# STUDIES OF BIODEGRADABLE POLYMER MATERIAL SUITABILITY FOR FOOD PACKAGING APPLICATIONS

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#### Abstract

Since its invention in the 1930s, plastic packaging has posed two challenges: its dependence on petroleum and the problem of waste disposal. Over the past five years packaging suppliers have been introducing various forms of biodegradable plastics made from a variety of plants, in the main corn. The market of biodegradable polymers at the present is growing based on projections that consumers and recycling regulations will drive demand for environmentally-friendly packaging. Market introduction has started successfully all over Europe. Most important application sectors of biodegradable polymers today: organic food and service packaging, shopping bags, catering products, bio waste bags, mulch films, horticulture auxiliaries. At the Latvia University of Agriculture faculty of Food Technology the following tasks of some biodegradable polymer testing for food applications were carried out:

- plasticized PHB films were used for sour cream and salad with meat and mayonnaise packaging;
- PLA film influence on the quality indices of rye bread at the storage time and their suitability for bread packaging was evaluated;
- with the aim to check the published data of biodegradable PLA packaging film special suitability to provide longer shelf life of fresh fruits and vegetables, some in Latvia cultivated fruit storage were tested.

Key words: biodegradable films, food packaging, rye bread, fruits.

## Introduction

Since its invention in the 1930s, plastic packaging has initiated two challenges: its dependence on petroleum and the problem of waste disposal. Most of today's conventional synthetic polymers are produced from petrochemicals and are not biodegradable. Theses stable polymers are a significant source of environmental pollution, harming organic nature when they are dispersed in the environment. The row materials such as fossil fuel and gas could be partially replaced by greener agricultural sources, which should also participate to the reduction of  $CO_2$  emissions (Narayan, 2001). Over the past five years packaging suppliers have been introducing various forms of biodegradable plastics. These materials are made from a variety of plants, in the main corn. The market of biodegradable polymers at the present is growing based on considerations that consumers and recycling regulations will drive demand for environmentally-friendly packaging. Some of the biodegradable polymers are already competitive alternatives to conventional food packaging, polylactate (PLA) is being one most important of them (Haugard, Martensen, 2003).

**State of the art of biodegradable polymer packaging.** According to the Biodegradable products Institute (BPI) a biodegradable plastics is one in which degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi or algae. This takes place in two-steps: degradation/defragmention initiated by heat, moisture, or microbial enzymes, and second step – biodegradation – where the shorter carbon chains pass through the sell walls of the microbes and are used as an energy source. The packaging is certified compostable and biodegradable according to European standard EN-13432, which is the internationally recognized standard for compostable packaging in Europe in 2000<sup>1</sup>. Biodegradable polymers are a growing field (Kaplan, *et al.*, 1993; Van de Velde, Kiekens, 2002; Rouilly, Rigal, 2002). Some micro organisms and enzymes capable of degrading them have been identified (Chandra, Rustgi, 1998; Kaplan, 1998). Depending to the evolution of

<sup>&</sup>lt;sup>1</sup> Drachman F. // Development in Biodegradable Plastics for packaging, Industry Insights, Intertech Pira 2007. Source: <u>www.intertechpira.com</u>; resource used on 10.02.2008.

