

Chapter 18

Starch-based plastics

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18.1. Introduction

Brazil disposes of approximately 240,000 tons of waste per day, an amount lower than that in the USA (607,000 t./day), but fairly above those in countries such as Germany (85,000 t./day) and Sweden (10,400 t./day). Of that total, a large amount goes to open waste deposits. Only a small quantity is disposed of in appropriate places. A city like São Paulo spends, per day, US\$ 300,000 with waste. According to the Instituto de Pesquisas Tecnológicas – IPT (Institute of Technological Research), only few municipalities have specific teams and public policies engaged in dealing with the waste. When it is not treated, waste becomes a serious sanitary problem, since it exposes the community to illnesses like diarrhea, amebiasis, and parasitosis, apart from contaminating the soil, waters and water tables.

Among solutions, there are the creation of sanitary landfills in appropriate places, adoption of selective collecting and recycling programs, conducting of campaigns with the aim of both making society conscious about the problem and demanding a greater participation of government authorities (Editora Abril, 2002). The manufacturing of biodegradable material offers an interesting solution for plastic materials. Like it happens with organic residues, such as foodstuff, elimination of biodegradable materials is not automatic and is considered as a recycling process by many experts. Biodegradable materials go through a composting process, for the obtaining of a stable compound, considered the final product of recycling.

The bioplastics found in the market are made mainly from starch. Starch-based bioplastics represent from 85% to 90% of market's bioplastics (Bastioli, 2000). Among starch bioplastics are those manufactured with native or slightly modified starches, either isolated or blended with natural or synthetic molecules. In addition, there is also the result from the lactic acid polymerization obtained through the fermentation of starch. Within this later category is the PLA (polylactic acid), considered the one with the largest potential for the next years.

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18.2. Biodegradable materials

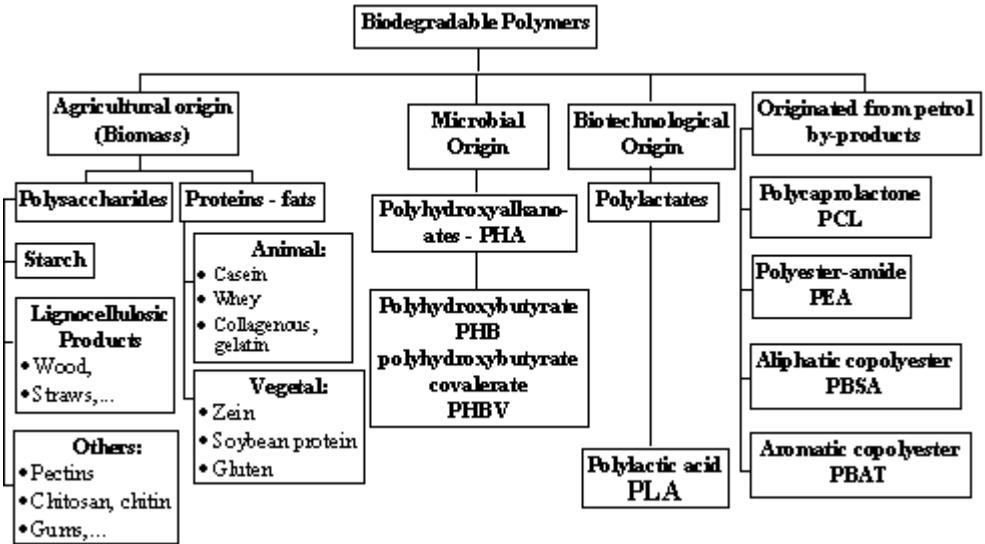
Guilbert (2000) defines three types of biodegradable materials:

- Agricultural polymers used alone or blended with biodegradable synthetic polymers;
- Microbial polymers, produced from the fermentation of agricultural products used as substrate. Averous (2002) identifies within this class the Polyhydroxy Alkanoates, or PHA. Its most widely known representative is the PHBV (Polyhydroxybutyrate covalerate).
- Monomers or oligomers polymerized by means of conventional chemical processes and obtained from the fermentation of agricultural raw materials used as substrate. The most well known material within this category is the PLA.

Averous (2002) includes a fourth class to the above-mentioned ones:

- Derivatives by means of synthesis, obtained from the petrochemical industry by the classic synthetic via. The latter one is represented by several polymers and subgroups:
 - The polycaprolactones: PCL;
 - The polyesteramide: PEA;
 - The aliphatic copolyester or Polybutylene Succinate Adipate: PBSA
 - The aromatic copolyester, such as the Polybutylene adipate co-terephthalate: PBAT.

PCL and PLA are the polymers most used in the market, except for starch derivatives (Averous, 2002). Figure 18.1 shows the different families of biopolymers, and their raw materials.



Source: Adapted from Averous (2002) and Weber (2000).

Figure 18.1.

Different families of biodegradable polymers and their raw materials.

Figure 18.2 indicates the chemical formulas of main biodegradable polymers.

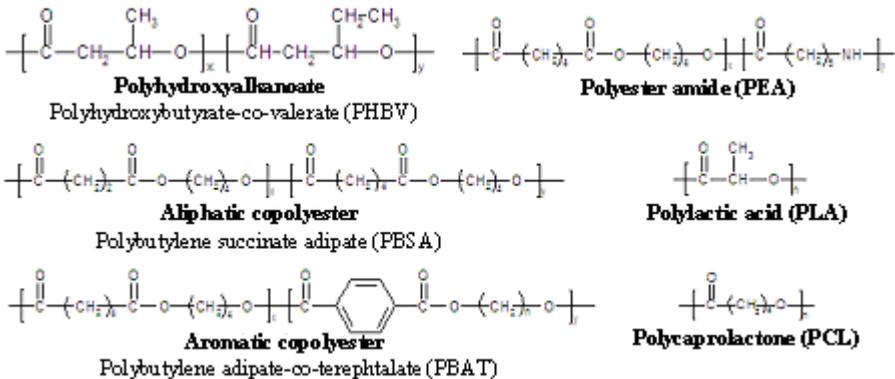


Figure 18.2.

Chemical structure of several biodegradable polyesters.

