food packaging have not yet been introduced commercially. Products based on a molding technique from a slurry phase (Earthshell (USA), APACK (D)) are close to market introduction. These products are produced from starch base slurries with inorganic and agro fiber based fillers. Other proposed techniques include loose-fill molding (Novamont (I), Biotec (D)), foam extrusion (Biotec (D)), and extrusion transfer molding (Standard Starch (USA)) and expandable bead molding (Tuil et al., (In press)). Foamed products based totally on PLA are still in a developmental phase (Claus 2000). In order to be able to use these starch-foamed products in food contact applications coatings should be applied on the starch-based foams.

Adhesion between the foam and the coating is of importance. Paraffin and other oligomer based coatings are proposed next to PLA and PHB/V based coatings. Protein and medium chain length PHA based coatings (ATO, 2000) are close to market introduction. Other proposed techniques include loose-fill molding (Novamont (I), Biotec (D)), and extrusion transfer molding (Standard Starch (USA)) and expandable bead moulding (Tuil et al., (In press)). Foamed products based totally on PLA are still in a developmental phase. In order to be able to use these starch-foamed products in food contact applications coatings should be applied on the starch-based foams. Adhesion between the foam and the coating is of importance. Paraffin and other oligomer based coatings are proposed next to PLA and PHB/V based coatings. Protein and medium chain length PHA based coatings (ATO, 2000) are close to market introduction (Claus 2000).

Coated paper

It is expected that paper will stay an important biobased packaging material. Paper and board materials have excellent mechanical properties; however, the gas permeabilities are too high for many food applications. The hydrophilic nature of the paper-based materials is a major challenge of these materials when packaging moist foods. To date, the paper-based materials have been coated with a thin layer of synthetic plastic which has provided the materials with the required gas property and water resistance. Alternatively, biobased materials might be used as coating materials thus paving the way for a 100% biobased packaging material. Paper-based materials coated with PE are readily repulpable as the hydrophobic PE is easily removed in the pulping process. Hence, paper-based materials coated with biobased, hydrophobic polymeric materials are, likewise, going to be repulpable (Claus 2000).

Additional developments

To be able to produce a 100% biobased packaging development of biobased additives is needed. Additives used in the production of packaging are plasticizers, UV-stabilizers, adhesives, inks and paints, natural pigments and colorants. So far, few developments have been made in this field and it is suggested to direct research to this area (Claus 2000).

Some Biodegradable Packaging materials available in the market

<table>
<thead>
<tr>
<th>Biopolymers</th>
<th>Manufacturing company</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB; PHV</td>
<td>Monsanto, UK, Biomer, UK</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Courtaulds, USA; Mazzucchelli, Italy</td>
</tr>
<tr>
<td>PLA</td>
<td>Cargill Dow Polymers, USA; Mitsui, Japan; Hycail, Netherlands; Galactic, USA</td>
</tr>
<tr>
<td>Starch</td>
<td>National Starch, UK; Avebe, Netherlands</td>
</tr>
<tr>
<td>Starch based blends</td>
<td>Novamont, Italy; Biotec, Germany; Earth Shell, USA; Biop, UK</td>
</tr>
</tbody>
</table>

V. CONCLUSION

The food industry has seen great advances in the packaging sector since its inception in the 18th century with most active and intelligent innovations occurring during the past century. These advances have led to improved food quality and safety. While some innovations have stemmed from unexpected sources, most have been driven by changing consumer preferences. The new advances have mostly focused on delaying oxidation and controlling moisture migration, microbial growth, respiration rates, and volatile flavors and aromas. This focus parallels that of food packaging distribution, which has driven change in the key areas of sustainable packaging, use of the packaging value chain relationships for competitive advantage, and the evolving role of food service packaging. Biopolymers have highly influenced the packaging sector greatly.

Environmental responsibility is constantly increasing in importance to both consumers and industry.
For those who produce biodegradable plastic materials, this is a key advantage. Biopolymers limit carbon dioxide emissions during creation, and degrade to organic matter after disposal. Although synthetic plastics are a more economically feasible choice than biodegradable ones, an increased availability of biodegradable plastics will allow many consumers to choose them on the basis of their environmentally responsible disposal. The processes which hold the most promise for further development of biopolymers are those which employ renewable resource feedstocks. Time is of the essence for biodegradable polymer development, as society’s current views on environmental responsibility make this an ideal time for further growth of biopolymers.

REFERENCES

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