the synthesis process, different classifications of biodegradable polymers have been proposed. There are 4 different categories of biodegradable polymers; only 3 of them have been obtained from renewable resources. Production capacity for biodegradable polymers worldwide has grown dramatically since the middle of 1990s. Demand for bioplastics in Europe experienced its first boom in 2006, according to a survey by the European Bioplastics Association. Currently bioplastics account only for less than one percent of the European plastics market. Prospective amount of biodegradable packaging market at 2010 could be about  $10\%^{1}$ . Renewable resource based biopolymers such as starch and PLA account for around 85% of the total production capacity with synthetic biopolymers accounting for the remaining 15%. Biodegradable polymers market introduction has started successfully all over Europe (Platt, 2006). European Bioplastics Association estimates the global production capacities of bioplastics to increase six times until 2011. The shares of the three material classes: synthetic biodegradable, biobased biodegradable and biobased non-biodegradable are expected to change significantly towards biobased non-biodegradable bioplastics. Their share is about 12 percent in 2007 of a total production capacity of 262000 tones in a year; in 2011 the share of biobased non-biodegradable plastics will be almost 40 percent of total capacity<sup>2</sup>. Most important application sectors of biodegradable polymers at the present time are mainly for organically produced foods packaging, conventional fruit and vegetables as well as bread and bakery products, ready-to-eat foods, service packaging, shopping bags, catering products, bio waste bags, mulch films, horticulture auxiliaries. Nets, trays and flow pack – from PLA, cellulose and starch materials - are being used as well. Not only the range of biodegradable products has widened but the number of those manufacturers, distributors and users has also increased. At present PLA is the most widely used biodegradable polymer for fresh-food applications<sup>3</sup>. A new study from Pira Intl. Ltd. estimated that biodegradable packaging will grow at a compound annual growth rate (CAGR) of 22 percent by introduction of lower-cost polyhydroxyalkanoate (PHA) in 2011<sup>3</sup>. Until today the poor barrier properties of uncoated biodegradable materials have prevented their use for products requiring a long shelf life. Currently Hycail Finland Oy have developed a new generation biodegradable PLA material -Hycail ® XM 1020<sup>4</sup>, which is ovenable and microwavable and can withstand temperatures over 200 °C. Compostable PLA trays to improve shelf life for meats and other food products by absorbing any liquids exuded during storage have been developed<sup>5</sup>. Biodegradable lidding film Alcan's CERAMIS<sup>®</sup>- PLA with high-barrier properties to seal food trays (for fresh meat, sausages, cheese and pasta packaging) has been introduced<sup>6</sup>. Presently, biopackaging can be found almost everywhere on the shelves in European supermarkets. Supermarket – Sainsbury in the UK was first who recognized the opportunities for compostable plastics packaging. Supermarket chains such as Delhaize (Belgium), Iper (belonging to the Carrefour group; Italy), Albert Heijn (Netherlands) and Migros (Switzerland) are actively placing their trust in biopackaging<sup>7</sup>. As an industry leader in research and development of biodegradable films is Treofan Company offering one of the broadest product lines for food packaging. Biophan

<sup>&</sup>lt;sup>1</sup> 1<sup>st</sup> European Bioplastics Conference, 21-22 November 2006, Crowne Plaza Hotel, Brussels. 2006. Source: <u>http://european-bioplastics.org/</u>; resource used on 09.02.2008.

 <sup>&</sup>lt;sup>2</sup> 2<sup>nd</sup> European Bioplastics Conference, 23 November 2007, Established as the place to be of bioplastics industry
Berlin/Paris. 2007. Source: <u>http://european-bioplastics.org/index.php?id=646</u>; resource used on 08.02.2008.

<sup>&</sup>lt;sup>3</sup> Biodegradable packaging to grow at CAGR of 22 percent, Packaging Digest, 08.01.2007. Source: <u>http://www.packagingdigest.com/article/CA6490177.html</u>; resource used on 11.02.2008.

<sup>&</sup>lt;sup>4</sup> Hycail launches first transparent, microwavable and ovenable biopolymer. Source: <u>http://www.hycail.com/pages/engels/nieuwsen.html</u>; resource used on 11.02.2008.

<sup>&</sup>lt;sup>5</sup> Compostable tray devised for meat packaging. 2008. Source: <u>http://www.foodproductiondaily.com/news-by-product/news.asp?id=82700&idCat=0&k=Biopak--meat-tray-Polylactic-Acid;</u> resource used on 12.02.2008.

<sup>&</sup>lt;sup>6</sup> <u>CERAMIS</u> PLA High-Barrier films Biodegradable packaging Films. 2007. Source: <u>http://www.publications.alcan.com/sustainability/2007/en/pages/review\_7\_innovation\_casestudies\_9.html</u>; resource used on 12.02.2008.

