Creating markets for recycled resources

LIGHTWEIGHT COMPOSTABLE PACKAGING: LITERATURE REVIEW

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Written by:

Professor Edward Kosior
Nextek Limited

Dr. Radek Messias Braganca & Dr. Paul Fowler
BioComposites Centre, University of Wales, Bangor, Gwynedd

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The Waste & Resources Action Programme
The Old Academy, 21 Horse Fair, Banbury, Oxon OX16 0AH
Tel: 01295 819900 Fax: 01295 819911 www.wrap.org.uk
WRAP Business Helpline: Freephone: 0808 100 2040

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Retailer Innovation Milestone Report

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1. Executive summary

In the UK where the total consumption of plastics amounted to 2,414 million tonnes, of which approximately 60% of which is packaging, that is discarded as soon as the package is open. Many of these plastics end-up in landfills where they will stay for centuries.

In recent years, many companies have introduced compostable polymers made from agricultural resources as substitutes of petroleum based thermoplastics. Compostable polymers are expected to lessen the environmental impacts of packaging by shrinking landfill requirements, while decreasing the dependence of non-renewable resources, provided measure that a number of barriers to their widespread use would be overcome, such as the existence of composting infrastructures, better understanding on how to use these materials in novel food packaging design that would subsequently improve retailer/consumer know-how, and a lowering of the unit price as a function of the increase of their market share.

An overview of commercially available materials shows that a number of compostable polymers exist now in the market, Polylactic acid (PLA), Polyhydroxyalcanoates (PHA), Thermoplastic starches (TPS), Cellulosic and whole plants materials, and a range of others aliphatic esters. In general, these materials are more expensive than petroleum based polymers, however analysts suggest that price of non-renewables thermoplastics is to increase drastically because of the exaustion of petroleum reserves, while the price of renewable based polymers is expected to decrease because of better processing technologies and increase of scale of production.

PLA, the most important material is presently produced from starch (by most producers), and whey residues (by Hycail in Netherland). This polymer use less fossil energy than traditional polymers, and completely compost in 45 days in a commercial composting facility. Unlike PLA, PHA will biodegrade in others environment (marine, soils, home compost), however this material use more energy than traditional plastics. Both PLA and PHA can be used to produce both rigid and flexible materials, and the commercially available resins have higher modulus than the ones of the plastics currently used in food packaging, indicating that thinner/stronger materials can be obtain. Like the PHA's, aliphatic polyesters cellulosic and TPS polymers can be composted in a variety of situations, but need lower fuel use and are far cheaper and as they don't have the same properties than the formers two classes of compounds, are expected to be used in blends that would reduce costs of materials.

Analysis of the properties of the novel renewable based materials indicate that they can be stiffer or with higher elongation than conventional plastics used in packaging, suggesting that it is plausible that weight of food packaging can be reduced by developing ultra thin materials reinforced with plants with microfibrils, or by using foamed sandwich materials.

On a short term, it is expected that Sainsbury, which consume 2000 tonnes of per year of rigid plastics for all produces, could save 300 tonnes of packaging by the introduction of ultra thin materials. If these results could be adopted by whole UK packaging sector than the saving would be 1900 tonnes (based on a 16% share of stream). Major savings, in terms of waste reduction could be achieved if foamed materials are to be used.

On a long term it is expected that technologies would be developed allowing a more systematic use of such materials in both packaging (bottles for soft drinks) and others uses (like foam for house insulation). These are expected to provide more reduction of materials going to the landfill.

2. Glossary of terms and abbreviations

PE, **Polyethylene** or **polyethene** is a thermoplastic commodity used in consumer products (over 60M tons are produced worldwide every year). Its name originates from the monomer ethene, also known as ethylene, used to create the polymer. In the polymer industry the name is sometimes shortened to **PE**, Polyethylene is classified into several different categories based mostly on its density and branching. Most important are : **High Density Polyethylene HDPE** is defined by a density of greater or equal to 0.941 g/cc**., and Low Density Polyethylene LDPE** defined by a density range of 0.910 - 0.940 g/cc. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. It has therefore less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. LDPE is created by free radical polymerization. The high degree of branches with long chains gives molten LDPE unique and desirable flow properties. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength.

PP, **Polypropylene** or **polypropene** (**PP**) is a thermoplastic polymer, used in a wide variety of applications, including food packaging, textiles, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. An addition polymer made from the monomer propylene, it is unusually resistant to many chemical solvents, bases and acids.

PS, **Polystyrene** is a polymer made from the monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum. At room temperature, polystyrene is normally a solid thermoplastic, but can be melted at higher temperature for molding or extrusion, then re-solidified. Styrene is an aromatic monomer, and polystyrene is an aromatic polymer.

PET, **Polyethylene terephthalate** (aka **PET**, **PETE**, **PETP**,**PET-P**) is a thermoplastic resin of the polyester family that is used to make beverage, food and other liquid containers, synthetic fibers, as well as for some other thermoforming applications. It is also one of the most important raw materials used in man-made fibers. Depending on its processing and thermal history, it may exist both as an amorphous (transparent) and as a semi-crystalline (opaque and white) material. It can be synthesized by a transesterification reaction between ethylene glycol and dimethyl terephthalate.

PVC, **Polyvinyl chloride**, (IUPAC Polychloroethane) commonly abbreviated **PVC**, is a widely-used plastic. Polyvinyl chloride is produced by polymerization of the monomer, vinyl chloride as shown. PVC is a hard plastic that is made softer and more flexible by the addition of plasticizers, the most widely used being phthalates.

Biodegradation is a process where different micro organisms break down organic matter and produce carbon dioxide, water, heat and humus, which is a relatively stable organic end product.

Composting, refers to an industrial/ small scale (home composting) biodegradation process which proceeds through 3 phases where different communities of micro-organism predominate during various composting phases.

3. Introduction

3.1 Objectives of the review

This document presents the current state of the art of commercially available renewables-based polymeric materials that might be replacements of conventional polypropylene (PP), polystyrene (PS), polyethylene terephtalate (PET) and polyvinyl chloride (PVC) for use in the manufacture of light-weight packaging by thermoforming. All the alternative polymers have been selected on the basis that they are compostable according to the European Norm EN13432.

The document begins with an overview of compostability, biodegradability, presents some definitions and the current state of thinking. A brief summary of the current use of synthetic commodity polymers used in packaging is followed by an analysis of commercially available, renewable polymers. This analysis presents an overview of technology of production, existing and emerging producers (looking to production capacity, planned increases) and pricing. Finally a comparison of materials' properties is made to signpost replacement of existing materials with emerging, commercially available renewable, compostable alternatives. Because of the large number of renewables-based polymers in development, analysis is limited to products that are commercially available, or close to being manufactured on a commercial scale and are expected to be used as packaging materials, i.e. starch, cellulose and whole crop polymers, and polyesters (polylactic acid, polyhydroxyalkanoate) and a range of compostable polyesters that are presently obtained from petroleum based resources, but can be obtained from renewables (polycaprolactone, polybutylene succinate/adipate, polybutylene succinate/carbonate, polyethylene succinate, polybutylene adipate terephthalate).

Finally, the document presents some conclusions about how, using these materials, a reduction in weight of packaging waste might be achieved within the current WRAP funded period (2006-2008), and on a medium term (i.e. next 20 years), looking additionally to ways to reduce the amount of food thrown away by consumers, and how to insure that more its collected for composting.

It is expected that polymers based on renewables, which are new in the market, would follow a similar development and uptake curve to established thermoplastic polymers, and therefore would follow a path of "material reduction"; that is, the down-gauging of film/substrate thickness, and the elimination of excess material through improved design. Down-gauging achieves the desirable combination of cost reduction and reduced environmental impact, and is a standard phase of the development of each polymer history. For example, between 1975 and 1990 the typical weight of a 1.5 litre PVC bottle fell by 27%, and that of a PET bottle fell by 33%, a typical PP yoghurt pot now weighs 7g compared with 12 g for a PS pot in the late 1960s, PE bread bags have been reduced to a thickness of 25 microns from an earlier thickness of 40 microns, the liners in cereal boxes have been downgauged by 12%, metallised film used in US multilayer snack food packs has been downgauged by 12 %. Because design/tooling learning from petroleum based plastics is transferred earlier in the products maturation curve, it is also expected that downgauging potential of biopolymers would be designed at an earlier stage.

An additional example of the potential of new bio-derived plastics in lighter/stronger materials is illustrated by the fact that Mazda, in May 2006,[1] announced the use of a new bioderived polymer to manufacture parts. In contrast to current petroleum-based polypropylene plastics, the new bioplastic also has comparatively higher rigidity, resulting in thinner moulds and fewer materials used. The newly-developed material is stronger--it has three times the shock impact resistance along with 25 percent higher heat resistance when compared to competitive materials. The novel bio-material also uses 30% less energy than polypropylene.

3.2 Compostability

The terms biodegradation, biodegradable materials and compostability are much used and abused by the layperson and purported experts alike. Here terms are used as defined by the standard EN13432, and as reported in the "Abreviation and Glossary of terms" parts of the report.

Attempts have been made to try to standardise a set of conditions, time scales and degradation products under which an item may be said to biodegrade. Only one European Standard currently exists for packaging materials, EN13432.

The standard is aimed at indicating the characteristics of the compostable packaging and the test methods needed to verify the conformity of the packaging under study with the requirements. This standard sets out a series of parameters under which a test specimen should be submitted to check for its biodegradability. These are done in 4 steps. In the first step, the material and all the components included are characterised and identified to guaranty absence of negative effects on the final compost.: ex. heavy metals. In the step two biodegradability is tested using small pieces in an aquatic or mature compost environment by measuring the carbon dioxide formed. This provides data for the calculation of the degree of biodegradation, which is defined as the ratio of the carbon dioxide produce to the calculated theoretical maximum value. Then, in the step three the product is tested for disintegration in fresh compost or mature compost, or in activated vermiculite under optimal conditions. **EN13432** standard stipulate the parameters which amount to active aeration of the item in compost at an elevated temperature (58 C +/-2 C) over a period of three months constitute conditions of composting. If after the three month period, the material is disappeared to carbon dioxide and water then the material is said to be biodegraded under active composting conditions. It is then decided if products are sufficiently disintegrated in composting establishments. The final step const in subjecting the material to a maturing stage of 3-6 months, afterwards for eco-toxicity and soil improvement.

At the present time, there are today no international/European standards for home compostable materials, or which include test methods and requirements related to home composting.

Test methods proposed by EN13432 and certifications refer to industrially compostable plastics.

3.3 Home compostability - concept and testing

Home composting implies that organic materials are transformed into humus by bacteria and other microorganisms under aerobic conditions similar to industrial composting. There are however a number of major differences. The time scale is different-composting cycle in industrial system is composed of a 3 months thermophilic phase, followed by a 3 months maturation phase. In home composting such time scale may not be so crucial, as longer periods may be acceptable. Control of humidity and temperature is not so clear cut, as it is accepted that these parameters may not only be lower, due to heat exchange with ambient temperature, and deficient aeration due to location of compost bins. The European Norm EN13432 for the Compostability of packaging implies the use of active composting. Active composting is the proactive management of a compost site at which the compost is turned, aerated and biodegradation is such that significant heat is generated as part of process. Indeed, the generation of heat significantly contributes to the ease and rate at which newly introduced material composts. It is unlikely that such temperatures will be sustained in a home composting situation, particularly in the winter months and/or when the compost bin is not managed. The altogether less efficient composting regime envisaged in a home environment places greater demands on packaging materials to be disposed of in such an environment at the end of useful life. For example, polylactic acid, although known to be compostable in an active composting scenario, will not, in any of its current known formulations, compost in the home environment.

Development of test procedure for home compostability is independently investigated by the Biodegradable Plastics society (BPS), in Japan, by AIB Vincote (a certification company in Belgium) which have developed testing procedures and certification procedures and awards the OK Compost Conformity Mark, and by the Swedish National and Testing Institute.

The methodology proposed by the Swedish National and Testing Institute assume that the process would be similar than industrial composting, but may be subject to freezing cycles, and would be allowed to take more time. Unfortunately testing methods have been validated by comparing the model with 6 separate assays of real home-compostability of a packaging material compostable at relatively low temperature (a starch polymer called Mater-Bi) in 6. It failed to compost in one of the assays where no thermophilic phase was obtained.

This raise the question of the behaviour in real life home composting situation of others materials that are reported to be home compostable, but would need temperature that would be higher than Mater-Bi.

3.4 Oxo-degradable polymers

Another element should be taken in consideration in packaging that may be compostable is the introduction in the market of oxodegradable and photodegradable polyethylene materials. In this case polyethylene is modified with proprietary chain breakers additives that designed for a "controlled lifetime". These in adequate environment catalyse oxidative or photochemical degradation of the polyethylene, which then fragments quickly and then undergoes degradation. More details can be obtained at the Oxo-biodegradable Plastics Institute (OPI) (www.oxobio.org). In the UK such technology is provided by Symphony Plastics and Ciba Speciality, and as been adopted for carrier bags by Co-OP (a retail and service group with strong ethical and environmental profile) Somerfield (a medium size supermarket chain) and (Tesco).[2] Symphony material is also sold by the Soil Association. In the US quality of such materials is guaranties by ASTM 6954 04, which has no equivalent in Europe. At the present a commission from BSI is discussing a potential standard (BSI 8274). In Germany the use of such material has been banned.

The only independent assessment, performed in the UK,[3] that could be found by the authors, indicate that, after composting of kerbside collection of organic waste in such PE bags, " the PE becoming increasingly visually obtrusive within the windrows", adding that "monitoring undertaken has demonstrated that although PE sacks are suitable for the collection of organic wastes, they are not compostable under open windrow conditions as a determining feature of a compostable polymer is its ability to undergo biological degradation at a rate consistent with other known compostable materials, in addition to leaving no visually distinguishable residues within the final compost product" to suggest necessary to screen the finished product after the composting process is complete, before marketing and delivery to the consumer. However, and because PE is not renewable based materials, it is not therefore focus of this review, and there is no more discussion on the subject.

3.5 Water soluble polymers,

These are also polymers dissolve easily in water (are used in laundry detergent packaging) and which public perception associate with degradability. The most common of them polyvinyl alcohol which is only degraded with very specific bacteria's,[4] and can not genuinely be considered bio-degradable.

3.6 Home compostability as a way to deal with packaging waste.

Different strategies are pursued to reduce waste plastic materials landfill and it is expected that, in the UK, two of them would form all part of a global solution, recycling and compostability.

The later is regulated in the UK/EU by standards dealing with the quality of the compost (BSI PAS 100), and by measure of compostability of an eventual material in an industrial installation (EN13432).

There are no international standards to certify home compostable materials, but some national or company standards. These assume that the home compostability process would be the same than the industrial one, but could take more time (up to two years in the Swedish Standard) and have intermittent periods of freezing.

A critical question that could be raised- mainly if home compostability is to be promoted in cold regions from the UK, is to know if relatively high temperature (to 60 ºC) could really be obtained in home composting situations. This question is very important because, as it can be seen later in more detail, some commercial materials only undergo biodegradation if submitted to such temperature.

In the study to check the methodology proposed by the standard, the Swedish Institution performed a cross study of 6 cases in real home composting situation in Norway/Sweden. In this study they used a material witch undergoes biodegradation at relatively low temperature (Materi-bi), but even with this material, in one case there was no biodegradation after one year, because no enough high heat could be generated to allow the suitable bacteria's to strive.

4. Commodity plastics presently used in food packaging

4.1 Consumption

Consumption of large-volume thermoplastic families [i.e. polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS & EPS) and polyethylene terephthalate (PET)] amounted to 26 million tonnes in Europe in 2003 (68% of total plastics' consumption). A major share of these is used in packaging. Many of these demonstrated substantial growth, in particular PET with 11% higher volumes over two years.

A similar situation exists in the UK where the total consumption of plastics amounted to 2,414 million tonnes, with a major share of polyolefins (LDPE/LLDPE), HDPE, OPP, PP and unspecified (79%) (Figure 1).