According to Weber (2000), starch-based packagings will continue developing with the support of their niches of traditional non-food markets. Later, starch biopolymers should enter the food market, after that resistance to humidity and cost-related problems are solved

18.3. Starch-based plastics

The use of starch in the manufacturing of bioplastics began in the 70's (Curvelo et al., 2001). Among its advantages, the starch is cheap, abundant and renewable. Besides, it is found in several forms due to the origin of its raw material (Lawter and Fischer, 2000).

In the granular state, it has been used as filling agent for polyolefin and as a component in synthetic polymers blends. According to Lawter and Fischer (2000), starches have also been modified by means of "grafting" with vinyl monomers (e.g., methyl acrylate), originating materials for injection in molds or extrusion.

It is possible to produce starch films through the grafting of polymers, such as Polyethylene (PE). Only the starch is biodegradable and these films are practically no longer used (Lawter and Fischer, 2000). According to Kaplan (1998), a silane with a general formula of $\text{CH}_3\text{-Si-O-(R}_1\text{,R}_2\text{,R}_3\text{)}$ can be added to a blend of PE to improve the compatibility of these two materials.

18.3.1. "Thermoplastic-like Starch" (TPS)

The TPS is a relatively new concept and, today, it is one of the main research hints for the manufacturing of biodegradable materials (Curvelo et al., 2001). The starch is not a real thermoplastic, but, in the presence of a plasticizer (water, glycerin, sorbitol, etc.), high temperatures (90 – 180°C) and shearing, it melts and fluidizes, enabling its use in injection, extrusion and blowing equipment, such as those for synthetic plastics. So as to obtain a thermoplastic starch, it is necessary that the starch maintains its semi-crystal granular structure and that it behaves in a way similar to that of a melted thermoplastic, obtained through a mono- or twin-screw extrusion with the use of mechanical and thermal energy (Lourdin et al., 1999).

The water added to the formula plays two roles: it is an agent that breaks the structure of the native granule, breaking the bonds of hydrogen chains, and it is a plasticizer. However, it is necessary to add an additional plasticizer besides water, such as polyol, which will be only slightly influenced by the atmospheric conditions in the sorption - desorption mechanism, and that will allow a melting phasis at a temperature lower

than that of the starch degradation (Averous, 2002)

During starch extrusion, the combining of shearing, temperature and plasticization allows the obtaining of a melted thermoplastic material (Averous et al., 2001-a). Afterwards, this material can be transformed by means of thermoforming or injection molding. The low resistance to water and the variations in mechanical properties under humid conditions affect the use of starch. Starch derivatives present a high permeability to moisture and degrade rapidly for many types of applications. Changes to remedy these problems make the final product more expensive, what limits any solutions (Lawter and Fischer, 2000). According to Averous et al. (2001-a), besides being susceptible to moisture, starch biopolymers have mechanical properties that change as time goes by, apart from their low resistance to impacts. Moreover, in the case of thermoformed products, the thinness of formed products limits the use of starch derivatives.

According to Levesque (2001), the use of starch and its derivatives as the only component of biodegradable materials was object of a number of surveys. Techniques on starch plastification were developed to allow the manufacturing of objects (usually massive objects), which, however, evolve rapidly due to the atmospheric humidity. To plastify the starch, it is necessary to use a large quantity of plasticizers or destructuring compounds (glycerol, carbamide, etc. ...) with hydrophilic properties.

This material can be processed in the same way as synthetic materials: extrusion, injection, etc. According to Lourdin et al. (1999), a plasticizer such as glycerol, sorbitol etc. is added in a ratio ranging from 20% to 40% to the starch weight. The plasticizer content is directly related to the mechanical properties and glassy transition of the material (Table 18.1).

Table 18.1.

Properties, initial and final formulation of wheat starch-based TPS, using different plastification levels.

	% Starch	Moisture^(*)	Glycerol Content (% starch)^(*)	Density	Glassy Transition (°C)	Module (Mpa)
1	74	16 (9)	14 (14)	1.39	43	997
2	70	12 (9)	26 (25)	1.37	8	52
3	67	9 (12)	36 (35)	1.35	-7	26
4	65	0 (13)	54 (50)	1.34	-20	2

Legend: (*) data in parentheses were obtained after formation (extrusion and injection molding), with a temperature balance at 23°C and 50% of relative humidity.

Source: Averous (2002).

The use of plasticizers also allows for a lower water activity (A_w), limiting the growing of microorganisms (Weber, 2000).

Table 18.2.

Conditions for the plastification of pea starch using a twin-screw extruder.

Start h rate of flow (kg/h)	Plasticizing rate of flow (L/h)	Screw rotation speed (rpm)	T. plastification zone (°C)	Product temp. when leaving the extruder (°C)	Die pressure when product leaves extruder (bar)	SME* (kJ/kg)
12	3.6 – 4.8	110-160	110-120	55-60	50-60	1,050 – 1,400

Legend: * SME : Specific Mechanical Energy

Source: Lourdin et al. (1999).

The properties of plasticized starches depend a lot on moisture. As water has a plasticizing power, the material behavior changes according to the relative humidity of the air (Averous, 2002), through a sorption-desorption mechanism. The higher the plasticizer content (polyol), the higher is the moisture content. At the same time, the properties of the material evolve as time goes by, even when moisture and temperature are controlled, translating into a lower elongation breaking and higher rigidity.

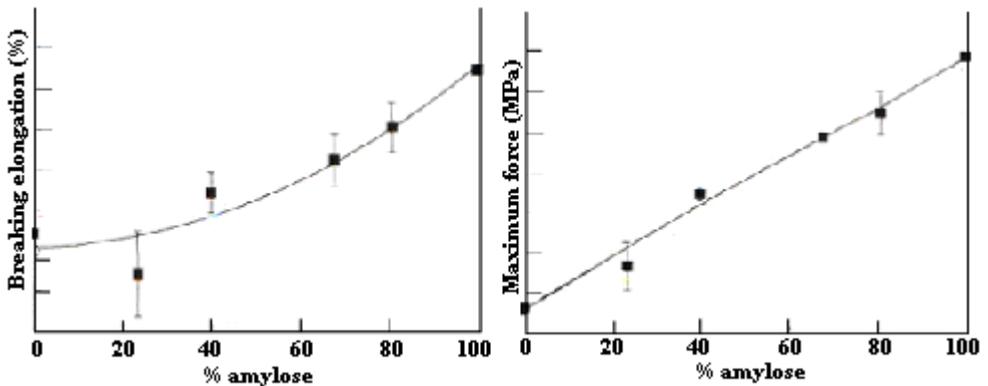
So as to improve the impermeability of starch biodegradable products, Averous (2002) suggests the possibility of incorporating biodegradable, renewable or synthetic polymers. These polymers can be blended with the starch or applied to multilayered films, with an internal layer of starch and two external layers of impermeable polymer. According to Averous et al. (2001-a) and Martin et al. (2001-a), starch films can be complexing with thermoplastic polyesters, such as polycaprolactone (PCL), and then processed through blowing or calendering, as with traditional plastics. As regards biodegradable films, the industrial process reaches a yield equivalent to 80% – 90% of that obtained for low-density polyethylene (LDPE) (Bastioli, 2000).