<sup>&</sup>lt;sup>7</sup> Packaging. Source: <u>http://european-bioplastics.org/index.php?id=133</u>; resource used on 08.02.2008.

films (thickness of 20 µm up to 50 µm<sup>1</sup>) have excellent product features: high transparency, exceptional surface gloss, high stiffness, resistant to oil, fat and alcohol, low water vapour barrier, high water transmission rate. The headlines of PLA properties and application for cheese packaging have been studied and presented in the EC funded framework project "Biopack" (Plackett, *et al.*, 2006). The market development of biodegradable plastics has been hindering by their high price. Since 2003 the gap between conventional petroleum-based plastics and biodegradable plastic prices has narrowed considerably due to the price jump of crude oil and energy as well as growing of biodegradable polymer production capacities. NatureWorks produced PLA (to compete directly with PET) price is 2.2–1.5  $\in$  per kg, while for PHB Metabolix it is foreseen 1.85  $\in$  per kg in 2008<sup>2;3</sup>.

The aim of this work is to batch information in general of the state of the art of biodegradable polymers for food packaging and to capsule the news about the studies carried out in Latvia on suitability of biodegradable polymers. In the laboratories of Department of Food technology as well as in the Latvia State Institute of Fruit-Growing, Dobele, the following tasks of some biodegradable polymer testing for food applications were performed:

- plasticized PHB films were used for sour cream and salad with meat and mayonnaise packaging;
- PLA film influence on the quality indices of rye bread at the storage time and their suitability for bread packaging was evaluated;
- with the aim to check the published data of biodegradable PLA packaging film special suitability to provide longer shelf life of fresh fruits and vegetables, some in Latvia cultivated fruit storage were tested.

# **Materials and Methods**

All published data on the studies of biodegradable packaging materials for food performed in Latvia University of Agriculture (LUA) were analyzed and accordance with them consequences were drown. In details the quality of fresh strawberries, black currents and raspberries at the storage time were tested. Two strawberry varieties: 'Tenira 'and' Pegasus', which have been commercially grown in Latvia, black current as well as late-bearing raspberries, were used for our experiments. For quality studies at the storage time the fruits were packed in polypropylene (PP) trays (210x148x35 mm) and sealed on the sealing equipment *Pratica* with oriented polypropylene (OPP) film with thickness 40 um, as well as the PP trays and Carton boxes as control packaging with berries were enclosed into pouches size of 200x300 mm made from biodegradable PLA films thickness of 25 (Treofan company) and 40 µm (MaaG company). All samples were stored in alight showcases at temperature +5±2 °C. To evaluate the packaging material influence on the ambience in packaging head space the gasses composition was measured by gas analyzer "OXYBABY" ECO. The moisture dynamics of the berries at the storage time was determined by sample mass change weighing on the scales at each day of analyzes. The weight losses were calculated as % of the initial weight.

# **Results and Discussion**

In the experiments performed at LUA several kinds of plasticized PHB were tested. The impact of plasticized PHB comparing with Lean Pouch, PE covered with light protective graphite layer films and PS cups of volume 250 ml usually used for dairy product packaging were evaluated on the quality indices of sour cream. It has been noticed that significant

<sup>&</sup>lt;sup>1</sup> European Bioplastics Member. Source: <u>Treofan GmbH</u> <u>http://www.european-bioplastics.org/index.php?id=356</u>; resource used on 10.02.2008.

<sup>&</sup>lt;sup>2</sup> Techno-economic Feasibility of Large-scale Production of Bio-based Polymers in Europe, European Commission, Directorate-general Joint Research Centre, EUR 22103 EN, December, 2005. Source: <u>http://www.biomatnet.org/publications/1944rep.pdf</u>; resource used on 06.02.2008.

