# Developments in recycling plastic food packaging: biodegradable plastics

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Recycling of plastics is routine since the beginning of industrial processing of polymers. However, most, if not all, was done on scrap that was produced during processing. It soon was found that adding oxygen or radical scavengers helped in maintaining polymer quality. Over the years these additives were developed to a point that by today plastics recycling from scrap can be considered as a mature process. R&D aims at still further improving the additives and at developing new approaches such as brighter colors or fluorescent whiteners to cache impurities.

Large scale recycling of soiled post-consumer materials is new. To ease the shortage of landfill sites and to calm the public distaste towards building new waste incineration plants in Germany the government outsourced packaging waste collection to those selling the goods (to the retailers). In addition it requested that high shares of the collected waste is recycled. This was the start of the consumer funded German Green Dot system. The request to recycle soiled consumer packages proved to be a total failure. One had to return to burning. Cement and steel producers were allowed to burn the waste. This now no longer is called "incineration", but "thermal recycling". Even so the costs exceed revenues by a factor of about 10. In spite of the sobering fact that the Germans now have to pay twice for waste disposal (the public system continued to operate, although at lower load, but not at lower costs) more and more countries including Japan, Taiwan, and South Korea introduced similar waste disposal legislation. California and Oregon asked that 25 % of post-consumer recycled plastic had to be added to rigid plastic containers. This requirement sounds beneficial to the environment. However it might be harmful to consumer's health considering food contact safety.

Polymer subunit recycling is an attractive alternative to material recycling. Hydrolysis is a favored approach because of the ease of operation. Costs are lower than material recycling and even lower if one uses the biocatalyzed approach: biodegradation in composts.

There are two types of biodegradable plastics: starch (renewable) and polyesters (oil derived and renewable). Novamont in Italy ultimately became the world's largest starch derived plastics provider. Its brand Mater-bi is used mainly in catering items and in packaging films. It excels by the ease of disposal (composting).

Polyesters are degradable because ester bonds are prone to be hydrolyzed, especially under hot and humid conditions. If in addition the subunits of the polyesters are metabolized by bacteria and fungi the resins might be considered as biodegradable. Polymer producers around the world sized the opportunity and developed polyester type of biodegradable plastics. Japanese companies were among the first to start. European and American companies followed, part in synthesizing new types derived from crude oil and part in further developing the natural biopolyester polyhydroxybutyrate (PHB).

The early synthetic polyesters were of the type glycol/butanediol-succinate/adipate copolymers. These monomers and thus the polymers are biodegradable. The various brands differ in composition and rations of the subunits. These synthetic polyesters have low melting temperatures and are not suitable for injection molding. However, the films produced from them have impressing mechanical properties.

Showa Highpolymers in Japan was the first to introduce a biodegradable polyester called Bionolle. Sky in Korea soon followed with SkyGreen. Bayer in Germany introduced additional amide bonds to defeat the thermal weakness. However it abandoned its BAK developments due to uncertain legislation. BASF and Eastman developed the semi-PET's Ecoflex and Ecostar. Both polyesters bypassed the weak properties of the synthetic aliphatic polyesters by introducing aromatic residues. Actually about 70% of the terephthalic acid residues of PET (copolyester of terephthalic acid and ethylene glycol) are replaced by succinate or adipate. Thus the ester bonds are more accessible to water hydrolysis than those in plain PET. The glycol and diacid subunits are biodegradable. Terephthalic acid also is known to be biodegradable, although at rather slow rates. Thus both semi-PET' s can be considered as biodegradable polyester. The slow degradation of terephthalic acid might pose a future problem. If semi-PET type biodegradables were introduced in large quantities into the environment, terephthalic acid could accumulate adsorbed to clay particles and river banks very much like the phthalates plasticizers (also known to be biodegradable).

In the seventies, initiated by the first oil crisis, many companies started R&D programs to use renewable materials. At the end of the crisis all but a few stopped such projects. The concept of renewable plastics more or less disappeared from the public perception until pressure against landfills and incineration became pressing. Then it was remembered that bioplastics, by their nature, are bio-recyclable (biodegradable).

ICI in England and PCD Polymere, Linz in Austria (now Borealis), were the two companies that continued to develop PHB after the end of the oil crisis. ICI discovered that the heteropolymer polyhydroxybutyrate-co-hydroxyvalerate (PHB/HV) was not as brittle as the homopolymer. It sold this heteropolymer under the trade name Biopol. In addition to reduced brittleness, reduced processing temperature was claimed as improvement over the homopolymer. Later it turned out that the extreme temperature sensitivity of the first batches were due to impurities. Thus the "reduced processing temperature" claim became obsolete. It also turned out that PHB/HV became as brittle as PHB during storage. In the aftermath of a management buyout the Biopol business of ICI became part of Marlboro Biopolymers. Zeneka, the "bio"-part of ICI after splitting the company, later bought the Biopol business back to sell it again some years thereafter to Monsanto that itself sold it to Metabolix.