The multilayered structure is more difficult to be produced than the blended one (Averous, 2002). The main manufacturing technique is the co-extrusion (with a flat die) for the production of a film that can be thermoformed for the manufacturing of, for example, trays. Hot compression can also be applied to the films, but, in this case, there is less adherence among the layers.

Not all materials are compatible among themselves, and they can come unstuck. In this case, compatibilizers are added (Averous, 2002). In the case of multilayered products, delamination is measured by means of a peeling test at 90 °. According to Martin et

al. (2001-a), the adherence among the films diminishes through the addition of more than 20% of glycerol. Averous (2002) classifies polyesters from the most to the less adherent one: PEA, PBSA, PCL, PLA and PHBV. For the author, another problem with multilayered films is the difference in the materials' rheological behaviours in the molten state, what brings about problems of instability in the layers interface, with uneven properties and permeability along the different parts of the film. Due to this, the surface of the films gets wrinkled.

According to Curvelo et al. (2001), the resistance to moisture can be enhanced by adding synthetic polymers, cross-linked agents, such as Ca and Zr, salts, or lignine. TPSs properties vary according to the type of starch used, emphasizing the amylose content. The almost linear increase of breaking forces and elongation according to the amylose content (Figure 18.3.) can be explained through the larger agglomeration capacity of linear macromolecules while ramified structures of amylopectin originate nodules. The amylose-rich corn starch (70% of amylose) or a specific pea starch (35% of amylose) is indicated to enhance the manufacturing of these materials. However, even that the values of maximum forces for breaking are acceptable (30 to 60 MPa), materials are fragile due to their low deformation (approximately 6%). This property explains the reason why it is necessary to add other components, such as plasticizers, able to enhance the plastic behavior (Lourdin et al., 1999).



Source: Lourdin et al. (1999)

Figure 18.3.
Influence of amylose content on the mechanical properties of starch films without additives.

According to Lourdin et al. (1995 and 1999), the effect of the amylose content is

considered a favorable factor when there is no plasticizer (Figure 18.3). When plasticizers are added, the effect is inverse, since films with a larger content of amylopectin react more and have a larger plasticity. In this case, starches with lower amylose content can be preferable.

Besides the blend of starch with other polymers and the use of plasticizers, many surveys have been conducted regarding the possibility of modifying the starch so that the TPS can acquire the desirable properties as regards both mechanical and moisture resistance. According to Thakore et al. (2001), the esterification of starch allows the increase of its thermoplastic characteristics, as well as its thermal stability, hydrophobicity and crystallinity. This is confirmed by Whistler and Hilbert (1944), who affirm that starch triacetates break easily and are fragile when the esterification reaction is applied to the whole starch or to the amylopectin fraction. When it is applied to the amylose fraction, films are more resistant and flexible. According to the authors, these characteristics are maintained even when plasticizers are added.

Fringant et al. (1998) used an acetylated starch, with a Degree of Substitution (DS) of 3, to improve the resistance of biodegradable materials to moisture. The coating effect was not good, due to the incompatibility between the material and the starch. The best effect was achieved with little trays produced by means of flash vaporization with 50% of pre-gelatinized starch and 50% of acetylated starch. The blend had approximately 15% of ethanol, used as a solvent. The coating of these little trays allowed an even higher effect, because the acetylated starch in the coating was compatible with the acetylated starch in the little trays paste. In the case of a little tray with 50% of acetylated starch, with no coating, the impermeability was only partial, and after seven hours the trays had already acquired around 50% of their weight in water.

Vilpoux, in unpublished data, produced flexible and resistant films, less sensitive to water, with a blend of acetylated starch with a DS ranging from 2 to 3 and PCL. However, the high production costs of highly acetylated starches impair the use of these films.

18.3.2. Starch-based films

Starch-based films found in the market are made mainly from starch complexed with thermoplastic polyesters, such as poly-epsilon caprolactone (PCL), to form biodegradable and compostable products (Bastioli, 2000). When used for the manufacturing of bags for the recycling of organic waste (composting), packagings, hygienic items and agriculture, the properties of these films are similar to those of LDPE (Low Density Polyethylene).

● Purchase Bags (Bastioli, 2000): were introduced in the market in 1999 and started being used in many supermarkets in Scandinavia and in the Mediterranean Coast. They were introduced in places where the collecting of organic wastes already existed and where they were accepted as biodegradable compost bags (Figure 18.4). These bags have a behavior similar to the bags made with LDPE as regards the maximum weight and most of its performances.



Figure 18.4.

Biodegradable purchase bags commercialized in a supermarket in Italy.

- Consumer goods packaging (Bastioli, 2000): the main market is that of silk paper, but there are markets for magazines wrapping and bubble films, mainly for electronic goods.
- Food packaging (Bastioli, 2000): the main markets are those of bags for fruit, vegetables and bakery products. The high cost of biodegradable products limits this market, but starch films have an advantage against traditional plastics, that is to say, they allow for a better breathing of the products.
- Composting bags (Bastioli, 2000): bags used in the selective collecting of organic waste, which will be treated to produce a compound. Millions of Europeans already use these bags.
- Hygiene – cosmetics (Thouzeau, 2001): in the hygiene line of business, biodegradable polymers are found in diapers, swabs and even in toothpicks (Figure 18.5).



Figure 18.5.
Starch-based toothpicks commercialized in Hong Kong.

- Funerary goods (Thouzeau, 2001): biodegradable plastics can be used to wrap corpses, in compliance with the rules on the use of biodegradable materials.