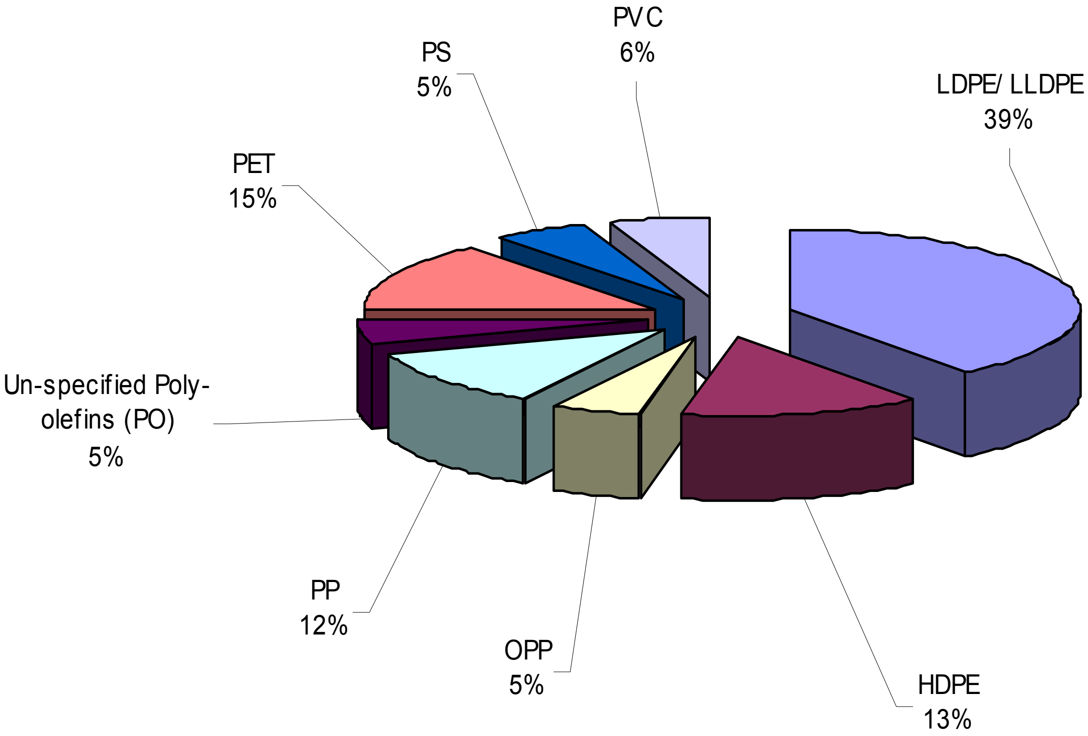


Figure 1. Commodity plastics used in packaging in the UK

(source WRAP, May 2006) <Paul.Davidson@wrap.org.uk>

4.2. Price structure of commodity thermoplastic polymers

The price ranges of commodity polymers are shown in Figure 2 and Table 1 and are logarithmic as a function of the volume of sales. It is expected that emerging prices of new polymers would also fit the regression curve; that is, the price of novel commercial biopolymers would decrease as their sales increase.

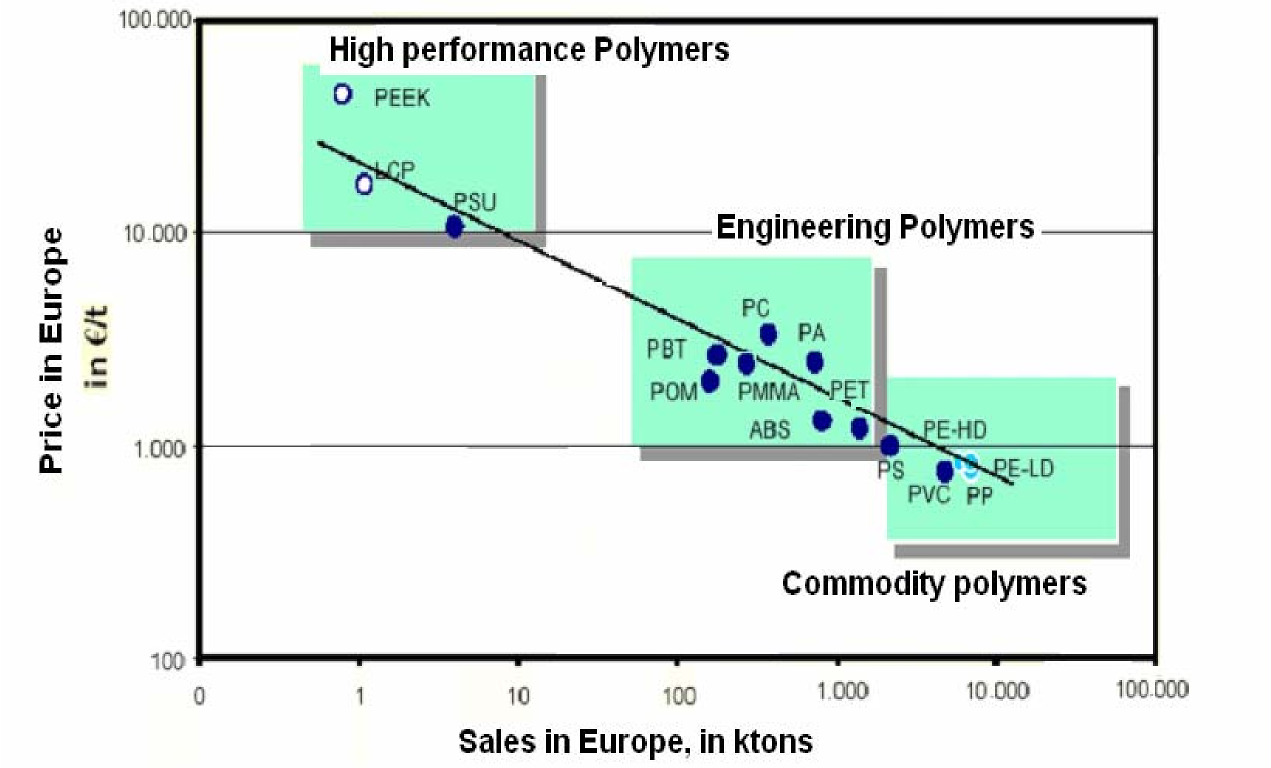


Figure 2 : Price of polymers as a function of volume of sales,

(*Personal Communication with Biomer* "Urs J. Haenggi" <haenggi@biomer.de>)

Material	***LDPE***	***HDPE***	***PP***	***PVC***	***Polystyrene (PS & EPS)***	***Polyethylene terephthalate (PET)***
Average price (€/kg) (2005)	**0.85**	**0.92**	**0.80**	**0.80**	**0.90**	**1.15**

Table 1. The average prices of commodity polymers;
(Source:www.polymer-age.co.uk)

The prices of all synthetic polymers are a linear function of the price of petroleum and the latter has been increasing in the last years. Figure 3a (from www.wtrg.com) illustrates the variation of petroleum price from 1947 to 2004

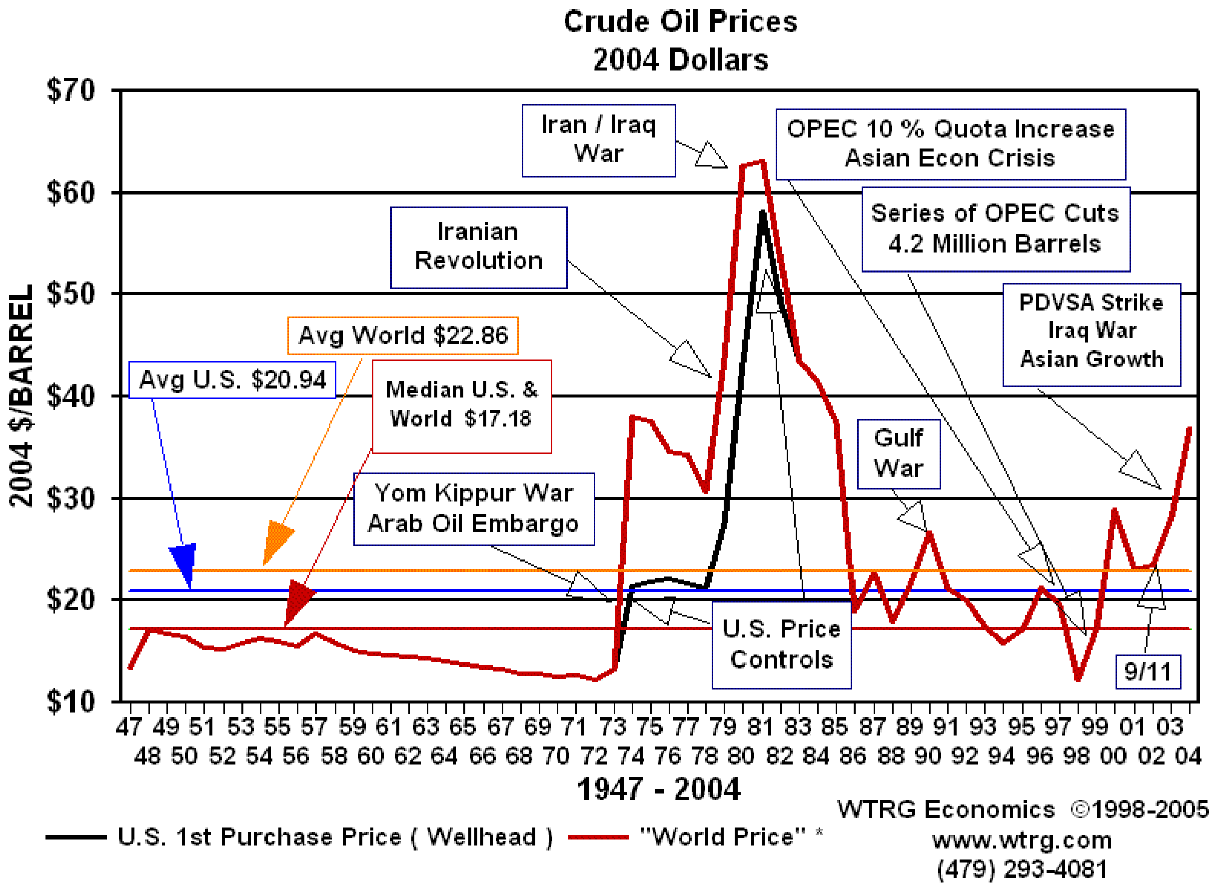
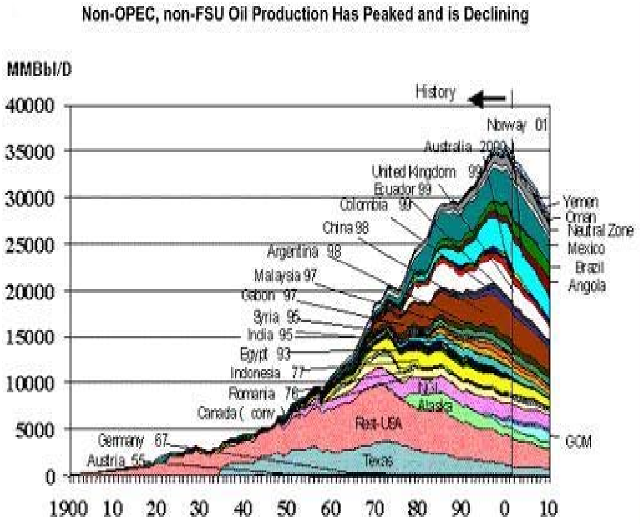


Figure 3 The variation of petroleum price with time, (Source www.wtrg.com)

Nobody can accurately predict the variation of the price of petrol in the next few years, but most answers are related to the extraction/depletion of the reserves, and the security of supply. World reserves of oil are estimated at roughly 1–1.5 × 10^7 tonnes, more or less 40 years of consumption at the present rate. However these values do not allow an easy correlation to the rate of petrochemical resource extraction and depletion. Many schools of thinking have emerged to try to predict this rate, some optimistic, others pessimistic with a range of opinions in between.

The optimist school, based mainly at the Massachusetts Institute of Technology, estimates that possible production/depletion is a function of the technical progress which would allow a better exploitation of existing reserves (by, for example, reduction of drilling costs, improvement of oil recovery and better geological estimates). Such technical progress is exemplified by oil extraction in Venezuela where, in the 1980s, extraction of heavy crude was considered feasible only when the price per barrel reached USD50. However, technological advances have reduced this threshold to USD15 by 2004.[5]



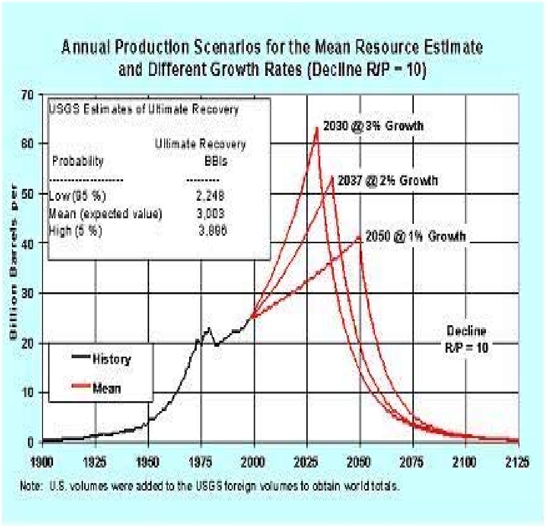


Figure 4a Predictions of oil reserves by the by the Association for the Study of Peak Oil & Gas

Figure 4b Predictions of oil consumption

Conversely, the most pessimistic analysis is presented by the Association for the Study of Peak Oil & Gas, which suggests that the global production of oil had already peaked in the spring of 2004.[6] (see Figure 3b) Furthermore, in March 2005, the Algerian minister for energy and mines stated that OPEC had reached its oil production limit,[7] while in September 2005, British Gas raised its prices blaming falling oil reserves.[8]

An intermediate vision is presented by the United States Geological Survey (USGS) which estimates that there are enough petroleum reserves to continue current production rates for 50 to 100 years. In 2000, a USGS study of world-wide oil reserves predicted a possible peak in oil production around the year 2037.[9] The US Department of Energy predicts that global oil production will peak somewhere between 2020 and 2050, but that the output is likely to increase at a substantially slower rate after 2020.[10] Price speculation is likely to increase petrochemical prices before peak oil production is reached. Figure 3b shows U.S. government predictions for oil production other than in OPEC and the former Soviet Union.

The above document has now disappeared from the US Department of Energy website. A copy of the report may be accessed here:
http://www.evworld.com/library/Oil_Shale_Stategic_Significant.pdf.

An updated version of the graph, presented in Figure 3c can be accessed at: http://www.energybulletin.net/2544.html.

It is now clear, that even if at the present moment, the price of renewable based polymer is high it may come down as their market share, and volume of sales increase (following the pattern in Figure 2), while price of the petroleum based polymers is expected to grow (with historical values presented in Figure 3a). Following oil consumption patterns expectative indicated in Figure 3b and 3c.

Another reason to focus on the sustainability of packaging polymers arises from the fact that consumption and subsequent disposal of petrochemical based resources leads to increased carbon dioxide emissions,[11] with concomitant effects on global warming. Thus, continued increase in petrochemical production requires an increased exploitation of non-conventional sources, suggesting market opportunities for new, renewable-based polymers.

4.3. Packaging uses of thermoplastic polymers

In the UK, plastics are used in packaging for a variety of end-uses, with the preponderance of bottles, films, bags & sheets, thermoformed packs and injection moulded articles, as shown in Figure 4.

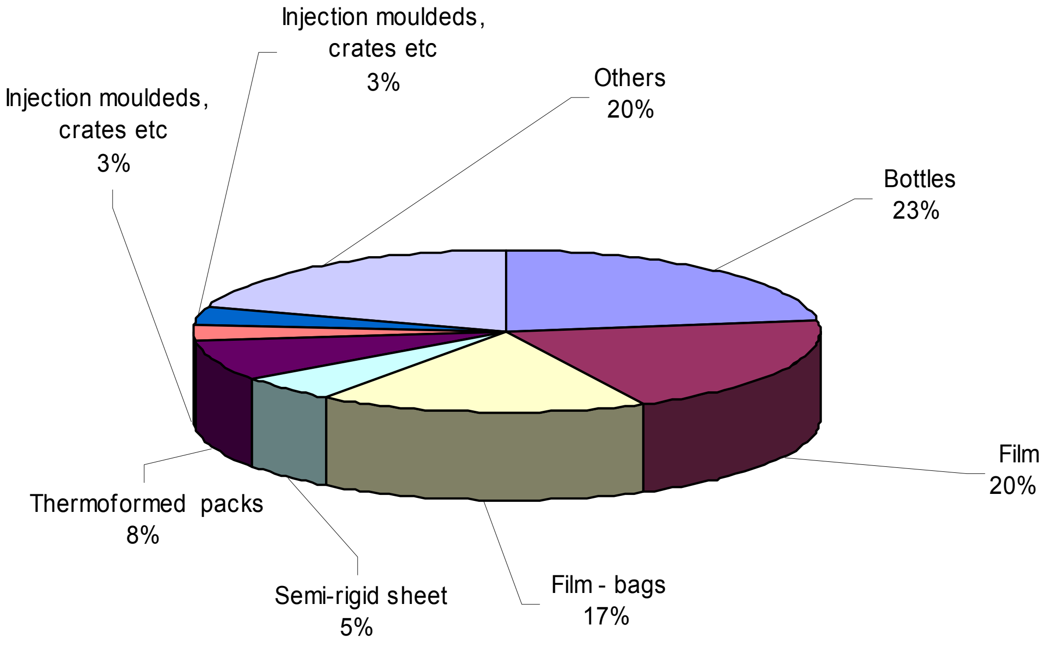


Figure 5 The end-uses of plastics used in packaging in the UK,

(Source WRAP, May 2006) <Paul.Davidson@wrap.org.uk>

These can be related to the properties of the basic commodity polymers as described in Table 2, overleaf.