PCD introduced a new bacterial strain that produces PHB during the growth phase of the bacteria. The bacteria used for the production of Biopol produce PHB only at the end of the growth phase. PCD also introduced a solvent extraction process that bypassed the impurity problems. PHB of PCD can be considered as thermally as stable as most commodity synthetic polymers. In 1994 PCD sold strains, patents, and know how to Biomer. Biomer focussed on transforming the biopolyester into a bioplastic by blending PHB with plasticizer, nucleating agents, and other processing aids. All the additives are selected to not to endanger biodegradability under no circumstances. Doing so Biomer developed formulations that had identical mechanical properties as PP or PE-HD, but that in addition are fully biodegradable, are of renewable resources, allow molding thinner walls, and have faster injection molding cycles[1]. Biomer formulations were spun into fibers with tensil strengths of up to 400 MPa[2]. In cooperation with pab productions it also developed formulations with particular adsorption properties that are used as immuno sticks[3]. Current R&D focuses on natural fiber composites and oxygen barrier films for food packages.

Tepha, a sister company of Metabolix (that itself focuses on genetic engineering and plant derived PHB), develops medical applications and new heteropolymers with long side chains (PHA' s) or with non-standard chain links (PHB/4HB) for flexible devices. The Procter & Gamble Company in the US and Kaneka in Japan develop high strength biodegradable films made of PHB/HH (hydroxyhexanoate)[4].

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1 see links "mech. Data" and "Properties" of www.Biomer.de

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Synthesis of PLA (polylactate), the other thermoplastic biopolyester, was explored by Cargill (USA), Hycail (NL), Neste Oy (FIN), Shimadzu, (J), and Mitsui (J). Mitsui used a solvent based process to remove the water in the polymerization process. Neste got high mw PLLA by joining low molecular weight precursors by urethane links. All the others use the dimer lactid process.

PLA is not hydrolyzed by microorganisms. However the ester bonds are attacked by water in humid and hot environments having temperatures over 55°C (e.g. commercial composts). The resulting lactic acid is a nutrient for microorganisms. For this PLA merits the label biodegradable. Temperatures of >55°C are needed to "thaw" PLA that behaves like a glass (frozen melt) below temperatures of 50-60°C. In everybody' s garden composts the hot conditions are present only during very short periods. Thus PLA is not biodegraded in home composts, only in professional ones.

The freezing-thawing phenomenon also is the cause for the limited resistance of PLA to heat. PLA is suitable for frozen food or for packages stored at ambient temperatures. It is not suitable for hot drinking cups or food that need to be sterilized or pasteurized in trays or cans.

On the other hand PHB is a highly crystalline material that withstands sterilizing at 120°C[5]. Its crystallinity also provides good vapor and gas barrier properties (oxygen, $CO_2$, water)[6]. Since PHB formulations are easy to mold, have a glossy

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Miguel O., Fernandez-Berridi M. J., Iruin J. J. (1997) Survey on transport properties of liquids, vapors, and gases in surface, and are totally biodegraded in soils and composts, PHB is a preferred packaging material for processed (sterilized or pasteurized) feed or food (e.g. yogurt: spoon it up and dispose the cup without washing with the kitchen waste). The fine surface of injection molded PHB parts prevents fast attack by microorganisms so that PHB also could be used for unprocessed, fresh food with limited shelve live such as butter, salads, dressings, cheese and others[7].

Biodegradable plastics, while helpful and interesting for industrialized countries, are of uttermost importance to developing countries. Today, these countries have low plastics consumption, but they will end up with amounts seen in the developed ones. In industrial countries, the development of consumer plastics and their use got hand in hand, so that there was plenty of time to adjust waste disposal systems. Developing countries have no such grace period. Biodegradable food and feed packages can alleviate that situation. Further, bioplastics like PHB can be produced locally using local agricultural feedstock without the need to import crude oil. The latter aspect, combined with the ease of molding, the mechanical properties, the shelve live, and the barrier characteristics classify PHB as a preferred food and feed packaging material for developing countries. For this it is not a surprise to see lengthy efforts to find new

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PHB producing bacterial strains and plants in India[8], Singapore[9], Mexico[10], Argentina[11], China[12], and Brazil[13].

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PHB currently sells for over 6 times the price of technical grade polyamides and about 10-20 times that of the polyolefines PP, PE, or PS This looks deceiving. However one has to keep in mind that PP or PE were about 4000 times as expensive as today. PHB will not fall in price to the same extend. However with increasing economy of scale it will sell at prices attractive to food packaging producers throughout the world.

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