According to Tuil et al. (2000), multilayered biodegradable films can be used as food packaging with either controlled atmosphere or gas. Starch packagings boast the characteristic of being an excellent barrier to O₂ and CO₂, facing problems only with water and water vapor. The application of layers of biopolymers resistant to water in the ratio of 10% allowed Tuil et al. (2000) to obtain films resistant to water with a thickness from 30 to 100 µm. This material is currently commercialized by AVEBE under the name of Paragon® and can be processed by means of blowing and used in multilayers with PLA or PHBV (Weber, 2000).

Table 18.3.
Biodegradable starch-based films and main manufacturing companies.

Brands and Companies	Activities	Patent Situation	Installed Capacity (t./year)	Applications
Biotec (Melitta) (Germany)	Blend of biodegradable starch and PCL. Packaging materials and waste collecting bags were its main markets, among others.	Acquisition of Fluntera patents	Pilot plant (\approx 1,000) Went out of business in 2002	Composting bags since 1995
BASF (Germany)	Manufacturing of synthetic copolyesters with starch-based blends, destined, among others, to the production of flexible films.			
Bayer/Wolf Walsrode (Germany)	On a pre-commercialization phase. Synthetic copolyester starch, biodegradable, destined, among others, to the production of flexible films.			
Mater-Bi (Novamont) (Italy)	Commercial business. Mixture of starch with PCL and/or polyvinyl alcohol. Also use of cellulose acetate.		4,000	Composting bags, laminated paper, packaging paper, cottons and cosmetics.
Novon (Ecostar)	TPS	Acquired from Warner Lambert in 1995	\approx 3,000 Went out of business in 2002	
Chisso (Japan)	Similar to Novon, but limited to Japan	Warner Lambert License		Composting bags employing old technology

Sources: Demicheli (2001); Bastioli (1998).

The production of small packaging bags is extremely important, since it accounts for 40% of the plastic packaging market (Averous, 2002). The formation of biodegradable material using the starch as a raw material can be done through blowing, but the material has to be adjusted. TPS, even with the adding of a large amount of plasticizers, does not react to the blowing process, mainly because of the amylopectin, whose

structure is much stiffer than that of polyethylene. So as to improve the formation of films, TPS is blended with polyesters (Averous, 2002), a system that permits the manufacturing of a film through co-extrusion and blowing (Figure 18.6).



Figure 18.6.
Descending film blowing equipment for plastic material.

Besides the biodegradable films used to replace plastic synthetics, it is also possible to manufacture edible films. Baldwin et al. (1996) affirm that edible films can propitiate a barrier to water vapor and other gases, allowing the creation of a controlled atmosphere around the product. The authors say that these films are also useful as additive carriers (intelligent films) such as antioxidants, acidulants, fungicides and preservatives and improve the preservation of food colors. The most efficient preservatives for fresh food are the sulphites, since they inhibit both the effect of enzymatic darkening and of microbial contamination (Baldwin et al., 1996). Nevertheless, the use of sulphites is subject to restrictions in some countries.

Cooksey (2001) highlights the possibility of using biodegradable products for the releasing of bactericides. The methylcellulose offers the best support to the potassium sorbate, a bactericidal agent. The creation of multilayered packagings, with methyl or hydroxypropyl methylcellulose, restrains the releasing of potassium sorbate in food. The adding of fatty acids, such as lauric, palmitic, stearic and arachinic acids, also diminishes the diffusion of potassium sorbate.

18.3.3. Starch-based expanded packagings

Bastioli (2000) defines two main markets for starch derivatives expanded products:

- Loose fill products: it is the main market of biopolymers. The average density of snack-type products is 8 kg/cubic meter, compared to 4 for EPS derivatives (expanded polystyrene). The main market is the United States.

- Disposable food serviceware (Bastioli, 2000): environmental problems led many Governments to either ban the use of EPS or starting levying taxes on them. Starch or polylactic-based extruded or laminated products are available in the market, and they are only slightly more expensive compared to traditional products. Thermoformed PLA products are also available. Products using bakery technology, following the principle of wafers production, are also found in the market, but only on an experimental basis (Figure 18.7). Tuil et al. (2000) affirm that expanded packagings made by means of bakery technology, or wafer technology, are about to enter the market.

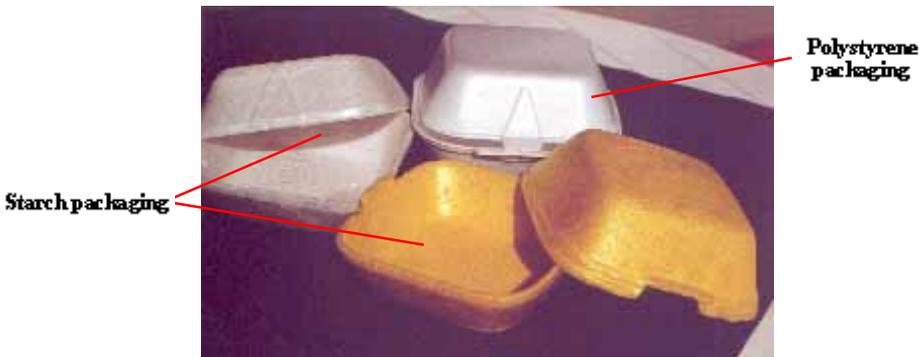


Figure 18.7.

Biodegradable packaging made in Brazil, with wafer technology.

Technologies developed and available in AVEBE allow the development of trays-type packagings with properties similar to those of XPS (Extruded polystyrene) and EPS, biodegradable and resistant to moisture. Products expanded entirely from PLA are still under study (Weber, 2000).

The blend of starch with PVOH (polyvinyl alcohol) was largely studied for the production of materials to replace expanded polystyrenes (Bastioli, 1998). According to Cha et al. (2001), a blend with 95% of hydroxypropylated corn starch with a high content of amylose and 5% of PVOH is used as a commercial alternative to the polystyrene. For Glenn et al. (2001-b), a blend of starch with PVOH, expanded by means

of wafer technology, leads to a decrease from 25 to 32% in water absorption. According to the authors, cross-linked agents decrease this absorption by 80%. Chandra and Rustgi (1998) affirmed that the isocyanide is a good cross-linking agent.

Table 18.4.
Main starch-based biodegradable expanded products and manufacturing companies.