Plastic type	End use in food packaging	Basic properties
Low density polyethylene (LDPE)	Pallets, film, bags, coatings, containers, squeeze bottles, carrier bags used in multilayer films, coating for disposable paper cups-not recyclable	High resistance to puncture/tear protection & heat sealability (used in multilayer films to improve other materials), low permeability to water
High density polyethylene (HDPE)	Containers, housewares, industrial wrappings and films for water sensitive products such as dry foods, in multilayer films to protect water sensitive EVOH used for packaging oxygen sensitive food	Lower water permeability; inert to acids, oxygen/carbon dioxide diffusion rate. Tough and flexible and used in films. More crystalline, and higher density than LDPE, it is stronger and stiffer and it is also used in containers
(OPP)	Multilayer films	Biaxially oriented PP films have modifier incorporated that dramatically improves resistance to moisture transmission, act as barrier against moisture and flavour loss.
Polypropylene (PP)	Film, microwave-proof containers, ice cream cups, lids, most thin walled containers are those used for butter, margarine and yoghurt.	Lower vapour and oxygen permeability. Inert to acids, good strength, stiffness fatigue resistance. Flavour loss barrier, clarity superior to LDPE. Oriented PP has higher strength and does not need impact modifiers.
Polyethylene terephthalate (PET)	Bottles, films, trays, boil-in-the-bag	High strength, high softening point. Available in moulded form, rigid clear, tough, creep resistance, wide range temperature resistance (–40–200 ºC).Gas barrier superior to PVC/PE but lower than polyacrylonitrile
Polystyrene general purpose	Rigid packaging, cosmetics packs, lids thermoformed containers, trays and boxes	
Polystyrene (high impact)	Thermoformed containers, yoghurt pots, ice cream cups, cream, cheese cartons, molded containers and lids, trays and boxes	Hard/rigid, opaque translucent, strength up to 7 times general purpose grade; other properties similar to general purpose polystyrene
Polystyrene (EPS)	thermal insulation, cups, plates, disposable fast-food packaging	Insulating material
Polyvinyl chloride (unplasticised)	Bottles for edible oil, thermoformed foil packaging of chocolate and biscuits, cap sealing	Clarity, oil resistance, maximum 22% plasticiser content, no phthalates, needs impact modifier to increase strength
Polyvinyl chloride (plasticised)	Cling film, shrink wrapping of pre-packaged meat, fruit and vegetables. Used to package biscuits and chocolate	Flexible, clear/opaque, durable, weatherproof, good impact strength, stretchable PVC-polyvinylidene chloride in multi-layer film, used as coating to improve the barrier properties of others films
Polyamide (PA)	Films for packaging of foods such as oil, films for vacuum packed food, cheese and boil-in-the-bag products, for high temperature engineering applications	Low gas permeability, translucent, steam sterilisable, high lipids barrier, creep resistant

Table 2. The uses of thermoplastics in food packaging

4.4 Basic properties of thermoplastic polymers

The thermo-mechanical properties of packaging films (Table 3) are as important to the application as are the barrier properties. Adequate mechanical strength throughout the service life of a packaging application is necessary to ensure the integrity of a film. Thermal properties are important not only because of polymer processing technologies but also because of food preparation conditions (sterilisation steps), storage conditions (for freeze packed food), and cooking conditions (in the case of microwave packed food).

The main purpose of packaging is not only to protect the product from its surroundings, but also maintain the quality of the product for its shelf-life, while addressing communication, legal and commercial demands.

In the subsequent discussion, a number of material properties of renewable based polymers are to be compared with their synthetic counter parts, such as physical and thermo-mechanical properties (for example, melt flow index, Vicat temperature (both related to processability of the polymer), tensile strength, elongation, tear strength, puncture resistance and sealability (related to the mechanical feature of the packaging), migration/absorption, chemical resistance (related to the ability to be in contact with such media without deterioration).

	LDPE	***HDPE***	***PP***	***PVC***	***PET***	***PS***
Physical properties						
Melt flow rate (g/10 min)	0.8–6	0.3–1.8	1.25	1.3–1.4		8
Density (g/cm^3)	0.91–0.94	0.92–0.96	0.91		1.37	1.04
Mechanical properties						
Tensile strength at yield (MPa)	7.6–22.1a)	21–42	36.3	47	110	48
Elongation at yield (%)	600	600-900	12	100	50–350c)	2
Flexural Modulus (MPa)	150–213	1300	1520	2200–2900d)	2750	3500
Izod impact J/m, 23 ºC			55		59	21
Thermal Properties						
HDT (ºC)	49	80	108		67	106
Vicat softening point (ºC)	94–120	121–129	156		78	99
Optical properties						
Haze (%)	9–12			15		
Gloss (%)	26–100b)					
Barrier propertes						
Oxygen transmission cc-mm/in^2-24h-atm @ 20 ºC & 0% RH	0.72–239	0.3–0.4			3–6	4
CO_2 transmission cc-mm/in^2-24h-atm @ 20 ºC & 0% RH	N/a	400–700	N/a	N/a	15–25	N/a
WVTR Moisture vapour transmission rate g-mil/100 in^2 day	N/a	130–185	N/a	N/a	1–2.08	N/a

Table3. Some thermo-mechanical properties of commodity films; (Source MatWeb online, average value: a) 12.5MPa; b) 75%; c) 130; d) 2650)

4.5. Thermo-mechanical properties

The first step in moulding thermoplastic polymers is, in a factory, to melt the polymer to introduce it gradually into the mould. A measure of processability in this stage is the melt flow index (MFI), a measure of the melt flow rate, i.e. an indication of the flowability of a polymer melt. Thermoformed products that are to be analysed in more detail in this report, are obtained in a two stage process. First, the polymer (with some additives) is used to obtain a sheet, which is subsequently softened by heat and moulded to obtain a finished packaging product. The Vicat softening point is the temperature at which a load can penetrate up to 1 mm, and characterise the temperature at which thermoforming can be performed.

Adequate mechanical strength throughout the service life of a packaging application is necessary to ensure the integrity of a film. Thermal properties are important not only because of polymer processing technologies but also because of food preparation conditions (sterilisation steps), storage conditions (for freeze packed food), and cooking conditions (in the case of microwave packed food).[12] Interactions between hydrocolloids, and small molecules, including water, plasticisers, lipids and others additives dispersed in the space of the matrix contribute to the thermo-mechanical parameters of the films.

Among the many thermo-mechanical properties of plastic materials are tensile properties. Tensile testing provides data on yield strength, fracture strength (ultimate tensile strength), modulus of elasticity (Young modulus), and elongation at break.[13] The maximum tensile strength is the maximum tensile stress that a film can sustain. Strain is the maximum change in the length of a test specimen before breaking. Elastic modulus is the fundamental measure of film stiffness.[14] Additives, and plasticisers in general, affect mechanical properties (as the content of plasticiser increases, tensile strength decreases and elongation increases).

4.5 Barrier properties

The barrier properties of packaging materials are as important to the application as are the thermo-mechanical properties A key characteristic of glass and metal packaging materials is their high barrier properties to gases and vapours. While polymers can provide an attractive balance of properties such as flexibility, toughness, lightweight, formability and printability, they do allow the transport of gases and vapour to some extent. The selection of a barrier polymer for a particular application typically involves trade offs between permeation, mechanical and aesthetic properties as well as economic and recycling considerations.[15] Quality and shelf life are reduced when the packaged product, through interactions with the outside environment, gains or loses moisture or aroma, takes up oxygen (leading to oxidative rancidity) or becomes contaminated with micro-organisms.[16,17]

2.5. Summary on information on commodity plastics used in food packaging

Plastics used are accountable for 2,414 million tonnes tonnes per year of landfill waste in the UK. They are mostly from five chemical families (polyethylene, polypropylene, polyvinyl chloride, and polyethylene terephthalate).

These are used to produce a range of flexible, and rigid packaging materials (see Table 1) due to their thermo-mechanical and barrier properties, and their price.

Studies suggest that these prices may soon increase due to the exhaustion of petroleum resources; non-petroleum based polymers, that would be less influenced by such price changes are promoted as alternatives and have the advantage to be compostable.

5. Emerging biodegradable and/or renewable materials

Biodegradable and compostable materials can be from either biobased or petroleum (non-renewable) source.

The later are mainly a range of polyesters, that are described in detail in the point 3.5 of the report, while an overview of the former category of renewable based (biobased) polymers is presented in the Figure , as the concept cover natural polymers extracted from biomass, polymers that are obtained by synthesis of bioderived monomers, or polymers produced by micro-organisms. In this review, polymers which are not available in commercial scale, or on which there is no indication of commercial uptake, or that are not used in food related applications, are not reviewed, because they could not be used within the current WRAP funded period (2006-2008) to afford a reduction in weight of packaging waste, this include proteins, nylons, polyurethanes, and non-starch non –cellulose based polysaccharides. Paper and molded pulp paper are also not reviewed because they have been part of others Wrap reports

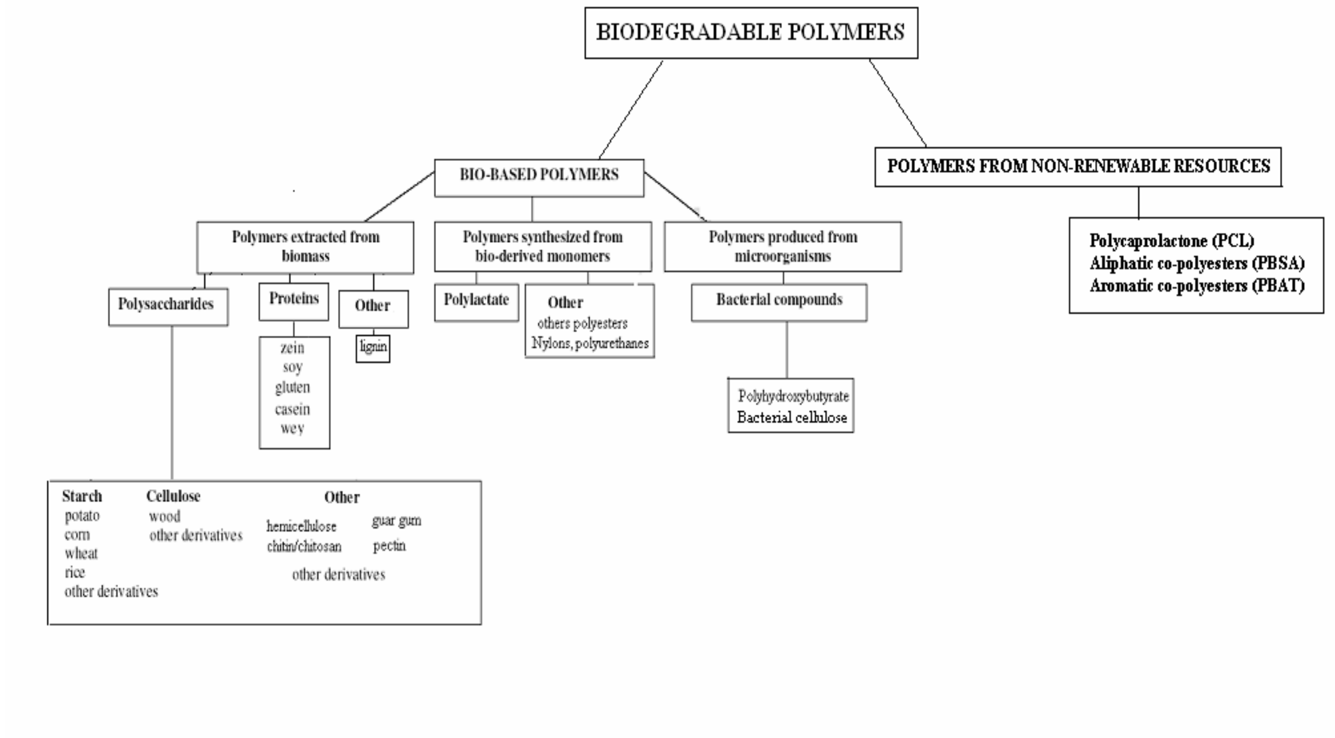


Figure 6 Biodegradable polymers

5.1. Starch polymers

5.1.1. Technology overview

Starch is a granular material from vegetable origin that is composed of two natural polymers: amylopectin and amylose. These are polysaccharides with different molecular weights and structures (the latter being almost linear, while the former has a highly branched structure). Pure starch provides brittle and friable materials, but this can be improved by destructurisation, a process in which the granular structure of starch is destroyed by the combined use of shear, temperature and time to provide a homogeneous material with both amylopectin and amylose dispersed uniformly through the material. The properties of this destructurised starch can be improved by complexing; that is, blending with other polymers (such as polycaprolactone, polyvinyl alcohol, polylactic acid and other polyesters), nanofillers, plasticisers and fibres.

A particular process uses technology developed by Rodemburg and involves the production of partially fermented starch polymers. The raw material is potato waste slurry originating from the food industry. The slurry consists of starch (72% of the dry matter), protein (12% DM), fats and oils (3% DM), inorganic components (10%DM), and cellulose (3% DM). The slurry is held in storage silos for about two weeks to allow for partial fermentation of starch to lactic acid. The product is subsequently dried (10% water final content) and extruded to obtain thermoplastic properties. Palm oil and additives such as titanium dioxide and calcium carbonate are added in the extrusion step to improve the properties of the product.

Commercial starch thermoplastic polymers are also prepared by chemical modification of starch (ester starch which is produced in a chemical reactor, dried and subsequently extruded with a range of additives). Reactive extrusion is a particular case of technology used for starch chemical modification, in which a monomeric reactant (e.g., caprolactone, or fatty acid) is reacted with starch inside an extruder. The system has been trialled in the UK and the properties of the resulting films are reported to be similar to those of LDPE. Reactive extrusion is claimed to be used by Plantic, a starch polymer processor.

An alternative approach to the production of packaging goods from starch is the adaptation of the food industry technique of wafer baking. In this process, a batter of starch, incorporating additives, is baked to afford a rigid form product using waffle-making technology in which only the mould is changed.

5.1.2. Current and emerging producers

Table 4 below shows the current and emerging producers of starch-based packaging materials. Trade names, production capacities and costs per kilos are presented in those cases where the companies have disclosed them.

Producer	***Region***	***Trade name***	***2006 Capacity (kt p.a)***	***2006 Price (€/kg)***
Avebe	Europe	Paragon		
Biop Biopolymer Technologies	Europe	Biopar	10 (17 in 2007, 100 in 2015)	1.50-4.5
Biotec	Europe	Envar, Bioplast, Bioflex,		1.50-4.5
Novamont	Europe	Mater-Bi	20[a)]	1.50-4.5
Plantic	Australia		NA	na
BioPearls	Europe	Pearls	NA	1.3-4
National Starch and Chemical	US	EcoFoam	NA	NA
Stanelco	Europe	Starpol, Bioplast	12	1.4-4.2
Rodemburg biopolymers	Europe	Solanyl	40	1
Japan Cornstarch	Japan	Cornpol	NA	Na
Nihon Shokukin Kako	Japan		NA	Na
PaperFoam	Europe	PaperFoam [b)]		na

Table 4. Current and emerging producers of starch-based packaging materials
[a)] in-house production in 2002 was12 kt; licenced production elsewhere 13 kt
[b)] baked starch

Novamont Spa, located in Novara, Italy started research in 1989 as a part of the chemical group Montedison. In 1996, Novamont was acquired by Banca Commerciale Italiana and Investitori Associati. It recently increased its capacity of production to 20,000 tpa. An additional 15,000 tpa (mostly loose fill) is produced off-site under licence agreements for which Novamont share agreement with National Starch and Chemical. The company has invested heavily in R&D and has acquired other businesses to consolidate its position as a leading company and pioneer in the field of starch based polymers. Acquisitions made include Warner Lambert's IP portofolio in 1997, the film technology company Biotec in 2001, and Eastman Easter in 2004.