<sup>&</sup>lt;sup>3</sup> Drachman F. // Development in Biodegradable Plastics for packaging, Industry Insights, Intertech Pira, 2007. Source: <u>www.intertechpira.com</u>; resource used on 06.02.2008.

differences of  $L^*$ ,  $a^*$  and  $b^*$ - colour values during storage time for 18 days exist among all sour cream samples packed in different kinds of materials; kind of PHB plasticizer slightly influences L\*, a\* and b\*- values during storage. Significant difference of secondary oxidation products acetaldehyde, pentanal and 2-methyl-1-propanol content among samples storage was observed as well. In general established that PHB based polymer films with various plasticizers (Dioctylsebacate or Bisoflex) might be suitable for different packaging technologies of dairy products (Muizniece-Brasava, 2006; Muizniece-Brasava et. al., 2006). The shelf life extension of meat salad in mayonnaise (cooked beef, potatoes, eggs, pickled cucumbers, salt, and mayonnaise) packed in pouches made from biodegradable commercially in Brazil produced plasticized PHB (poly- $\beta$ -hydroxybutyrate) films thickness of 60±5 µm was determined. pH of samples packed in plasticized PHB film under vacuum significantly decreased after 10 days refrigerated storage at +4 °C. A favourable impact of biopolymer packaging material – plasticized PHB film on total color changes of salads at the storage time has been observed. The growth of micro organisms in meat salad in mayonnaise demonstrated that storage time of salads in a vacuum packaged pouches made from plasticized PHB could be not more than 10 days (Muizniece-Brasava et al., 2007). Treofan Company as producer of biodegradable PLA films suggest their Biophan films for use in bread packaging because it is transparent, it allows preserve freshness and crispiness of bread products, what is provided by high water vapour permeability of the material. Our experiments showed that after 21 days of storage rye bread samples packaged in environmentally friendly PLA material films loosed 22.01-22.80% of their initial moisture content, as well as moisture loss from sweet-and-sour rye bread within 28 storage days reached respectively 30.05% and 33.11%. The mentioned moisture loss is too high and bread becomes stale – unacceptable for Latvian consumer. The results show the optimum shelf life for rye bread packaged in PLA film is up to one week, when moisture loss is still negligible. For longer term storage materials with better barrier properties should be used (Straumite et al., 2007). In the same way, vacuum-packaged cakes in PLA film due to its high water vapor permeability rapidly loses moisture and hardens faster then control sample in air ambiance, therefore can not be recommended in packaging technologies for shelf life extension of cakes (Muizniece-Brasava et. al., 2007).

As an example the dynamics of oxygen and carbon dioxide in the MAP packaged black currents container headspace at the storage time is shown in Fig. 1.



Figure 1. The dynamics of oxygen and carbon dioxide at the storage time in the headspaces of different containers with packed black currents (Latvia State Institute of Fruit-Growing, Dobele)

As the sealing of packages was performed at atmospheric ear ambiance, the initial content of  $CO_2$  was presumed closely to zero and  $O_2$  according as in atmosphere – 21%. The gas composition in packages established at the storage time depends from the barrier properties of films used for packaging. As a result of berry's breathing the  $CO_2$  content in the head space of

packages has been raised accordingly  $O_2$  content – decreased. The highest  $CO_2$  content 18% have been observed in the PP trays sealed with OPP film after 25 storage days. It could be explained by low  $CO_2$  permeability of OPP film, which promotes  $CO_2$  accumulation in the packages. The more acceptable concentration of  $CO_2$  for storage of berries has been observed in the carton boxes inserted in PLA pouches thickness of 40 µm (MaaG company) – 11 to 12% and  $O_2 - 4\%$ , which could be assessed as adequate to equilibrium modified atmosphere (EMAP) for minimal breathing of fruits at the storage time. In the PP trays enclosed into pouches made from biodegradable PLA films thickness of 25 µm (Treofan company) the content of  $CO_2$  was acceptable, whereas  $O_2$  content decreased close to zero, the oxygen free ambiance could not provide the fruit quality at the storage time. The mass of berries packed in PP trays and sealed with OPP film accordingly to OPP inherent moisture barrier properties does not changes for 21–25 storage days.

## Conclusions

A rapid growth of biodegradable packaging materials in European countries started since 2006, the global production capacities of bioplastics will increase six times until 2011. At present PLA is the most widely used biodegradable polymer for food packaging. The experiments performed in LUA proved about the suitability of biodegradable packaging

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materials for food application, for all that the experiment should be followed up.

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