Brands and Companies	Activities	Patent situation	Installed capacity (t./year)	Applications
Mater-Bi (Novamont) (Italy)	Commercial business. Mixture of starch with PCL and/or polyvinyl alcohol. Use of cellulose acetate		4,000	Expanded products and bones for dogs.
Envirofil (Enpac) joint-venture Dupont- Conagra	TPS	Warner Lambert license, limited to loose-fill	5,000 (with sublicensed)	Loose-fill
Ecofoam (National starch)	TPS with a high amylose content	Warner Lambert license	≈ 5,000	Loose-fill and expanded products
Biopac (Haas)	Waffer technology		≈ 500 Went out of business in 2002	Food trays

Sources: Demicheli (2001); Bastioli (1998).

According to Glenn et al. (2001a), the extrusion technique is useful for the loose fill production, but is not appropriate for the production of materials with other shapes. So as to tackle this problem, there is the possibility of compression/explosion, or flash vaporization, another technique that deserves deeper researchs.

Flash vaporization is described by Glenn and Orts (2001) and comprises the pressurizing of starch with a low moisture content (10 to 12%) in a heated mold. Pressure is suddenly suppressed, allowing the expansion of the product in the mold. Processing takes only 10 seconds. Nevertheless, the explosion process is limited given it propitiates simple and thick shapes (> 1 cm) (Glenn et al. 2001b).

Table 18.5.
Comparison of some biodegradable expanded products with EPS and XPS.

Material	Density (kg/m³)	Ø cells (mm)	Maximum Pressure (Mpa)	Elasticity (%)
XPS	45.6	0.55	0.140	72.8
Expanded with potato starch	34.5	0.14	0.170	55.3
EPS	9.6	-	0.082	79.3
Mater-Bi	16.8	-	0.040	62.3
Eco-foam	19.1	-	0.055	70.7

Legend: -: unavailable data.

Source: Tuil et al. (2000)

Glenn and Irving (1995) describe the possibility of obtaining starch-based expanded materials by means of aerogels, produced after the elimination of water in starch gels, given rise to a spongelike structure. The removal of water goes firstly through the replacement of this solvent by acetone or ethanol, so as to avoid that the material gets cracked. Aerogels have an extremely high porosity, with a diameter from about 3 to 60 nm. Aerogels, like all starch derivatives, are very sensitive to humidity.

18.3.4. Blend of starch with cellulose derivatives

The incorporation of cellulosic fibers to TPS can improve mechanical properties, permeability to gas and resistance to water (Averous et al. 2001-b), because cellulose is less hydrophilic than the starch. Cellulose-starch interactions mobilize sites previously used by water molecules (Averous et al. 2001-b). Nevertheless, the incorporation of fibers is limited due to the difficulties of dispersion (Dufresne et al., 1997.). According to the authors, the presence of pectin increases the cohesion of fibers with the material, increasing pressure forces, mainly in environments with low humidity. With the increase in relative humidity, pectin, which is more hydrophilic, absorbs a larger quantity of water and gets softer, impairing the material's mechanical properties.



Figure 18.8.

Disposable food servicewares made in Thailand, mixing cassava starch and fibers.

According to Glenn et al. (2001a), wood fibers with a length from 5 to 7 mm greatly improve the flexibility and other functional properties of starch derivatives processed by means of wafer technology.

Table 18.6.

Properties of starch extruded films, with and without fibers.

Composition	Module E (Mpa)	Max. pressure (Mpa)	Deformation in breaking point (%)
0% fibers	52	3	126
15% fibers	430	13	31
30% fibers	670	22	19

Legend: Pressure strengths estimated from the movement of pincers of 50 mm/min, at 23°C and 50% relative humidity.

Source: Averous et al. (2001-a)

The production of vegetal polymers-based composite materials is still in the early stages of development. It consists of formulations associating vegetal polymers to a linking or thermoplastic matrix (starch, resin) and several adjuvant elements. It is possible to mention products, like FASAL and NAPAC which are appearing in Germany, Switzerland or Austria, for the production of parts molded by thermopressing or injection processes. The polymer made of triglycerides and polycarbonate acid anhydride, developed by PREFORM in Germany, is used as a linkage for fibers (wood, straw...) in the production of extruded parts or formed panels. In Brazil, little pots made with fibers and a starch based link are being tested for eucalyptus and pines plants production (Figure 18.9.).



Figure 18.9.
Pots for production of plants like eucalyptus and pines.

According to Arvanitoyannis and Biliaderis (1999), methyl cellulose provides a homogeneous dispersion with the starch and it is less hydrophilic, allowing the starch to enhance its weak barrier to moisture. For the authors, the hydrophilic character of the blend increases with a higher content of plasticizing elements (water or a blend of water-sugar-glycerol). However, despite the enhancements, films are still not very resistant to moisture.

18.3.5. Polylactic acid (PLA)

PLA is an aliphatic polyester, with glassy transition temperature (T_g) of 55°C and fusion point at 170°C . A low breaking deformation value limits the use of PLA (Martin and Averous, 2001-b). To deal with this problem, many researchers added plasticizing elements, such as citrate ester (produced by SIGMA), PLA oligomer (OLA), glycol polyethylene (PEG) (also produced by SIGMA), monoester glyucose and partial esters from fatty acids.

PLA properties depend on the type of polyester, with conformation L or D (Weber, 2000). The use of 100% of PLA-L results in a product with high fusion temperature and high crystallinity. The use of an equivalent blend of L and D drops T_g to 60°C , a temperature that may be considered too low for some uses.

The main PLA is NatureWorks produced by Cargill / Dow Polymers (Dumoulin, 2001). This PLA is derived from corn starch or sugar beet (other types of starches or sugars may also be used), and its biodegradation takes from 4 to 6 weeks in pilot composting

equipment. It can be used to make films for agriculture, yogurt plastic bottles, diapers or textiles and hygienic products (together with cotton).

Nonwovens, with DÉPOSA and Galactic, a Belgium organization specialized in lactic acid and lactate production but which invested in PLA production, are included among the competitors of Cargill / Dow (Dumoulin, 2001).

PLA production requires from 20 to 50% less fossil fuels than petrol plastics, nevertheless the energy consumption in the production is higher than that in most of the petrochemical processes (Gerngross and Slater, 2000). According to the authors, this consumption is 50% higher than the necessary for the polyethylene (PET), but it is 40% lower than that for nylon, another PLA competitor.