Biotec Biologische Naturverpackungen GmbH is a German company that developed starch destructurisation. It produces about 2000 tpa of starch based materials. In 2005, it was bought by Stanelco and Sirap Gema, two major conglomerates involved in packaging industry.

BIOP Biopolymer Technologies AG is a Dresden-based company that has switched production from the Netherlands to Schwarzheide, Germany, where (in 2005) it has constructed a €7m, 10,000 tpa plant to make potato starch-based resin.

In Japan, Japan Corn Starch produces ester starch under the brand name of CornPol. The company is involved in basic R&D as well as pilot/demonstration projects. Also in Japan, Nihon Shokuhin Kako produces a modified starch under the trade name of PLAcorn.

Rodemburg is a company located in Oosterhout, Netherlands. It produces Solanyl, an extruded granule of thermoplastic potato starch, starting from by-products of the potato processing industry. The company has an installed capacity of 40,000 tpa, which would be the largest starch polymer plant worldwide, but the interviewed representative was not at a liberty to disclose any sales figures.

BioPlastics Inc, in the US, is currently manufacturing bags with LDPE-like mechanical properties by extrusion of PCL with destructured starches.

Biopearls, and Supol did not disclose their company profile.

Plantic Technologies Ltd was formed in 2001 to commercialise technology developed at the Australian Cooperative Research Centre for International Food Manufacture and Packaging Science from Queensland University (Australia). The lead products of the company are biodegradable extruded sheets and packaging containers called Plantic®, supplied to chocolate companies.

Cortex is an American company that has introduced in the market a range of biodegradable starch based materials (starch-polyesters) for packaging and agricultural applications. Its Eco Wrap^{TM} stretch film is 60% stronger than PE stretch films, and it has developed an food packaging grade film EcoFilm^{TM} which maintain strength and usability even at very high/ very low temperatures.

Another major American company is Cereplast which is selling a range of modified starches as resins for the production of films and rigids materials.

Paperfoam (Netherlands), Biosphere (US), PotatoPak (UK) and Earthshell (US) are companies that use the wafer baking technology. They do not provide raw materials but packaging products made of starch. The first two companies are technology providers, selling turn key plants for production. The United States Department of Agriculture is providing a number of formulations to produce baked starch products in the literature, but all these companies also have proprietary formulations.

5.1.3 Cost structure and expected evolutions

The current prices for modified starch polymers range from €1.50 per kg for injection moulding foams to €4.50 per kg for films and speciality products. The average price is around €2–3 per kg. Rodemburg’s polymer, Solanyl, is sold at €1 per kg. (Solanyl is cheaper than most starches based bioplastics, because its raw material, potato waste, is cheaper, its processing is simpler- see 3.1.1., but it is contaminated with a range of chemicals unsuitable for direct food contact. These results from a process known as Maillard reactions where sugars and proteins react in high temperature/pressure and shear conditions to provide a range of condensation products/aldehydes and others little known chemicals).

The cost of starch is higher in Europe than in the rest of the world. However, according to Bastioli (2003), the cost of native starch is not the overriding factor in the cost structure of polymer production, but rather the cost of the modification, an area in which there is considerable potential for improvement. Confirming this, a cost structure analysis of Biotec/ Stanelco products indicate that the cost of the different raw materials, and energy accounts for a small fraction of the total manufacturing cost. Companies indicate that price is expected to decrease to €0.7-0.9 per kg, once higher sales volumes, and better/larger extruders and formulations would be developed.

5.1.4. Technical substitution potential

Table 5 describes some physical and mechanical properties of starch-based resins.

	Starch (>85%) co-Polyester Mater-Bi a) NF01U	***Starch/ PCL Mater-Bi a) ZF03U/A***	***Starch/ cellulose acetate Mater-Bi a) ZF03U/A***	***Starch/ cellulose acetate Bioplast b) GF105/30***	***Ester starch Cornpol c)***
Physical properties					
Melt flow rate (g/ 10 min)	2–8			5–6	5–6
Density (g/cm^3)	1.3			1.21	1.21
Transparency					
Mechanical properties					
Tensile strength at yield (MPa)	25	31	26	44,38	30
Elongation at yield (%)	600	900	27	400–500	600–900
Flexular Modulus (MPa)	120	180	1700		10–30
Thermal Properties					
HDT (ºC)					
Vicat softening point (ºC)				65	105–125
Melting point (ºC)	110	64			

Table 5. Some thermomechanical properties of starch-based polymers
a) Novamont , b) Biotec, c) Japan Corn Starch

Potential substitution of traditional non-renewable polymers Stanelco indicated that they range of tailored PVOH/starch blends have advantageous property combinations for a wide range of packaging applications which exploit their advantageous properties beyond simple biodegradability and compostability. These fall into the following main areas:

5.2.Cellulosic and whole crop polymers

5.2.1. Technology overview

Cellulose is a linear homopolymer of glucosic residues comprising β-(1→4) bonds. Cellulose-based films have an extensive history and technology. A common characteristic is that such films are produced by chemical, mechanical or combinations of chemical and mechanical processing of structural plant matter to provide a sheet-like matrix. This matrix contains dispersed or partially disintegrated cell walls and may contain numerous additives to improve processing or end-use function. The most prevalent commercial form is paper and paper related constructs such as cardboard or corrugated cardboard. This report will concern itself no further with paper. Cellulose may be used to make flexible and transparent films. The best known example is cellophane, a regenerated cellulose, obtained by extrusion of an alkaline dispersion of xanthate of cellulose in an acid bath. A film is obtained after treatment with a plasticiser (glycerol) and drying. Esters and ethers of cellulose can also be obtained. Some, like cellulose acetate, propionate and butyrate are thermoplastic products of commercial importance. From an environmental point of view, these processes have been criticised because they are energy intensive, and create large amounts of carbon dioxide emissions.

5.2.2. Whole plant/plant waste polymers/packaging products

The processing of whole crops relies on the fact that some crops are high in natural polymers like starch/cellulose/hemicellulose/lignin that in some conditions can be extruded to a plastic material. Whole plant polymers are presently produced in the south of France, where maize is directly extruded and pelletized to give a thermoplastic material.

5.2.3. Existing and emerging producers

Table 6 shows current manufacturers of cellulose-based packaging materials.

Producer	***Region***	***Trade name***	***2006 Capacity (kt p.a)***	***2006 Price (€/kg)***
Eastman	US	Tenite		Na
Lenzig		Lyocell		Na
Accordis		Tencell		Na
Mazzuccheli	EU	Biocetta		na
Innovia	EU	Natureflex		3.3
FKuR Kunststoff GmbH	EU	BioFlex		2.1
Weyerhauser, US	US	Cellulon		20
Ajinomoto, Japan	US	N/a		N/a
Vegemat, France	EU	Vegemat	5	1
Grenidea	Asia			1
Ecopack	Asia			1

Table 6. Current manufacturers of cellulose-based packaging materials; [a)] rIn 2005 the total volume of biocellulose produced was 40,000 tons, according to a Non Food Crop Centre document, "Landscape for Biopolymers" accessed on May 2006

Innovia is a UK-based company producing high performance cellulose-based films under the brand name NatureFlex™ which are suitable for both industrial and home composting. Products have high barriers to gases and aromas. Moisture permeability can be tailored to the product's needs, allowing increased shelf life (by comparison with polyolefins) of vegetables and fruits. The films can be used in combination with other biodegradable packaging materials (e.g. peelable lid on a rigid biodegradable tray).

FKuR Kunststoff GmbH manufactures cellulose blends (Biograde) with processing characteristics and mechanical properties similar to polystyrene. The products are white or may be coloured and produced with natural fillers and a vegetable oil. They also have high thermal stability and can be moulded on standard machines with a general-purpose screw. The material is notable for its low shrinkage and virtual absence of warpage, according to the company. Up to 20% regrind can be processed without deterioration of properties.

Vegemat is a producing a whole maize based plastic (Vegemat) in the south of France. The company was established in 2003 and has introduced into the market a very cheap (€1/kg), high flexular modulus thermoplastic material.

Grenidea and Ecopack have introduced in the UK market palm pulp molded trays.
These are produced using technology used by the paper pulp industry, but are reported to be cheaper than PS trays, with the advantage to be totally biodegradable. These are reported to be trialled by Sainsbury, Information could not be verified independently.

5.2.4. Properties of cellulosic polymers

Table 7 shows some thermomechanical properties of cellulose-derived polymers.

	Vegemat E4589	***Biocetta***	***Biograde 200C***
Physical properties			
Melt flow rate (g/10 min)	2–8		1–5
Density (g/cm^3)	1.45	1.25	0.99
Transparency			
Mechanical properties			
Tensile strength at yield (MPa)	22	27	
Elongation at yield (%)	0.67	62	3.13
Flexural Modulus (MPa)	3300		6531
Thermal Properties			
HDT (ºC)		77	65
Vicat softening point (ºC)		111	181
Melting point (ºC)			

Table 7. Some thermomechanical properties of cellulose-based polymers

Cellulose acetate films comprise a mature industry, however the whole plant plastics and the use of agri-waste to produce packaging is also expected to increase.

5.3. Polylactic acid

5.3.1. Technology overview

Lactic acid is produced by the fermentation of carbohydrate material, usually glucose derived by hydrolysis from starch. The fermentation route can provide either enantiomer of lactic acid in high purity and dominates over chemical routes. The structure of lactic acid contains one asymmetric carbon, and can therefore exist as two stereoisomers. L-Lactic acid is present naturally in numerous organisms, whilst the mirror image D-lactic acid is very rare in nature.

Two routes are currently used to obtain polylactic acid, via polycondensation of lactic acid or via lactide (a dimer of lactic acid) ring opening. The direct synthesis of PLA by polycondensation features the typical drawbacks of step growth polymerisation, i.e. obtention of low molecular weight PLA, unsuitable for most thermoplastic applications. High molecular weight polymers are obtained in relatively low yields, and these are very sensitive to the presence of impurities such as ethanol or acetic acid arising from the fermentation process. Nevertheless, high molecular weight PLA (300,000) can be attained by employing highly pure lactic acid and removing the water formed during the polycondensation, and another solution has been provided by the use of chain extenders to couple oligomers to provide high molecular weight products.

However, ring-opening polymerisation of the lactide, as practised by Cargill, appears more advantageous.[1] The latter is polymerised in the presence of tin/zirconium or titanium catalysts (this technique is also used to polymerise lactones, e.g., caprolactone on the large scale). Lactide, rather like lactic acid, but now possessing two asymmetric carbon atoms within its structure can exist as three stereoisomers: L-lactide, D-lactide and the *meso*-lactide.

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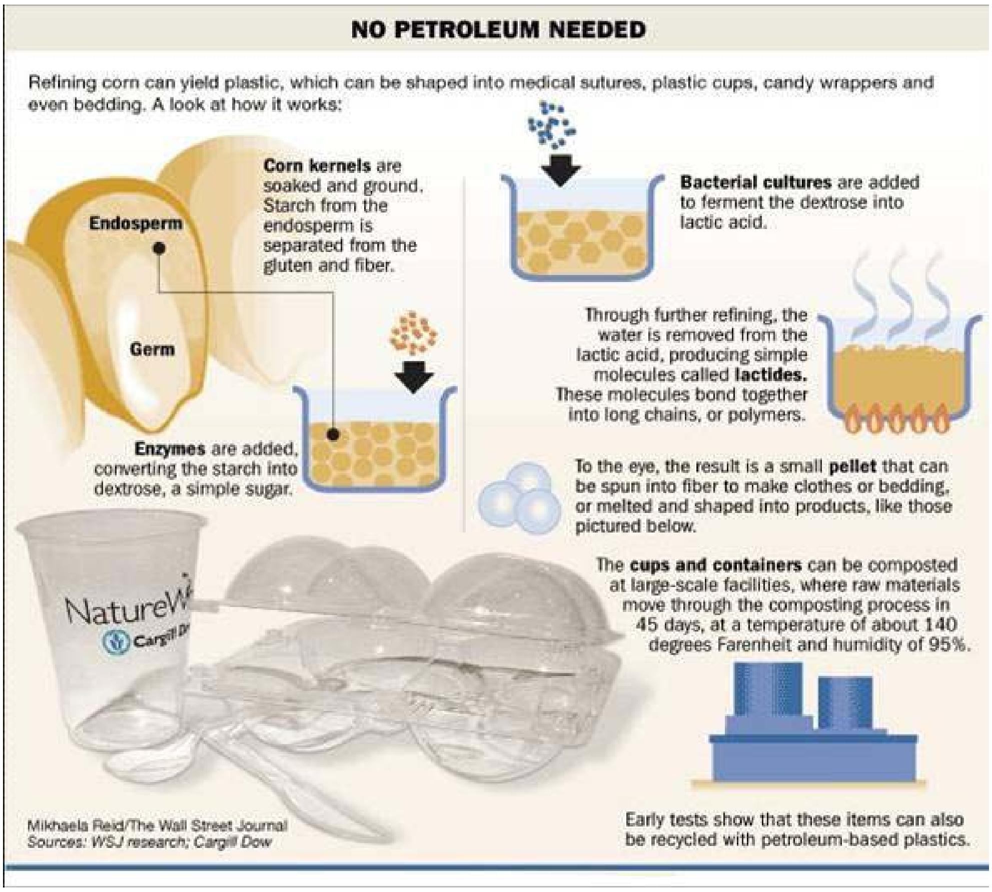
[1] Mitsui has developed direct polymerisation to an industrial scale, but signed an agreement in 2001 to be supplied by Cargill for the Japanese market, according to a press release from Cargill in September 2001.

Polymerisation of L-lactide affords a semicrystalline polymer with a melting point of 170–180 °C and a glass transition temperature around 60 °C. However, an amorphous material (no melting point and no glass transition temperature) is obtained from the polymerisation of the *meso* material. An overview of the process as described by Cargill to the Wall Street Journal is provided in the Figure.



Refining corn can yield plastic, which can be shaped into medical sutures, plastic cups, candy wrappers and even bedding. A look at how it works:

Corn kernels are soaked and ground. Starch from the endosperm is separated from the gluten and fiber.

Enzymes are added, converting the starch into dextrose, a simple sugar.

Bacterial cultures are added to ferment the dextrose into lactic acid.

Through further refining, the water is removed from the lactic acid, producing simple molecules called **lactides.** These molecules bond together into long chains, or polymers.

To the eye, the result is a small **pellet** that can be spun into fiber to make clothes or bedding, or melted and shaped into products, like those pictured below.

The **cups and containers** can be composted at large-scale facilities, where raw materials move through the composting process in 45 days, at a temperature of about 140 degrees Farenheit and humidity of 95%.

Early tests show that these items can also be recycled with petroleum-based plastics.

Mikhaela Reid/The Wall Street Journal
Sources: WSJ research; Cargill Dow

Figure 7 The production of PLA described by Cargill and reported by the Wall Street Journal

5.3.2. Existing and emerging producers

Table 8 summarises existing and emerging producers of polylactic acid-based plastic and packaging materials.

Producer	***Region***	***Trade name***	***2006 Capacity (kt p.a)***	***2006 Price (€/kg)***
Biomer			0.05	10–12
Birmingham polymers, Inc			N/a	
Boehringer Ingelheim			N/a	N/a
Natureworks (Cargill)		Natureworks (Mitsui Lacea in Japan)	140	**1.8-2.4**
Dainippon.			N/a	N/a
Hycail		Hycail HM, Hycail LM	1	**1.8-2.9**
Mitsubishi Plastics			N/a	N/a
FKuR Kunststoff				**2.85–3.70 a)**
Toyota		Toyota-Eco-Plastic	50 (2004)	N/a
Kaneka Corporation			N/a	N/a
Toyobo			N/a	N/a

Table 8. Existing and emerging manufacturers of polylactic acid-based plastic and packaging films. Manufacturers unable to supply data where figures are missing

Cargill uses corn due to its low cost/availability for its current process. Expansion plans are for two additional plants of similar capacity to the first, to be built wherever the market develops first. Combined production capacity is expected to reach 500,000 tpa. A third plant is earmarked for construction within a ten year framework. Cargill intends to use cheap biomass as the primary feedstock; that is, lignocellulosics from corn stover and to increase its sustainability profile by deriving its process energy from biomass/wind. Supply to Europe is achieved from GMO-free materials.