PLA seems to be the only plastic from vegetal source with chances to be commercialized, due to its low consumption of energy and high conversion rate, which is of about 80% of each kilo of sugar. Despite these advantages over other vegetal originating competitors, PLA emits more gases responsible for the greenhouse effect than the majority of its competitors coming from the petrochemical industry (Gerngross and Slater, 2000).

For food packaging, the best opportunities for PLA are in bi-oriented films and thermoformed material. In the past, PLA has been used by the Danone Company to produce thermoformed packaging for yogurt, being abandoned soon after. According to Bastioli (2000), if production raises, prices can be set between US\$ 2 and US\$ 4 per kilo. In case of prices around US\$ 2, it is possible to believe that a larger number of markets would be reached, as PLA has similar characteristics to PET and PP. Moisture barrier of biopolymers is higher than that of other materials derived from starch, whereas their gas barrier is lower.

After it is used, PLA can have its chemical components hydrolyzed for reutilization or recycling. PLA is a polymer that can degrade in much the same way as the paper in local composting facilities. It is degraded mainly by some microorganisms like *Aspergillus fumigatus* (solid medium) and *Agrobacterium radiobacter* (solid and liquid media) (Gattin et al. 2002). Due to these reasons, PLA may reduce the community dependence on fossil fuels while providing products adapted to traditional residues treatment methods.

18.4. Production, use and properties of starch biopolymers

Among TPS, Averous (2002) describes products such as Biopac, made of starch molded for manufacturing packaging (Mac Donald, IKEA, DO and CO), BIOTEC for manufacturing garbage plastic bags (FARDEM), Eco-Foam (National Starch and Chemi-

cal) and FLUPIS (PSP) for gluing (Projet Agromat, 2001).

Under the brand Mater-Bi, Novamont produces 4 types of biodegradable materials, all of them based on starch blended with other synthetic component (Bastioli, 1996). These products can be classified as:

- **Class A** – Biodegradable non-compostable materials (degradation within 2 years in liquid medium). Products made from starch and vinylic ethylene alcohol copolymers.
- **Class Z** – Biodegradable compostable materials, mainly for manufacturing films and sheets (biodegradation within 20-45 days in composting conditions). Material made from starch and PCL, in 50% ratio.
- **Class V** – Biodegradable compostable and soluble materials, as substitutes for EPS packagings (biodegradation faster than Z). Starch content in these products is over 85%.
- **Class Y** – Biodegradable compostable materials, for injection molded, rigid and dimensionally stable products. Materials made of entirely natural raw materials, such as those derived from cellulose.

The problem with synthesis biodegradable polymers is that they are expensive (generally priced over 3 US\$ / kg), in comparison with common used polymers, such as PE (0.8 to 1.1 Euro /Kg) (Thouzeau, 2001). According to Bastioli (2000), the price of bioplastics is constantly reducing and in 2000 it ranged from 1.2 to 4.0 US\$/kg, allowing the competition with traditional materials in some areas. In 2000 the annual market of bioplastics derived from starch was approximately 20,000 tons, 75% of which destined to packaging s (Bastioli, 2000). Their use in food industry was very limited, consisting mainly of kitchen utensils. In the same year, PLA market share was only 3,000 tons.

According to Ginon (2000) about 120,000 tons of biodegradable plastics are annually produced worldwide³, but North American studies estimate that this production can total 500,000 tons up to 2005. Roughly 90% of this production comprises packaging and composting bags (selective waste collection), but other markets are under development or in initial stage of commercialization, such as disposable cutlery for collective restaurants, office items, hygienic products and, mainly, films for agricultural mulching.

United States, Germany and Japan are the major patent holders of biodegradable products, followed by France, Italy, England, etc. (Nieddu et al., 1999). Germany's find-

³ - This figure is quite different from the one reported by Bastioli. The difference probably results from the incorporation or not of blends of starch with plastics derived from petrol in biodegradable plastics.

ings are concentrated in fewer companies than in the United States, where a larger number of small companies and individuals hold relevant patents. American companies tend to merge more than the German ones, as, for instance, Cargill with Dow Chemical and Monsanto with Penford Products Co. According to the authors, the findings focus mostly on packaging (bags, fast-food cutlery, etc.), followed by absorbent materials, diapers for babies and toilet tissues.

According to Nieddu et al. (1999), while biodegradable biopolymer prices remain stable, applications are focused on classical chemistry. In parallel, there is a tendency for acquisitions between companies, some of them investing in production capacity and alliances for a better market positioning in the near future. According to the authors, large companies are very optimistic about the genetic modifications of plants, seen as the element that will allow costs to be reduced and biodegradable products to compete with the plastic.

According to Demicheli (2001), natural biodegradable polymers are expected to show an annual increase of about 30% in Europe and in the United States in the next 10 years. This growth is the result of policies from the government, from ecologist consumers associations and from environmental protection movements.

No precise data on biodegradable plastics consumption in the European continent are available. It is well known that Germany is the largest consumer. Some estimates provide the following data on Europe's consumption in 1999 (Thouzeau, 2001):

- Composting bags: 5,500 tons.
- Waste packagings: 2,000 tons.
- Paper coating: 1,000 tons.
- Food packagings: 700 tons.
- Various: 800 tons.

The main market for bioplastics derived from starch, because of its water sensibility, is in the form of snacks, like loose fill and other expanded products, as substitutes for PS (Polystyrene) (Bastioli, 2000).

18.4.1. Food packaging

Packaging used for food must have special characteristics (Haugaard et al., 2001):

- Barrier to water, gas, light, flavor, etc.
- Optical properties (transparency);
- Resistance, weldability and moldability;

- Printing properties;
- Resistance to chemical products and temperatures;
- Aesthetic properties;
- Easy utilization;
- Competitive price.

Packaging lifetime should match with that of the packaged product. In this way, packaging must resist within this period of time (Haugaard et al., 2001). Packaging must keep the food quality, which is defined by Haugaard et al. (2001) according to the following criteria:

- Sensorial attributes: appearance, flavor, smell, texture, etc.;
- Nutritional content;
- Feeding safety: free of microorganisms, residues;
- Aethical properties: packaging production process;
- Food price.

Simoneau (2000) maintains the same factors, adding the need for resisting under different conditions of moisture and temperature and for providing for a good protection not only against microorganisms but also against insects and rodents. Weber (2000) mentions that 15% of foods are damaged by the action of rodents and insects. Nevertheless, there is no evidence that biodegradable packaging attracts more insects and rodents than traditional packaging, on the contrary, the cellulose acetate is very resistant to insects.

Simoneau (2000) alerts to the possibility of dried or dehydrated foods reabsorb moisture due to the hydrophilic properties of biodegradable packaging. According to the author, European regulations require that food biopackaging prevents foods from the migration of packaging contaminating substances and the amount of ingredients allowed in packaging must be respected.

Packaging with high water activity can help the development of microorganisms, what is considered as a negative factor (Haugaard et al., 2001). The microbial contamination of biodegradable packaging is low according to Weber (2000), as production conditions sterilize the material. Contaminations may occur mainly during storage, transportation or use. Generally, traditional or biodegradable food packaging contamination is well below the authorized regulations, with the exception of the corrugated paper and the cardboard made of recycled paper (Weber, 2000).

According to Glenn et al. (2001), Earthshell has launched food packaging made with

wafer technology. This packaging is made of potato starch, water, wooden fibers, CaCO₃, demoldings and thickeners, and is coated with an impermeabilizing substrate. Earthshell's (USA) products are not yet on the market and testes are still being held.

18.4.2. Biodegradable packaging in agriculture

According to Dumoulin (2001), the use of plastic materials is a common component of modern life. With plastic consumption increasing by 149% from 1985 to 1999, agriculture has followed the same trend. In 1970 the designation of mulched cultivation was created, and since then the use of plastic materials has been showing a steady growth.

Among the major plastics in use are PE, PP, EVA (Ethylene vinyl acetate) and PVC. Photodegradable polyethylene films can be used, but they are only fragmented and not totally degradable (Halley et al., 2000). According to Jouët (mentioned by Dumoulin, 2001), worldwide consumption of agricultural plastics is estimated to be 2,847,000 tons, distributed as follows:

- Greenhouses and large tunnels: 450,000 t
- Small tunnels: 168,000 t
- Mulching: 650,000 t (Figure 18.7)
- Canvases: 40,000 t
- Microirrigation and hydroponics: 645,000 t
- Silage : 540,000 t
- Others : 354,000 t



Figure 18.10.
Mulching in China for tomato production.

The Figure 18.10 indicates the use of mulching in China, the country with the largest area covered with plastic in the world (Table 18.7).

Table 18.7.

Agricultural surfaces using plastic in mulching, in major using countries (1997).

Regions	ha
Europe	380,000
• Spain	100,000
• France	100,000
• Italy	60,000
• Portugal	23,000
• United Kingdom	9,800
• Greece	4,600
• Hungary	2,000
America	200,000
• Mexico	9,000
Asia	3,500,000
• China	2,000,000
• Japan	150,000
• Turkey	1,000
Africa	15,000
• Morocco	6,700
• Israel	4,000
• Egypt	2,025

Source : Colloque Bbiomatériaux (2001).

According to Dumoulin (2001), distribution of plastics used annually in France is:

- PE: 95,000 t., with 25,000 t. for thin films;
- PP: 35,000 t.;
- PVC: 35,000 t.;
- Others : PS, polyester, PU: 5,000 t.

Dumoulin (2001) describes the characteristics of these polymers:

- PE: thick films (150 µm to 180 µm) are used for silage, mulching of greenhouses and livestock facilities. Thin films (25 µm) are used for straw and hay packaging or mulching (17 a 50 µm). They can also be found in macro perforated flat canvases, nets, windbreaks, films for protection against hailstorm and for shadow.
- Ethylene vinyl acetate (EVA): Covering of tubular greenhouses.
- PP: production of strings, non-woven flat canvases, glasses and big-bags envelopes.

- **PVC**: draining and irrigation pipes, semi-rigid sheets for greenhouse covering, small tubular greenhouses.
- **Other materials**: EPS is used for isolation plates, polyurethan foam (PU) is used as substrate for hydroponic culture and as isolator. Polycarbonates and methyl polymetacrylates serve as division walls and greenhouse walls, saturated polyesters (or PE tereftalate) for water tanks and greenhouse walls. Polyamids are used in the manufacture of nets.

The success of plastic is explained by its qualities (Dumoulin, 2001):

- **Lightness**: density close to 1. One m² of P.E film. (180 µm) weighs 165 g.
- **Resistance**: a P.E film. (180 µm) is twice as resistant as the glass used in horticulture, a string of PE is hard to split.
- **Inalterability**: resistance to corrosion, to chemical and biological agents.
- **Harmlessness**: no danger for plants and animals.
- **Impermeability** or selective permeability.

However, there are also technical use restrictions, such as sensitivity to tearing, inflammability, dilatation, aging, etc. Since the beginning of 2002 in Europe only the residues classified as final (that cannot be treated or degraded) are allowed to be thrown into discard. Recycling is a viable solution for greenhouse mulching films, which can be recycled at a competitive cost because they are clean (dirty rate ranging from 10% to 20%). This is a more complicate solution for films used in mulching, as recycling is much more expensive. Generally, these films are thin and have from 60 to 80% of dirt. In this case, recycling cost is estimated to be over 75 Euro / ton, including material and labor cost for collection and cleaning. This cost must be paid by farmers.

Commonly used, mulching has many advantages but some disadvantages too, mainly in relation to its elimination (César, 2001). This technique is used primarily to increase the soil temperature, to prevent weed infestation and to reduce some phytosanitarian problems. In the last two cases, the restrictions on phytosanitarian products allow environment protection.

This technique also takes part in soil and groundwater level protection, with the reduction of leaching of mineral elements. The problem with mulching is the generation of a large quantity of residues that are very dirty and difficult to eliminate. The valuation of the material after being used is not enough adapted and the energetic valuation is still a doubt (César, 2001). According to the author, a biodegradable material destined to agriculture should meet agro-economical criteria, such as:

- To show agronomical qualities similar to traditional non-biodegradable materials;
- To have a cost compatible with a healthy management of horticultural explorations;
- To allow the use of farm machinery.