One of the biggest perceived barriers to the adoption of NatureWorks PLA in the EU market is that it is GM-based.

Until recently Cargill was offering two possibilities to its EU customers:

1. Have the NatureWorks PLA resin they order certified as having no genetic content;

2 Participate in a source off-set program for non-genetically modified (GM) field maize purchases; in this case for every pound of NatureWorks PLA delivered to the participating customer, NatureWorks purchase the amount of non-GM field maize needed to produce it – approximately 2.2 pounds (3.0 kilograms). Delivery of the offset amount will occur within one calendar year of an order, to account for growing seasons and the required source verification.

A third option (presently under discussion with Biotec/Stanelco in the UK) is a purchase identity-preserved NatureWorks PLA with specified seed-to-finished-product traceability. This product grade allows customers to verify the source of the dextrose and the absence of any genetic material from the point of origin (delivery of the specified maize to the wet mill and segregation of materials at each manufacturing phase) through all steps of production of the resin. Terms of discussion refers to a minimum order volume and multi-year supply contracts. Independent certification is expected to be available as part of the deal as NatureWorks offers third-party certification that verifies and documents that there is no genetic material in the PLA resin customers order. Technical analysis and paperwork would be provided provided by GeneScan, Inc., which is internationally recognized by governments and non-government organizations (NGOs) as the leading authority for testing food, feed and raw materials. Program is expected to be tailored to meet specific customer documentation requirements of major end-users as Sainsbury/ Coop etc....

Due to the importance of the European market, it is believed that agreement would be reached soon between Cargill and customers requiring non-GMO products across the continent.

Hycail, a spin-out company from the University of Groningen, was set up in 1997 to investigate the production of PLA from lactose and whey permeate, a by-product of cheese manufacture. In 1998, Dairy Farmer of America was interested to add value to its whey production and acquired a share in Hycail. However, in 2006, Hycail was bought by Tate and Lyle. In December 2005, Hycail was operating a semi-commercial pilot plant producing 1000 tpa of high molecular weight PLA (Hycail HM) for pellets, films and bags, and a 10–20 tpa unit for the manufacture of low molecular weight PLA for hot-melt adhesives.

Biomer, a biotechnology company located in Krailing, Germany, has recently begun producing PLA on a small scale basis. The product is sold to converters for the production of transparent packaging films and other speciality injection moulding.

In Europe, other companies with interest in large volume PLA manufacture include the Belgian company Purac, a producer of lactic acid and derivatives, Boehringer Ingelheim, a major German producer of fine chemicals and intermediates, and Inventa-Fisher GmbH, a German engineering company, which is offering turn-key plants with capacity of 3,000 tpa.

FKuR Kunststoff GmbH manufactures PLA/co-polyester blends (Bio-Flex) and cellulose blends (Biograde). FKuR was established in 1992 to recycle plastics and launched its biopolymer business in 2000. FKuR Kunststoff GmbH, in collaboration with the Fraunhofer Umsicht Institute in Oberhausen, Germany, developed a PLA/polyester blend that reportedly processes like LDPE film. Tests show that the new Bio-Flex 219F material can be processed on conventional blown film lines without modification. The company claims easy processing results from the high compatibility of the blend components. The formulation consists of more than 10% PLA (purchased from NatureWorks LLC) plus a biodegradable copolyester and special additives.

FKuR says a special combination of compatibilisers permits coupling between the PLA and the copolyester. The compound is homogeneous, which allows the film to be drawn down to 8 microns. Film up to 110 microns thick is 90% degraded after 12 weeks in industrial composting conditions. Company has no data on home composting. Bio-Flex 219F is targeted for shopping bags, mulch film and laminates for trays. FKuR has also developed Bio-Flex grades with higher stiffness. Grade 466F (more than 20% PLA) and grade 467F (more than 30% PLA) are for shopping bags. Grade 482F, with more than 70% PLA, is for cast film. The company has capacity of more than 3,000 tpa and claim 25% p.a. growth (2005). Products range in price from €2.85–3.70 kg.

In Japan, Mitsui Chemicals is selling PLA using Cargill technology under the name of Lacea. Shimadzu Corporation formerly produced PLA via the ring-opening polymerisation route, but sold the technology to Toyota Motor Corp which has now set up a pilot-facility to produce PLA using sweet potato. In its annual report of 2003, Toyota indicated that ¼ of its future sales are planned to be of PLA, sold to itself- (i.e. for car parts manufacture) and to other users. Other companies involved in producing PLA in Japan are Kaneka Corporation and Toyobo. No information on production capacity was obtained in communications with company representatives.

Sukano (Switzerland) and Polyone (Belgium) are other compounders with PLA-formulation know-how to: a) improve transparency of PLA based materials; b) reduce adhesion to rollers during film processing; c) reduce brittleness during cutting; d) improve punching resistance; and e) enhance thermal stability. Materials are sold for the manufacture of bags, thermoformed trays and bottles.

Stanelco/Biotec, in the UK, provide blends of PLA, with other biodegradable components have recently been developed by Stanelco (Starpol^{TM}), Biotec (Bioplast)[51]. The Starpol^{TM} and Bioplast materials both contain 60% PLA together with other unspecified components.

BASF also provide a blend, Ecovio^{TM} containing 45% PLA together with an aliphatic/aromatic copolyester. Levels of PLA claimed by Novamont are 6-30% and by Cortec 5-50%.

Flexible grades for film blowing contain low amounts of PLA (10-30%) while stiffer grades for casting contain more than 40-70% PLA. Therefore PLA blend materials are suitable for both flexible and rigid applications, including making film, sheet, thermoformed shapes and injection- and blow-molded articles.

As described below, these blends can have significant advantages over 100% polylactic acid for many applications, e.g. lack of low-temperature embrittlement, improved barrier properties towards oxygen and carbon dioxide, faster crystallization, somewhat higher use temperatures, and easier processing. They are particularly advantageous for food packaging applications to provide completely biodegradable packaging and are significantly less expensive than other similar biodegradable materials.

The additional advantages of the blends are that they can be processed more easily and at higher output than 100% PLA without the need for equipment modification and with only minor temperature adjustments. Extrusion and die temperatures of 160-165°C are effective, which is considerably cooler than the extrusion temperatures required for 100% PLA of 180-210°C.

5.3.3. Expected developments in costs structure and selling price

NatureWorks, currently the only large volume supplier of PLA in Europe, supplies a large number of customers [such as, in Europe Carolex, Cedax, Folietechniek BV (all for sheets), Sidaplax, Treofan (for films), Sidaplax (labels), Autobar, Ampirica, Huhtamaki, Vitembal (for thermoformed sheets)] at the a price of £1.50/kg. The price is set at a level at which PLA is able to compete with PET, as Natureworks views it as a speciality polymer moving towards commodity polymer. After 2010, the use of lignocellulosic biomass and renewable energy in the production of polymer is expected to generate further improvements in price and competitiveness.

5.3.4. Technical substitution potential

The following discussion is based on the polymer material properties of polylactic acid which are shown in Table 9 overleaf.

	NatureWorks PLA	***Biomer L9000***	***Hycail HM1***
Physical properties			
Melt flow rate (g/10 min)	4.3	3–6	
Density (g/cm^3)	1.25	1.25	
Transparency	2		
Yellowness index	20–60		
Mechanical properties			
Tensile strength at yield (MPa)	53	70	102
Elongation at yield (%)	10–100	2.4	7
Flexular Modulus (MPa)	350–450	3600	350
Thermal Properties			
HDT (ºC)	40–45,135		
Vicat softening point (ºC)	–	56	
Melting point (ºC)	55–65		

Table 9. Some thermomechanical properties of polylactic acid-based polymers

It should be noted that there are very different grades of PLA due to molecular weight, macromolecular structure and degree of crystallisation. As stated earlier, PLA is known to have three possible isomeric forms. By varying the relative concentration of isomeric forms, the resin morphology can be tailored across a spectrum from always amorphous to readily crystalline. Amorphous PLA is transparent. The molecular weight of PLA varies from 100,000 to 300,000 similar to PET which varies from 170,000 to 350,000. With increasing molecular weight (as for polymers in general) strength increases due to the decrease in relative motion of the chains as they become longer. In addition, resistance to solvents increases and the melt point/glass transition temperature increases. The melt viscosity increases and the ease of fabrication (moulding, extrusion shaping) decreases.

A schematic evaluation (Table 10) of the potential for substitution was facilitated by interviews with a large production manufacturer (Natureworks), a potential large production manufacturer (Hycail) and a speciality chemical producer (Biomer). At the time of writing, Hycail has been bought by Tate and Lyle and is to be reorganised. Data reported have been cross-checked with literature reports of end-users and academia.

	LPDE	***PP***	***HPDE***	***PS***	***HI-PS***	***PVC***	***PET***	***PA***
Potential	+	+	+	±	±	–	++	±

Table 10. The potential for substitution by PLA
(++ = probable, + = possible, ± = doubtful, – = unlikely)

5.3.4.1. Bottles

Most current plastics used in the manufacture of bottles (for soft drinks and beer) is PET. PLA has high gloss and high transparency (haze of 2.1%), and mechanical properties (hardness, stiffness, low impact strength and elasticity) similar to PET. Additionally, the specific gravity of PLA

(1.25 g/cm^3) is lower than that of PET (1.34 g/cm^3), suggesting that it would be advantageous to substitute current PET by PLA.

But substitution has been marginal (a small number of companies in the US (but not in Europe or in Japan) began to bottle water in PLA bottles in 2004–2005) because PET has better barrier properties than PLA. PLA exhibits higher transmission rates for water and oxygen by a factor of 8–10 times compared with PET.

A recently published study by Corpoplast (a global supplier of packaging material, plant systems and services for the beverage industry that invented the stretch blow technology used to make blowable PET), shows that cycle time is slower for PLA, which needs a lower temperature but a higher mould temperature. The advantages in the process are that PLA can be blown in the same machines as PET, at higher speed, needs less heat than PET to be reheated, and pending further research, PLA may be blown at lower air pressure. However, PLA bottles have low burst pressure resistance and are instable thermally as evidence by bottle shrinkage when bottles are rinsed in aseptic applications. This implies that PLA packaging would need to a) have reinforcing feature such as ribs to prevent collapse of the side wall and b) only applications for non carbonated beverages are feasible, i.e. packaging water-but with short shelf life or cold chain applications with limited barrier requirements.

Also very recently, Toyota has published work showing that the use of nanofillers (in very small percentages) could improve drastically water & gas barriers, mechanical and thermal properties of PLA, suggesting that with some additional research restrictions to the use of PLA in the manufacture of bottles could be solved/reduced. Cargill/Corpoplast are investigating another approach, which is plasma coating with SiOx (ultra thin glass). These initial performance results look however promising, as developing PET-based bottles needed 10 years of R&D, and far shorter timeframe are expected to provide meaningful results with PLA.

Several studies have demonstrated the effect of PLA, alone or with other antimicrobials to inhibit microorganism on fresh or further processed food products. A study reported effect the anti microbial effect of 2% low molecular PLA alone and a synergetic in combination with with nisin or lactic acid against E.Coli on raw beef during irradiation and refrigerated storage. Another study shown that when applied to ground pork, ground beef or breakfast sausage inoculated with E.Coli and subjected to long term refrigerated staorage resulted in up to 1.7 $\log_{10}$ reduction of the pathogen, subsequent studies have shown that low dose PLA, in combination with low-dose radiation (2 kGy), followed by long term refrigerated storage could reduce population of E.Coli and S. Typhimurium up to 99.999% on beef surfaces. The level of irradiation did not affect the tensile strength of packaging materials.[18]

5.3.4.2. Rigid packaging materials

Thermoformed materials are generally made of PET-A (PET-amorphous), bi-axially oriented polystyrene (OPS) or styrene-butadiene styrene (SBS) polymers. PLA is as transparent as PET-A and more transparent than either PP, SBS or even OPS. The density of PLA, at 1.25 g/cm^3, is lower than that of PET-A (1.34 g/cm^3), but densities of PS (1.05 g/cm^3) and PP (0.9 g/cm^3) are well below that of PLA. Stiffness of a thermoformed article is critical for its stability and is directly proportional to the required thickness of the material. Different plastics are usually compared by way of the modulus of elasticity. Figure 6 compares the modulus of elasticity of different materials with a correction for density. General purpose polystyrene has the highest modulus of all the styrene materials. However it is very brittle and only used with special designed equipment.

At 3500 MPa, PLA has the highest modulus of elasticity of all the polymers compared. After correction for its density, PLA is neck and neck with PP. A similar position arises when the materials are price corrected, indicating that PLA is now price competitive. An additional important characteristic in thermoforming is the Vicat softening point which for PLA is the lowest, showing potential savings in energy during the moulding operation. Semicrystalline materials show greater shrinkage than amorphous materials. PET, PLA and PS are amorphous polymers, with low shrinkage. This means that PLA can be processed on existing PS and/or PET-A tools.

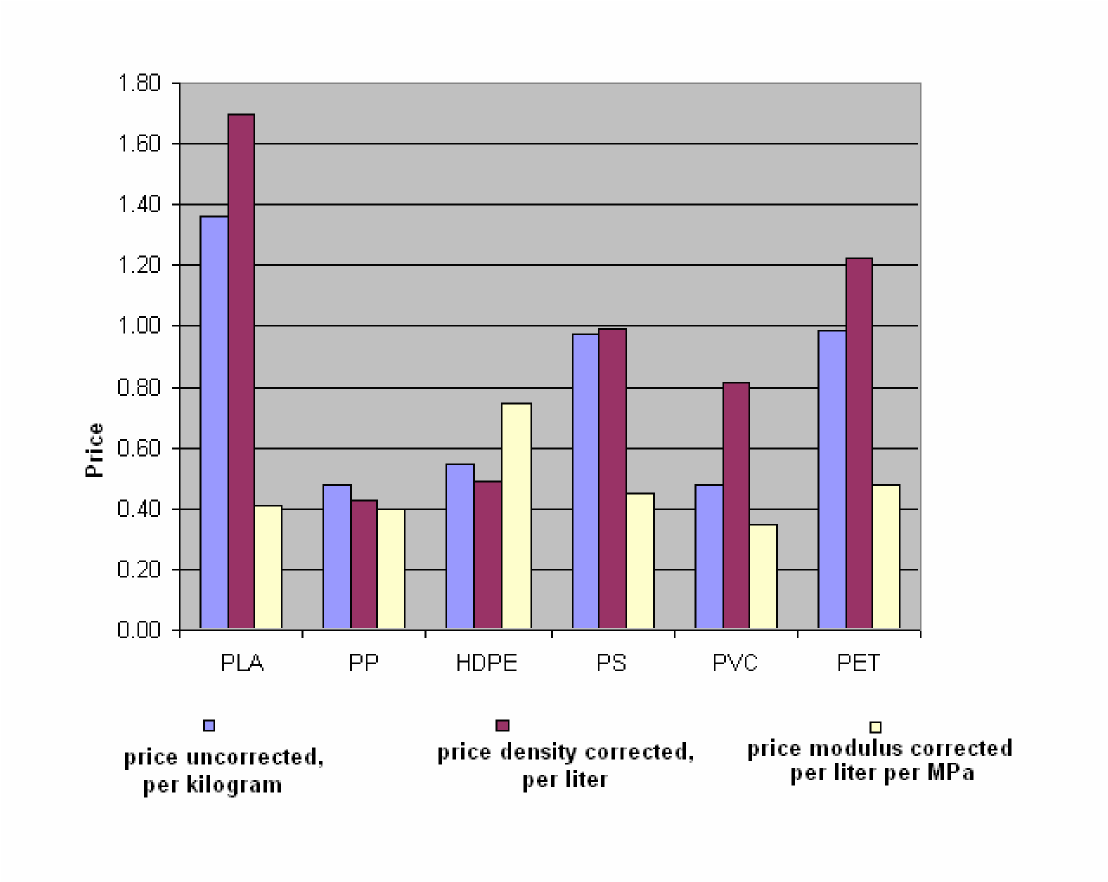


Figure 8 A comparison of the modulus of elasticity of different materials with a correction for density

The main disadvantages of using PLA over other materials is that the maximum operating temperature is approximately 45 ºC, and therefore is not suitable for hot filling. It is worth to note that it is possible to increase the modulus of PLA either by manipulation of the polymer (by introducing co-monomers during the polymerisation step) or by using nano-fillers. Indeed, various reports indicate increases up to 40% by using up to 6% nano-clays.[19, 20]

5.3.4.3. Films and flexible material

As indicated in Table 2, polyolefins, PET and PVC are used in the manufacture of different films/flexible packaging used by the food industry.