Biodegradable materials must be actually biodegradable according to established rules (César, 2001):

- To provide only biomass, water and CO₂, or CO₄ in case of anaerobic degradation, and possibly mineral residues at the end of the biodegradation chain, without affecting the nature.
- To generate no molecule or residue harmful to the environment during biodegradation.

Still according to the author, biofragmentable materials must be excluded from the biodegradable ones because:

- They disappear quickly from the sight, but remain present into the ground as small particles and microfibers for many years;
- They frequently make use of adjuvants in their compositions (peroxidizing agents, plasticizers, lubricants, coloring, metals, etc.) whose degradation and (or) accumulation may be toxic for the environment.

Table 18.8.
Different types of biodegradable films for “mulching” in agriculture.

Origin	Composition	Company	Products	Category
Natural direct origin	Paper: cellulose + additives	Ahlstrom	Black paper	Papers
		Ajo	<i>Sequana</i> Pink / black paper	
	Novamont	<i>Mater-bi</i>		
Natural origin by biotechnology	Starch + synthesis biological additives : PCL	UCB	<i>Cellophane UCB</i>	Bioplastics
	Cellophane			
	Bacterial fermentation from sugar or starch ⇒ molecules: PHB, PHV, PHVB		Integrated to composite materials	
Artificial origin (synthesis)	Aliphatic and aromatic polymers : polyester, polyesteramide, copolyester	Prosyn	<i>Biopolyane</i>	
		Polyane	<i>Biofilm</i>	
		Babier BASF	<i>Ecoflex</i>	

Source: Mazollier (2001).

According to Mazollier (2001), mulching with paper has several problems, making it less polyvalent than mulching with usual plastic film, and limits the possibilities of use for this material:

- Mechanical resistance of the paper is inferior to that of plastic mulching. During the placement of the paper there is a greater risk of tearing it, be it a manual or mechanical process.
- Paper film is thick and the bobbins can weigh up to 100 kg, requiring the use of an adapted unwinding machine, mainly to limit the reels maintenance.
- Paper degradation is very fast, especially in the portions that are underground. Sequana product degrades within 3 weeks in summertime.
- The porosity of mulching with paper is superior to that of the plastic film:
 - It needs an adapted procedure of irrigation, with higher frequency mainly in greenhouses or in summer cultivations in open air.
 - It can let more air pass through during rainy periods, in the open air, allowing the weed to grow.
- Paper shows contraction under heat conditions, a phenomenon observed in sheltered summer cultivations.

Depending on the conditions of the mulching at the end of the cultivation, it is necessary to define the best degradation conditions of the material: either placing it underground at the end of the cultivation or by composting together with the cultivation residues. If the material is buried, it is necessary that the film degradation occurs rapidly: residues from non-degraded films may hamper the installation of the next cultivation, especially if it is a seeded field (Mazollier, 2001). This is the case of photodegradable films.

Table 18.9.

Classification of mulching materials, according to their efficiency.

Best results obtained with	<ul style="list-style-type: none"> • Non-degradable opaque polyethylene • Opaque polymers considered as biodegradable • Papers considered as biodegradable • Chemodegradable / photodegradable translucent polymers
	
Worst results obtained with	<ul style="list-style-type: none"> • Bare soil

Source: César et al. (2001).

In the agronomical sector, tested biomaterials are efficient enough to prevent weed infestation, not only in greenhouses but also in open air. The cost of these materials per

square meter is high, about three times the price of PE, but it is constantly falling (4.5 Euro/kg in 1998, 3.8 in 1999, less than 3 in 2001), whereas PE price has risen regularly. Thermal properties of biodegradable plastics are not as good as those of PE, but they are better than bare soil or soil mulched with paper. This type of films may be buried at the end of cultivations without problem (César, 2001). Cheaper materials are being tested in Brazil, with the use of natural latex together with starch. These materials, totally natural, have a good resistance to humidity but low resistance to UV from the sun, which is the main problem to be solved.

Enimont, with the product Mater Agro, also has a film used for mulching. This company states that the biodegradation of Master-Bi film used in mulching begins by the buried edges, since a higher concentration of microorganisms is into the ground. The biodegradation of the portion of the film that is on the ground is, on the other hand, much slower. At the end of the cultivation cycle, it is necessary to turn over the field to allow the film that is not totally biodegraded to finish its degradation process.

The different experiments done by Novamont society have shown that a Mater-Bi film used in mulching lasts from 2 to 5 months, after placement, depending on climatic conditions and temperature (De Boissoudy, 2001).

18.5. General considerations

There are several surveys concerning starch for the production of biodegradable plastics. Nevertheless, starch limitations with reference to its moisture resistance and its mechanical properties restrict its use significantly. To deal with these difficulties, starch is used in mixtures with plasticizing elements and other biodegradable polymers. As biodegradable polymers are more expensive, these mixtures raise the cost of the products, reducing consumption in some market niches. Cost reduction implies additional research and increase of production.

In the last few years, biopolymers derived from fermentation, such as PLA produced from sugar or starch, have been in an outstanding position. A better resistance to moisture makes them suitable for use in several markets.

Besides PLA, many companies have made bulk investments in biotechnologies, with the aim of getting polymers directly from the plants. Achieving these goals will allow cost reductions and significant energy savings, making the production of polymers feasible.

However, a major restriction to this production is the biodegradable polymer fractioning and its purification phase. These phases must be performed at an acceptable cost and with feasible conditions from the ecological point of view, particularly in relation to

the use of organic solvents and the consumption of energy in the developed processes. With this prospect, it is likely that starch-based bioplastics will occupy only specific market niches, leaving the bulk of the market to PLA and to biopolymers coming from biotechnology. The loose fill products as well as all filling products for electric-electronic materials and other fragile and moisture-sensitive materials are included in the market niches where starch by-products have a competitive advantage.

The development of these materials, in addition to their properties, depends on the legislation evolution in every country. This could benefit, especially for packaging, the composting process in relation to the valorization of the material or to the production of energy. Uniformity among the countries is required to establish criteria, such as biodegradability and compostability. The different rules (ASTM, CEN) present diverse composting conditions (temperature, time, moisture), hindering results comparison. In order to facilitate the development of these materials, it is necessary an international logo to label the material as compostable so as to make it recognizable by the consumers. In parallel, the consumer needs to be educated to avoid the material dispersion in the nature, even if it is biodegradable.

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