PLA compares with polyolefins (LDPE/HDPE/PP) and PVC unfavourably in terms of density and of water barrier propertybut this is compensated favourably in terms of a) flavour, odour and grease barriers (resistant to most of the oils and fats found in foodstuffs); b) stiffness and tensile strength; c) the fact that it has higher modulus (would enable the production of hard packaging and injection-blow moulded products with smaller thickness); (a discussion on minimum attainable thickness is provided in the last chapter of this review) d) good heat sealability (could be processed at 80 ºC, providing a heat seal strength > 0.13 bar). Compared with PP, PLA has a smaller fatigue modulus, so it is inferior in hinges in packaging. This kind of problem can be overcome by alloying (i.e. blending PLA with other polymers). The fact that it has a lower water barrier is an advantage for packaging fruits/vegetables, as humidity in the pack can be smoothly removed, without creating haze, or fog on the film. Furthermore PLA is a polar material, with high critical surface energy and it is easier to print than commodity polymers. It is possible to print PLA using natural dyes and pigments which are metal-free and thus eligible for compostability. A partial substitution is to be expected.

5.3.4.4 Foams

PLA foams have been introduced in the market first in Japan by Mitsui,[21] Unitika,[22] Kanebo ltd,[23] Toray ltd,[24] , JSP Corp.,[25] and recently by CoopBox (in Italy). From press release and patent analysis, it is understood that Unitika made maximal use of clay- nanocomposites to raise the heat resistance of the material up to 120 degrees Celsius, making it microwave-safe and hot water resistant. For reasons explained in paragraf 5, this technology is also more adequate to obtain lighter foams than the technology patented by Coopbox which use only foaming agent and matrix resin. These manufacturers are promoting foams for use in food packaging, i.e. for the use of meat, vegetables, noddles, and (in the case of Japanese companies) for the automobile and construction industries.

An interesting claim of trays made of PLA foams, is that when used to pack meat, they naturally absorb the meat juice eliminating the need of absorbent pads.

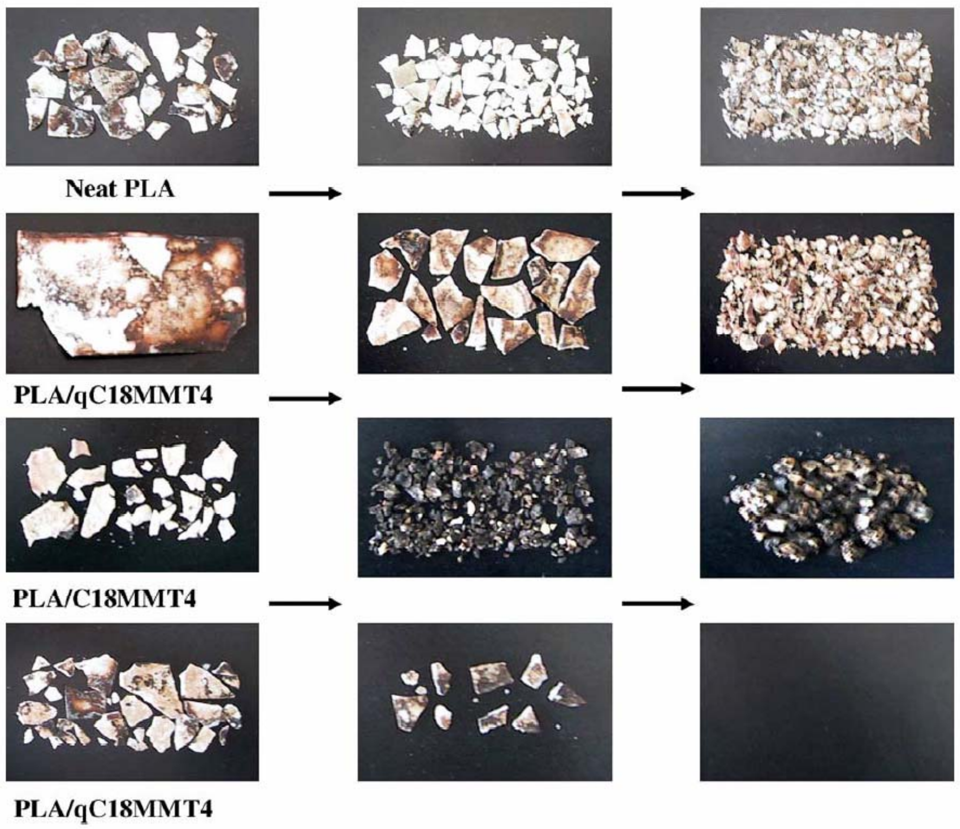
5.3.5. Biodegradation and home compostability

Despite erroneous public perception, PLA is not home compostable.

It only in industrial composting situations, where the temperature is high enough (more than 60C) to initiate hydrolysis of the polymer it can be mineralised to CO_2, water and a small mount of biomass, typically after a period of 4-6 weeks.

Despite the considerable number of reports concerning the enzymatic degradation of PLA and various PLA blends,[26] there have been relatively few reports on biodegradability of PLA in soil and how addition of fillers and others polymers may affect the compost degradability of PLA except three Japonese reports, the former indicating that molecular weight which claimed that molecular weight of PLA in PLA/starch 70/30 moldings decreased by about 60% after burial in soil for 45 days versus 10% for PLA alone, while the second one claimed acceleration of PLA in blends with polyethylene glycol and cellulose.

The most recent publication from which Figure 7 was obtained.[27] Figure 7 shows the real picture of the recovered samples of neat PLA and three different kinds of PLA/nanoclay nanocomposites from the compost with time. There was no major difference between the first two composites and only the latter showed enhancement of the biodegradability. Up to one month, both the extent of molecular weight loss and the extent of actual weight loss were almost the same level for both pure PLA and the latter preparation. However, after one month, a sharp change occurs in the weight loss of the nano-composite, and within two months, it was completely degraded in compost. Detailed condition of the composting where however not provided in the paper.



Real picture of biodegradability of pure PLA and various nanocomposites recovered from compost with time. The initial shape of the crystallized samples was $3 \times 10 \times 0.1$ cm^3

Figure 9 Pictures of biodegradability patterns of different PLA nano-composites subject to composting situation.

The investigators also conducted a respirometric test to study the degradation of the PLA matrix in a compost environment.[28] Unlike weight loss or fragmentation, which reflects the structural changes in the test sample, carbon dioxide evolution provides an indicator of the ultimate biodegradability, that is, mineralization, of the test samples. Data obtained indicate that the biodegradability of the PLA component in the nano-composite was enhanced significantly.

Furthermore, the investigators reported that compost degradation of PLA occurs by a two-step process. During the initial phases of degradation, the high-molecular-weight PLA chains hydrolyse to lower molecular weight oligomers. This reaction can be accelerated by acids or bases and is also affected by both temperature and moisture. Fragmentation of the plastic occurs during this step at a point where the M_n (number average molecular weight) decreases to less than about 40,000. At about this same M_n, microorganisms in the compost environment continue the degradation process by converting these lower molecular weight components to CO_2, water, and humus. Therefore, any factor which increases the hydrolytic tendency of the PLA matrix ultimately controls the degradation of PLA. These data indicate that the incorporation of different types of nano-fillers in the PLA matrix resulted in a different mode of attack on the PLA component of the test samples that might be due to the presence of different kinds of surfactants and pristine layered silicates. Since PLA is an aliphatic polyester, it is conceivable that incorporation of different types of nano-fillers resulted in a different mode of disruption of some of the ester linkages due to the presence of different kinds of surfactants and layered silicates. The disruption of ester bonds is a function of the chemical nature of the nano-filler. Therefore, this observation indicates a possible role of nanofiller to enhance the rate of biodegradation of pure PLA and the biodegradability of PLA can be controlled by judicious choice of additives.

5.4. Microbially synthesised polyhydroxy alkanoates

5.4.1. Technology overview

5.4.1.1. Poly-3-hydroxybutyrate (PHB)

Poly-3-hydroxybutyrate (PHB) is a biopolyester accumulated as a reserve of carbon and energy by a number of bacteria. It is located in the cytoplasm in the form of granules of approximately 0.5 µm size. Under suitable conditions, up to 90% polymer can be accumulated with respect to bacteria dry mass.

Isolation of the PHB requires breaking the cell walls by means of mechanical shear or enzymatic digestion followed by extraction of the polymer. This can be performed by means of washing in a centrifuge. PHB was produced on the kilogram scale in the 1960s, but its stereo-chemical regularity led to progressive crystallization with aging, thus making it brittle. This has been overcome by incorporation of co-monomers by grafting or by the use of suitable formulations (plasticizers and others additives).

5.4.1.2. Polyhydroxybutyrate-co-3-hydroxyvalerate (PHBV)

In the 1970s, PHBV (polyhydroxybutyrate-*co*-3-hydroxyvalerate) was successfully produced by using specific additives in the growth medium. Such an approach, whilst it improves the properties of PHB, is not cost effective, because the copolymer costs are higher, and its toxicity to the bacterium leads to lower production yields and also its presence affects PHB crystallization kinetics, which results in longer processing cycle times.

Nevertheless, PHB could be toughened by the process of annealing by conditioning in an oven, a process that widens its application possibilities. By comparison to PHB, which melts at 180 °C, the melting point of PHBV can be lowered to 137 °C by the introduction of 25% hydroxyvalerate. This greatly improves thermoplastic processability. In addition, mechanical stability is improved by an order of magnitude.

5.4.1.3. Polyhydroxybutyrate-co-hexanoate (PHBH)

Procter & Gamble and Kaneka have introduced a range of polyhydroxybutyrate-*co*-hexanoate, PHBH, under the trade mark of Nodax. The properties of Nodax are a function of the concentration of the hexanoate, which vary from hard with some flexibility (4%), hard elastic (6%), soft elastic (8%) to soft rubbery (18%), allowing to manufacture a range of materials (injected moulded, films, or fibres).

5.4.2. Current and emerging producers

Table 11 lists current producers of biodegradable polyesters derived from microorganisms.

Producer	***Region***	***Trade name***	***2006 Capacity (kt p.a)***	***2015 Capacity (kt p.a)***	***2006 Price (€/kg)***	***2015 Price (€/kg)***
Metabolix & ADM	North America		5	50,000	10-12	2.5
Procter&Gamble/ Kaneka	North America	Nodax	N/a	N/a	N/a	N/a
Biomer	EU		0.5	0.5	10	
PHB Industrial	South America		0.05	10	9	
Biomatera, inc	North America		N/a	N/a	N/a	N/a
Mitsubishi Gas Chemical (MGC)	Asia		N/a	N/a	N/a	N/a

Table 11. Current producers of polyhydroxy alkanoates

The main company with plans for large production is Metabolix. Procter and Gamble which in association with Kaneka Corp, Japan, was introducing Nodax has ceased R&D in the field. Smaller companies, like Biomer, Germany and PHB Industrial, Brazil, have a different market focus with limited supply of PHB for medical implants\z and analytics. However, both of them expect that in the near future (from next year) most PHB would be used in packaging.

In the late 1980s, PHBV was commercialised by ICI under the trade name of Biopol. By 1996, the technology had been sold consecutively to Monsanto and to Metabolix, which is currently coordinating a $1.6 million project funded by the US Department of Commerce Advanced Technology Program, the goal of which is to re-engineer the central metabolism of *E.Coli* for more efficient conversion of renewable sugars into PHB. Metabolix is also coordinating a parallel investigation into the production of PHB in crops focusing on a target yield of 10% transgenic rapeseed. In 2001, Metabolix commenced coordination of a $15 million shared cost project funded by the Department of Energy to investigate the production of PHB in green tissue plants, with a number of critical hurdles to be addressed that include the need to preserve the genetic identity of the crop, public opinion related to genetically engineered crops, and technical questions related to feedstock storage, yield improvement, and extraction and purification of PHA from the plant. In February 2006, Metabolix and ADM announced a partnership to build a new $272m plant in Clinton, Iowa, capable of producing 50,000 tons of plastics per year. Currently under construction, the plant is to open in mid-2008. Metabolix has signed a partnership agreement with BASF to develop products for the polymer industry.

Procter and Gamble in a partnership agreement with Kaneka Corp, itself in partnership with Tsinga University in China and the Riken Institute in Japan, have developed a range of applications for PHB polymers (trademark-Nodax) as fibres, non-wovens, aqueous dispersions and hygiene products. However at the time of writing, Nodax technology is to be sold.

Biomer is a German company located in Krailing, which produces PHB on commercial basis for speciality applications. In 1993, Biomer acquired the know-how and microbes from the Austrian company PCD for its PHB products and in 1995 registrated the trade name Biomer. Biomer considers that in the near future 70% of the market for PHB will be in packaging.

PHB Industrial Usina da Pedra-Acucar e alcool, Serrana Sao Paulo, Brazil is a new company planning to enter the commodity market. It is a joint venture between sugar and alcohol producer Irmaoes Biagi and the Balbo Group. The company has been running a pilot plant of 50 tpa, and has commissioned a 10,000 tpa plant which is due to start up in July 2006.

Biomatera Inc, Canada is specialised in the manufacture of PHA by fermentation of agricultural residues. The biopolymers are used in the manufacture of creams and gels that are developed to be used as slow release agents in drug manufacture and as cosmetic agents and tissue matrix regeneration.

In Japan, Mitsubishi Gas Chemical (MGC) has made an in-depth development study of the production of PHB from methanol fermentation (trade name BioGreen).

5.4.3. Cost structure and expected evolutions

The current cost of PHB is €10–12 per kilo. This price is higher than starch polymers and other bio-based polyesters due to high raw material costs, high processing costs (particularly the purification of fermentation broth) and small production volumes. Raw material is reported to account for 30–40% of the total cost of PHB. Metabolix claimed that its recent scale-up exercise demonstrates the possibility to produce PHB at a cost well below $2.5 per kilo at a full commercial scale, which is expected to be introduced into the market by 2008.

5.4.4. Technical substitution potential

The chemical, mechanical and thermal properties of PHAs are shown in Table 12 below. A distinction will be drawn between poly 3-hydroxybutyrate [P(3HB)] the homopolymer produced by Biomer, poly 3-hydroxybutyrate-*co*-3-hydroxyvalerate [P(3HB-C-3HV)] the di-copolymer as produced by Metabolix and poly 3-hydroxybutyrate-*co*-3-hydroxyhexanoate [P(3HB-co-3HHx)] the polymer introduced as Nodax. PHAs are available in the molecular weight range from 1000 to one million. Variation of the chain length in the monomer unit affects the hydrophobicity and a number of other properties including the glass transition temperature, melting point and level of crystallinity. PHA films are translucent and injection moulded products from PHA have high gloss.

Metabolix/P&G PHAs cover an enormous range of physical properties. PHB can behave both as traditional thermoplastic polymers and as elastomers. While some polymers such as polyethylene, flexible PVC, and thermoplastic elastomers have high elongation at break, they yield irreversibly at high levels of extension. Metabolix has developed truly elastomeric grades that have high levels of recovery (typically >80–90%), even under high levels of deformation (e.g. >500% ultimate elongation at break). These materials can be used for adhesives, stretch coatings, and as fibres, and have properties competing with some vulcanized rubbers.

	P(3HB) (Biomer PL9000)	***P(3HB) (Biomer P226)***	***P(3HB-co-3HV) (Biopol)***	***P(3HB-co-3HHx)***	***PHB Biocycle***
Physical properties					
Melt flow rate (g/ 10 min)	38	5–7	9-13	0.1–100	43.74
Density (g/cm3)	1.25	1.25	1.25	1.07–1.25	1.23
Mechanical properties					
Tensile strength at yield (MPa)		24			32
Elongation at yield (%)	2.4	19			1.89
Flexular Modulus (MPa)	35	1750			2710
Thermal Properties					
HDT (ºC)					
Vicat softening point (ºC)	56	96			

Table 12. Some thermomechanical properties of polyhydroxyalkanoates.

However it should be noted that potentially properties of PHB can be modified to cover virtually all fields of applications as suggested by the illustration obtained from Metabolix publication.

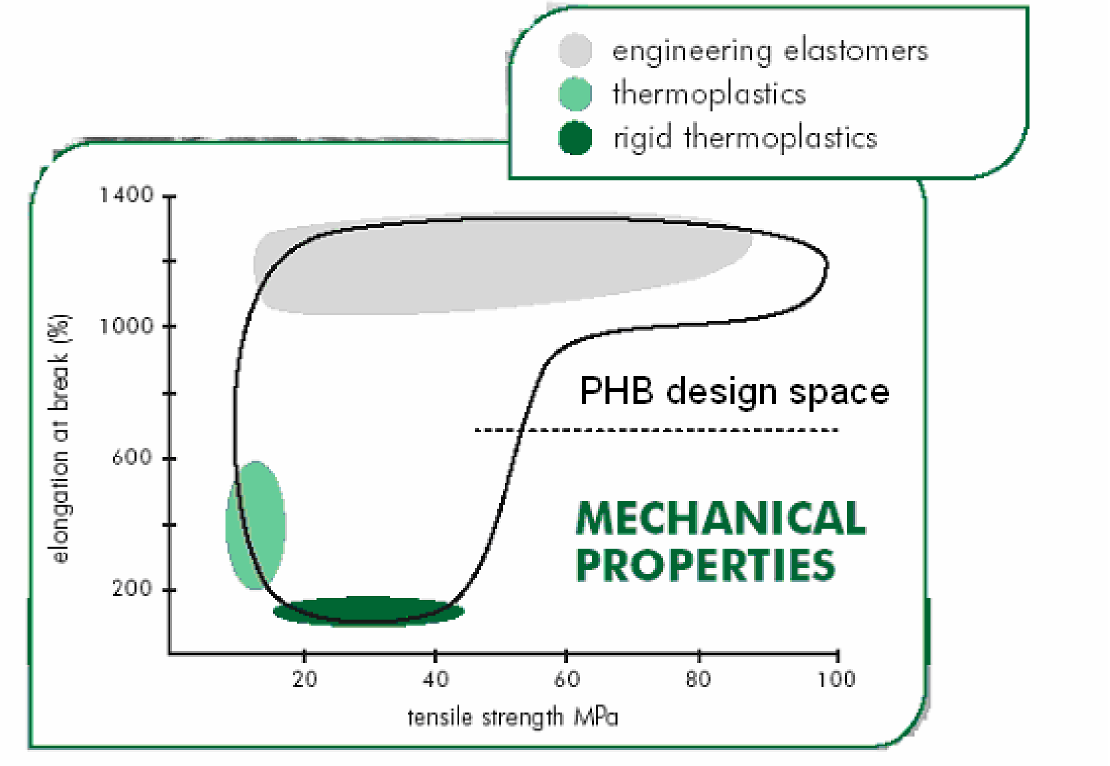


Figure 10- Mechanical properties of Metabolix PHB

(the thermoplastics and rigid thermoplastics are the two grades that may be used in food packaging)

A potential for short term substitution was also discussed in interviews with two speciality chemical producers (Biomer, PHB Industrial), and a large manufacturer (Nodax, a partnership between "Procter and Gamble", and Kaneka). A schematic evaluation is presented in Table 13. At the time of writing, the business strategy of Nodax is being refocused developing products for the market in Japan first. The collected information has been cross checked with Metabolix own published claims.

	LPDE	***PP***	***HPDE***	***PS***	***HI-PS***	***PVC***	***PET***	***PA***	***PBT***
Metabolix	++	+	++		±	+	++	±	−
Biomer	−	++	++	+	−	−	−	−	−
Nodax	+	++	++	-	−	+	+	−	−
PHB Industrial	−	++	++	+	−	−	−	−	−

Table 13 The potential for substitution by PHA films (++ = probable, + = possible, ± = doubtful, – = unlikely)

The major difference between polyhydroxyalkanoates and all other biopolymers, is their cost (present and in the near future), and their outstanding humidity barrier, which suggest their possible use in the manufacture of multi-barrier films that would be home compostable.

5.5. Other aliphatic polyesters

5.5.1. Technologies overview

Apart from PLA (described in Section 2.3) and polhydroxyalkanoates (described in Section 2.4), a number of polyesters which can provide biodegradable/compostable materials are available in the market. These are polycaprolactone (PCL), polybutylene adipate terephtalate (PBAT), polybutylene succinate (PBS), and poly(trimethylene terephthalate) (*PTT) all obtained from petroleum sources, but the last two are close to production from bio-based monomers.

Polycaprolactone (PCL) is obtained by a ring opening polymerisation of the corresponding lactone. Its main application is in the formulation of polyurethane, but high molecular weight polymers are used in film manufacture. It is also widely used to modify starch.

Polybutylene adipate terephtalate (PBAT) is produced by condensation of terephthalic acid and adipic acid with butanol. It provides a range of biodegradable polyesters.

Polybutylene succinate (PBS) has a melting temperature of 114 °C, and crystallises at about 75 °C. Blown films have mechanical properties similar to LDPE films. Incorporation of adipic acid into poly(butylene succinate-co-butylene-adipate) (PBSA) increases the degradation rate by lowering the crystallinity.

Poly(trimethylene terephthalate) (PTT) is a linear aromatic polyester produced by polycondensation of 1,3-propanediol and terephthalic acid. Recently, Dupont with Genencor and Tate & Lyle have developed a novel bioroute from glucose as the feedstock. Dupont has introduced petroleum-derived PTT into the market as yg6 x 3GT.

5.5.2. Existing and emerging producers

PCL is produced in the UK by Solvay (5,000 tpa), Dow in the US (5,000 tpa), and Daicel in Japan (3500 tpa). PTT is to be produced by Dupont. Shell has also announced a join venture with SGF Chemie JV to produce PTT (under the brand name of Corterra), in Montreal Canada, but using a continuous hydroformylation of ethylene oxide with newly developed catalysts.

PBS and PBSA are produced (10,000 tpa) by Showa Denko under the trade name Bionolle. Mitsubishi Chemical and Ajinimoto are reported to be developing a route to succinic acid, and claim that PBS obtained this way will be cheaper than PLA.

SK Polymers (Korea) is also reported to have a small plant producing PBS and PBS-A under the trade name Sky Green.

It should be noted that Bayer Corp. stopped producing its aliphatic polyester polymer line, BAK, more than a year ago because it did not see a profitable future, according to Josef Hirschman from Bayer Polymers Division.

5.5.3. Price structure

Showa High polymers sells Bionolle PBS for €3.5 per kilo, but expects that the price will decrease. It is expected that PBS produced from a bio-derived source will be priced to compete with Mitsubishi's target PLA price.

5.5.4. Technical substitution potential

From the data presented, it has been suggested that PTT could substitute nylon, PC, and PP (in some applications). PTT has a similar molecular weight distribution and strength in the same range as PET. PTT elongation is significantly larger than PET or nylon suggesting improved tear strength. Some thermomechanical properties are shown in Table 14.

PBS is a white crystalline thermoplastic with density of 1.25 g/cm3 (equal to PLA). It has in general excellent mechanical properties and processability. PBS may be processed using conventional polyolefin equipment in the temperture range 160–200ºC. New grades of PBS have been recently introduced into the market allowing the production of highly expanded foams and to prepare stretched films.

	PCL (Solvay) CAPA 650	***PBS (Showa Denko) Bionolle 310***	***PTT (Dupont) Sorona***	***PBT (Basf) Ecoflex***
Physical properties				
Melt flow rate (g/ 10 min)				
Density (g/cm^3)	1.11	1.23	1.35	
Transparency		1–2		
Mechanical properties				
Tensile strength at yield (MPa)	17.5	62	67.8	
Elongation at yield (%)	>700	710		
Flexular Modulus (MPa)	190	470	2760	
Izod impact J/m, 23 ºC				
Thermal Properties				
HDT (ºC)				
Vicat softening point (ºC)				

Table 14. Some thermomechanical properties of other biodegradable polyesters

Both Mitsubishi and Showa have shown that PBS can substitute polyolefins and PET. In Japan, PBS is used to manufacture mulch films, packaging bags, flushable hygiene products and as a non-migrating plasticiser for PVC. Mitsubishi is targeting the market developed by Cargill for PLA, i.e. fibres, mulch films and packaging.

Currently, because of their high cost, and the fact that they have high elongation these materials are blended with either starch or PLA which have higher stiffness to obtain suitable materials.

6. New Packaging formats and potential for weight reduction.

A major objective for this report was to analyse techniques that could be used to reduce food packaging weight, concomitantly looking to possible use of compostable renewable based packaging.

6.1. Influence of additives on the mechanical and barrier properties of renewable based and major synthetic polymers

On the account that most commercially available renewable polymers are used as blends, it is important to compare mechanical and barrier properties of the commercially available renewable based polymers with the major synthetic ones, and to understand how properties can be modified.

6.1.1. Mechanical and barrier properties of renewable/ compostable based polymers

For the production of rigid materials (trays), the most important mechanical properties are the stiffness measured by the modulus. For non-foamed rigid trays, the modulus is inversely proportional to the minimum required thickness. For flexible materials, like films, elongation at break is the most critical property. These two parameters are represented in the Figure, showing that renewable/compostable materials (PHB, PLA) are stiffer than non-compostable alternatives (HDPE, LDPE, PP, PS, and PVC), while others compostable materials (PBS, PCL) also present higher elongation. Mixtures of these could theoretically have all range of intermediate properties.

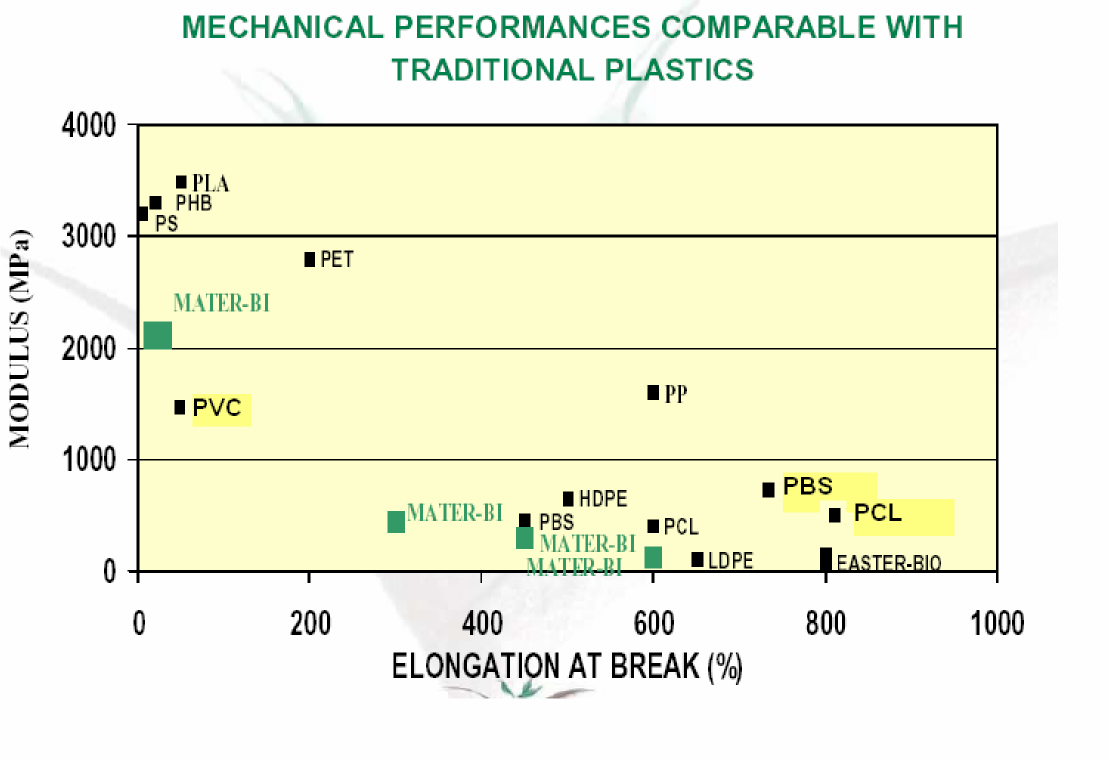


Figure 11- Mechanical performances of bioplastics

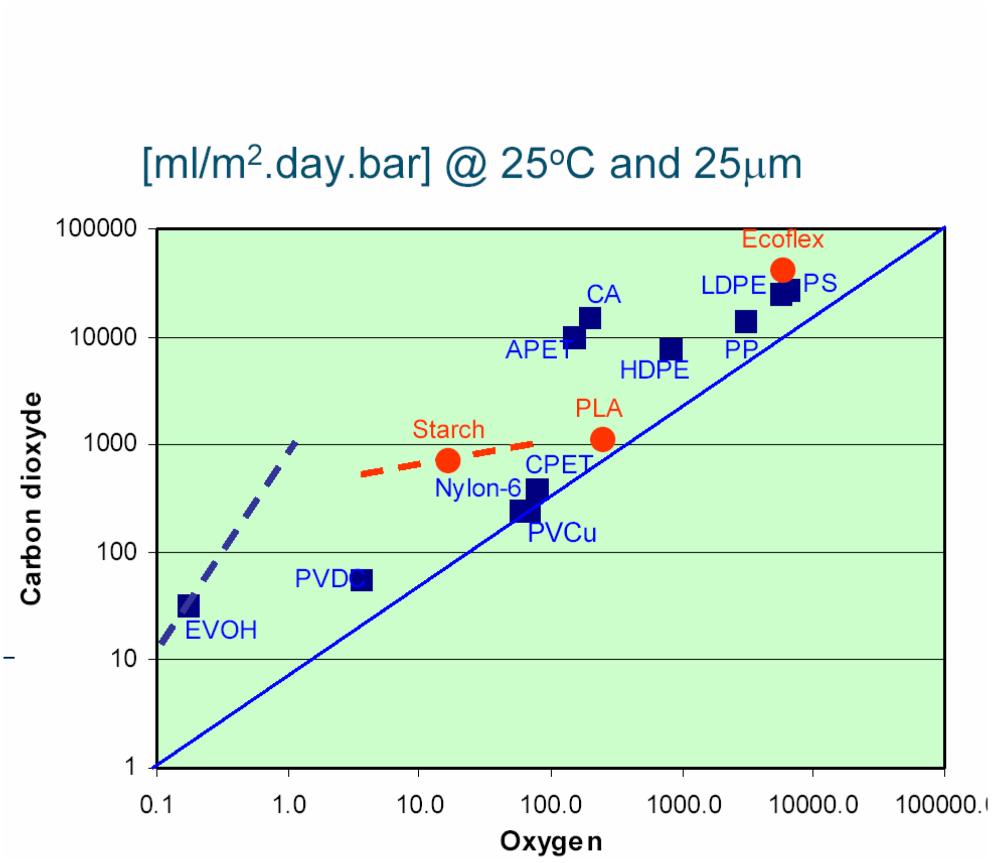


Figure 12 Data on gas permeation are presented for a range of polymers

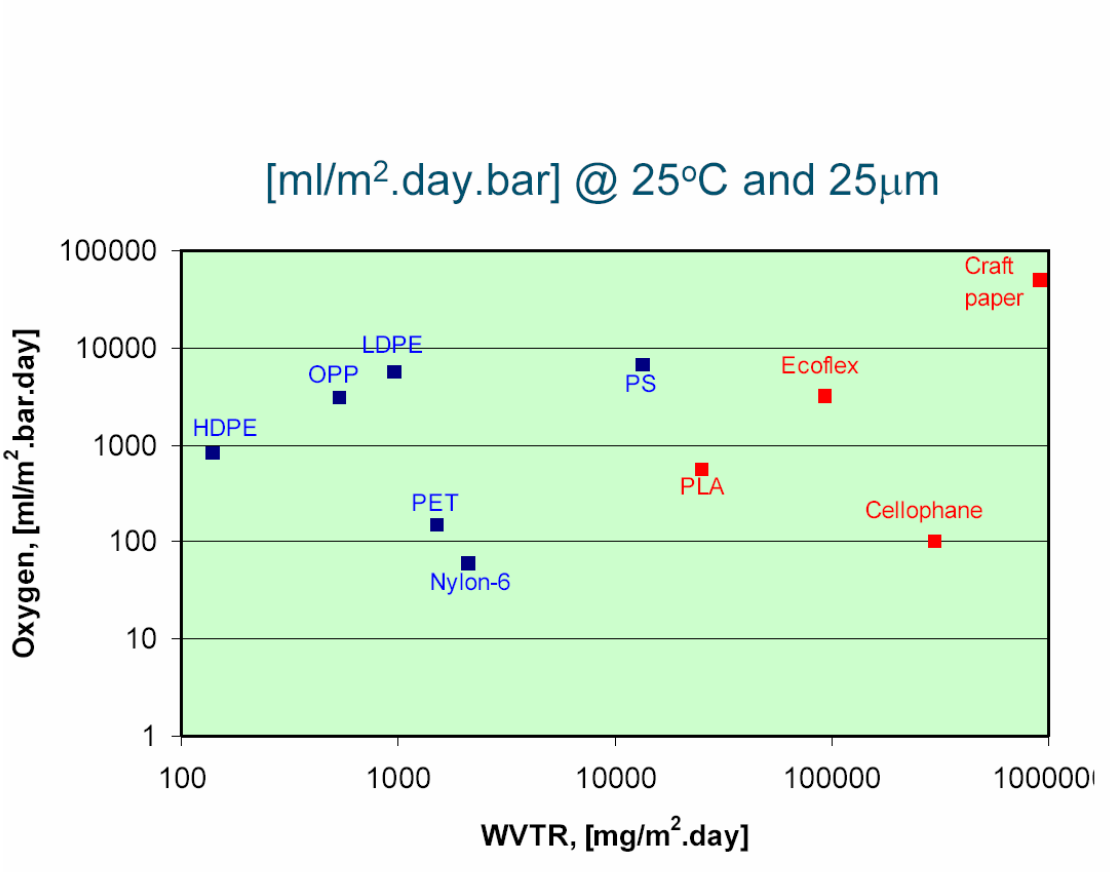


Figure 13 Data on Water vapour transmission for a range of polymers

6.1.2. How to improve these properties

6.1.2.1. Multi layers structures

As could be seen from the graph, most renewable based materials have very poor water barrier properties in comparison with existing petroleum based materials. This would limit potential uses in the packaging of products that need to retain moisture. Materials with higher barrier properties like PHB, or esters starches are either very expensive (PHB) or have very weak mechanical properties (like ester starches). A potential solution to accommodate these weakness is the use of multilayer structures. These techniques are also used with conventional materials (laminates and co-extrusions) and being good barriers to moisture, gases (oxygen, nitrogen and carbon dioxide), while providing adequate mechanical protection to the contained product they are known to increase shelf life and quality of various packaged food such as cheese, meat, fish, poultry, snacks coffee, and ready made meals.[29] Multilayer structure are flexible enough to allow pouches to be manufactured or rigid enough to assure thermoforming.

The use of such technology to process materials from renewables is expected to be easily accepted by industries not only because of the merits of the packaging materials but also because the fact that existing processing units, which transform conventional materials may also be used for such modification

6.1.2.2. Fibres, clays fillers, inorganic coatings,

Recent literature shows that a range of fillers have reinforcing effect on the polymers. These are clays and fibres.

A range of natural fibres as seen in the Figure that could be used as been suggested recently by American authors.[30] These are reported, in a recent review to provide major savings not only in cost but also in carbon dioxide emissions (up to 44%).[31]

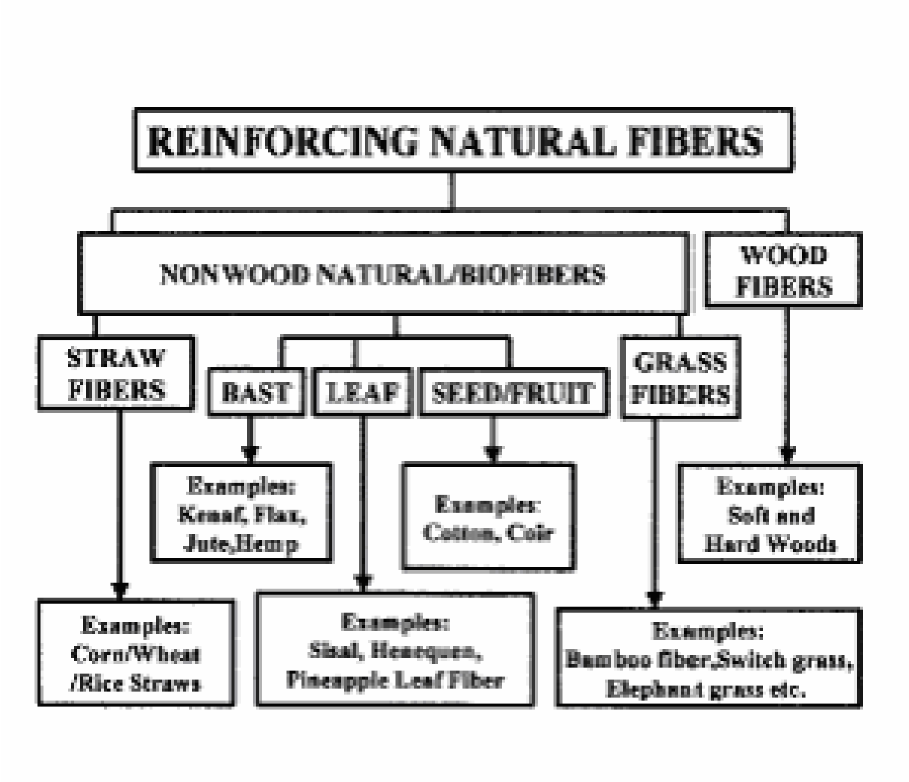


Figure 14: Potential new biofibres

Effect of these fibres would depend of a range of factors as the interfacial adhesion between the fibres and the matrix polymer, the dimensions and the morphology of the fibres. To illustrate the potential of the fillers to increase significantly the modulus, some examples from recent literature are provided in the Table.

Matrix polymer	**Modulus (MPa)**	**filler**	**Concentration (%)**	**Modulus of the composite (MPa)**	**source**
TPS	47.2	Ethanolamine activated montmorilonite	5	145.5	[32], by melt intercalation
TPS	87	Medium size fibers	5	190	[33]
TPS	87	Medium size fibers	12	522 a)	
PBSA	38	Wheat straw fly ash	10	80	[34]
TPS	80	Cellulose microfibrils	10	3000	[35]
PLA	2700	Recycled newspaper	10	5300	[36] [37]
PLA	3500	flax	30	8000	[38]
TPS	81.5	montmorilonite	20	850	[39]
Wheat starch filament	1390	cotton microfibril	5	9340	[40]
TPS	45	Waxy maize starch crystals/	5 b)	298	[41]

a) as a comparation the author also reported that HDPE module only increased two times with 12% fibres, b) 20 % glycerol as a plasticiser

Table 1: Influence of fillers on the modulus of some renewable polymers based composites.

Fillers, mainly the ones with small dimensions, are also known to improve barriers, due to a phenomenon known as "the tortuous path", as water or gases have to travel a longer path through the material to cross from one interface to the other. This is illustrated in the figure 14 produced in a recent research,[42] which shows the variation of water barrier properties of thermoplastic starch as a function of clay content.

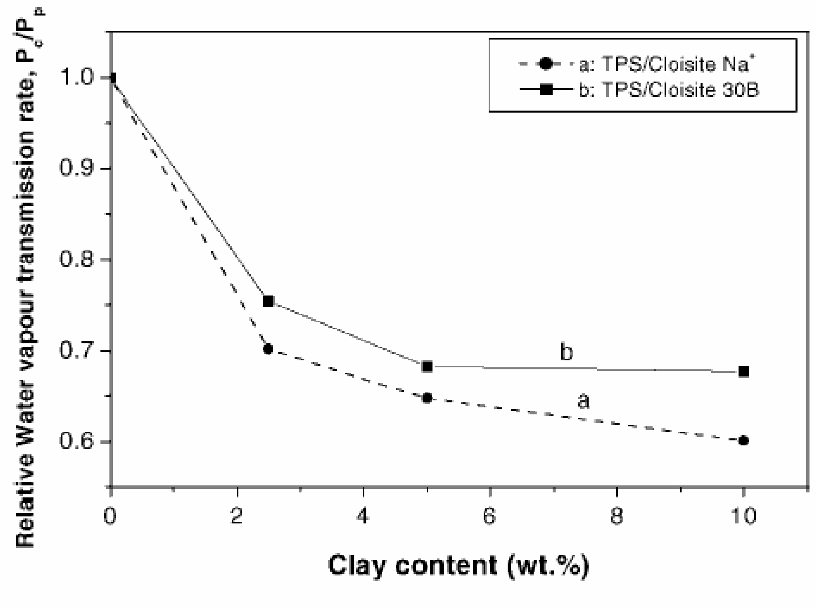


Figure 15

6.2. Potential techniques for weight reduction

Having analysed how mechanical properties oif the new renewable materials could be manipulated, and how the modulus of polymer matrix can be drastically increased, it is appropriate to analyse how feasible weight reduction of food packaging made of conventional non-renewable polymers with the new materials. 3 base cases are to be discussed, the case of ultra-thin trays/films, the case of foamed trays and the case of bottles.

6.2.1. Ultra thin trays/ films

Using the symbols w–weight of material, d-density of material , T-thickness of material, E-modulus of the material, we can describe the opportunity to reduce weight when using PLA instead of PP to produce trays with similar area for similar products.

$C. W_{pla} = W_{pp}$

Where c is a coefficient indicating the weight reduction

$C. T_{pla} .A. d_{pla} = T_{pp} .A. d_{pp}$

$C.T_{pla} d_{pla} = T_{pp} . d_{pp}$

$C = T_{pp}/T_{pla} \; d_{pp} / d_{pla}$

Assuming that the tray would behave like a beam, it could be deduced from the classical engineering bending equation, that the minimum thickness of trays is inversely proportional to the cubic root of the modulus, therefore :

$C = (E_{pla}/E_{pp})^{0.33} \; d_{pp}/d_{pla}$

$C = (2.3)^{0.33} * 0.77 = 1.01$

However if we consider that PLA tray would be reinforced with 10 % cellulose microfibrils, we could expect a 2.5 increase of the modulus. In this case the proportionality coefficient would be:

$C = (2.3 . 2.5)^{0.33} * 0.77 = 1.7.$
This predicts that a fibre reinforced PLA may offer up to 70% weight savings.

On the account of the errors in the assumptions, i.e. of a) the fact that the tray may not behave totally like a beam, and that b) the increase of the modulus may not be the expected one, c) the density of PLA microfibrils is similar to the one of PLA, it is safe to consider that a reduction of at least 15% is possible.

6.2.2. Foamed materials

As seen in points 5.3.4.4, and 5.1.4.3.foamed materials in both starch polymers and PLA have been developed. A possible method of reducing weight and raw materials costs is the development of sandwich foamed material, with a core in starch , and a skin in more expensive PLA.

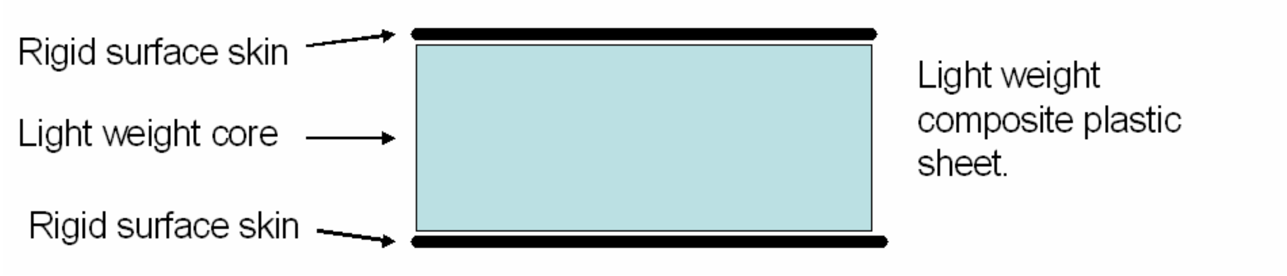


Figure 16 Scheme of a sandwich foamed material

A demonstration similar to the point 6.2.1. could be performed to estimate the weight reduction in the case foamed materials. However the models is more complicated, so applying a rule of thumb which validity has been proven for others thermoplastic materials, it is possible to state that a 50 % weight reduction for the same stiffness would be possible.

6.2.3. Long term benefits

It is expected that the techniques to be developed in these additional material science research would provide the basis to analyse others packaging. This is, novel forms to increase stiffness of renewable materials and technologies to improve barrier properties and compostability rate would allow these materials to be used in others more complex forms of packaging- like beer and soft drink bottles, punches, etc… This work is also expected to provide basis for use in others areas of materials, spanning outside the packaging areas and providing data for potential savings in construction materials and others consumers goods.

6.2.4. Opportunities for weight reduction

On the basis of the presented information it is acceptable to consider that savings in weight packaging can be obtained by using stiff and thin materials, and sandwich foamed trays, using polymeric materials from renewable resources.

Sainsbury’s presently uses 2,000 tonnes of rigid packaging, so that a conservatively estimated 15% saving is expected to correspond to 300 tonnes of reduction in the weight of packaging. The fact that material may be home compostable is expected to divert additionally a fraction of the remaining material from the landfill. If these results could be adopted by whole UK packaging sector than the saving would be 1900 tonnes (based on a 16% share of stream).

Major savings, in terms of waste reduction could be achieved if foamed materials could be used.

7. Conclusions

This report is based on peer-reviewed literature and others publicly available information (patents, newspapers), information obtained by contacting the three main societies of renewable polymers (i.e. European Bioplastic (formely IBAW), in Europe, The Biodegradable Plastics Society in Japan and the Biodegradable Products Institute in the US, and direct contact with several major players in the field. It is accepted that some information may be incorrect (mainly the referring to volumes of sales/ production processes used by companies or referring to moulder/packaging manufacturers existing in the US/Australia/Japan). Patent database analysis shows that in addition to work done (on the investigated matter) in this part of the world, research is also being carried out in China..

It has also been explained that most observers believe that price of petroleum and of commodity polymers presently used in packaging is to increase in the near future, which would therefore increase the price competitiveness of renewable based materials.

This document has dealt with three issues:

(1) the use of starting raw materials from renewable sources;
(2) the development of packaging solutions fit for purpose
(3) end of life disposal by composting

On the basis of the foregoing discussion, it is clear that the number of available renewable raw materials for the commercial production of compostable packaging is very limited. Indeed, the only renewable raw materials available in significant (1000s tonnes) quantities at the present time are either cellulose pulp, starch or polylactic acid derived. Of these, only starch and polylactic acid may be rendered thermoplastic for processing by conventional extrusion and conversion techniques. It should also be noted that the installed production capacity of polyhydroxybutyrate is 500 tonnes per year. This quantity represents a viable volume for the commercial production of packaging solutions where it is used as a non-structural, water-proof coating of otherwise water sensitive base substrates.

Significantly at the current time, these raw materials are combined with synthetic biodegradable polyesters such as polycaprolactone to afford a final product with appropriate functional properties and therefore none can be said to be wholly bio-derived. Without such additions, prototype packages may, for example, be too brittle or too water sensitive in use.

It is in trying to meet the requirements of issues (2) and (3) above that compromises and balances have to be met with the current state of the art renewables-based polymers. In fulfilling the requirements of issue (2), packages are conferred with hydrophobicity (made more waterproof) but this impacts on issue (3) rendering the package less biodegradable.

As stated above the main techniques that could be used to bring about weight reduction in rigid food packaging are related to (a) increasing the rigidity of a material and corresponding reduction in thickness; and (b) foaming the material to reduce the density while increasing the mechanical rigidity of the composite.
The model described in section 6.2.1 shows that a target of 15% weight reduction in comparison with a standard polypropylene tray presently used for packaging tomatoes is plausible. Testing is necessary to validate the demonstration and check shelf-life and production technology.

In order to fulfil the requirements of weight reduction, fitness for purpose and compostability at end of life, two candidate solutions emerge, based on already commercially available starting materials, that should be tested.
The solutions are:
(1) production of a co-extruded 3-layer PLA-foamed starch-PLA tray;
(2) production of blends of thermoplastic starch with other biodegradable polymers;
(3) reinforcement of thermoplastic blends with cellulose fibres and clays.

In the longer term, other modifications to foaming and fillers, both fibrous and particulate, may be developed that could allow weight further weight reductions to be achieved.

8. Appendix 1 References

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