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Evaluation of the biopolymer

Poly-hydroxi-alkanoates

-for use in Tetra Pak packages

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Abstract

Biopolymers are interesting materials from a sustainable point of view. Especially since consumers increasingly demand environmental friendly packages as well as more convenient packages with easy open and close features on the packages. The demands for convenient packages lead to more and more plastics in the packaging industry.

The purpose with this project is to find out typical properties of the biopolymer, polyhydroxyalkanoate (PHA) and to evaluate chemical, mechanical and barrier functions of the polymer PHA. The purpose is also to indicate if this polymer is useful in different Tetra Pak applications and define possibilities and restrictions leading to a final recommendation of what application the polymer is useful for. The main focus when it comes to Tetra Pak applications is on Tetra Brik Aseptic (TBA) and caps for the TBA. Tetra Recart (TRC) was also included in the project.

The scientific attitude used in this thesis is a system theory. Both qualitative and quantitative research approaches have been used. The thesis is based on literature studies, interviews, pilot study and laboratory evaluation. The material is then analysed with the SWOT (Strengths, Weaknesses, Opportunities and Threats) method.

Poly-hydroxi-alkanoates is a family of bio-based polyesters that serve as a energy reserve and is produced by fermentation of carbon substrate within the microorganism. PHAs are fully biodegradable in both aerobic and anaerobic conditions. Three different suppliers, Metabolix, BioMatera and Nodax, of PHA were invited to take part in this evaluation of PHA by Tetra Pak. Nodax was not able to deliver any material and thereby were excluded from further investigation in this thesis.

The pilot production including injection moulding and extrusion coating shows that the PHA requires changes in the process, in order to be used. A big difference between the PHA and the materials used today is the slow crystallization that is possible to speed up by using warm tools when injection moulding and a warm chill rolls when extruding.

The laboratory testing of the material properties indicates that most of the tested properties of the PHA both from Metabolix and from BioMatera are in need of improvement to match the materials used today and to measure up to the demands. In the laboratory testing of recycling properties the PHA extruded on carton did pulp readily and no flakes of fibres could visibly be noticed. The breakdown of the polymers into smaller pieces indicates that the polymers are more brittle than LDPE, which could be an issue in the recycling of paper.

The conclusion of this thesis is that the Poly-hydroxi-alkanoates possess good and needed properties compared to other biopolymers. But there are still properties needed to be improved and they are not as easy to process as the materials used today. The tested PHAs are all in need of improvement to be able to use in the laminar packaging materials for TBA, TRC or in a cap.

The recommended next step is to contact the potential suppliers in order to discuss the result of the laboratory testing and the possibilities to make improvements. If the discussion is successful and new and improved grades are processed, I suggest further testing of the material. If it does not result in a new modified PHA grade I suggest further research for other potential suppliers.

Preface

This thesis is written as the final task of my Master of Science education in Machine technology. The thesis is written at Tetra Pak R&D in Lund. Tetra Pak gave the research task and the frames for the project.

I would like to thank Tetra Pak R&D for giving me this opportunity to see the company from within and to write my thesis in such an interesting area. I would also like to thank my supervisors Lars Sickert at Tetra Pak R&D and Märit Beckeman at LTH without whom this would have been an impossible task to carry trough. I would also like to thank Daniella Nae, Lena Dahlberg and Ann-Christine Bengtsson whom has helped me with the testing at the Tetra Pak Laboratory and especially Keihan Lindborg that has put up with my never ending questions. Other persons at Tetra Pak that has contributed to my thesis are Kjell Asplund, Tommy Nyström, Nils Toft, Rune Sjölin, Roger Lindgren, Sara Granholm, Marlene Kjellstrand, Hanna Andersson, Fredrik Ullman and Mikael Berlin for which I'm very grateful.

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1. Introduction

In this first chapter the reader will be introduced to the background of this thesis. The problem formulation, purpose and limitations of this thesis will also be presented to the reader.

1.1 Background

"Aktiebolaget Tetra Pak" was registered in December 1950[1]. Ruben Rausing was the founder of Tetra Pak and by motivating his people to look beyond the obvious, he led the development of a unique innovation that has changed the way food is distributed around the world[2].

Today Tetra Pak develops, produces and markets complete processing, packaging and distribution systems for food products. Tetra Pak have manufacturing facilities for packages and packaging material all over the world. Tetra Pak has expanded its business to include much more than the packaging of liquid food products that the company started with. Today, ice cream, cheese, dry foods, fruits, vegetables and pet food are examples of what can be packaged in Tetra Pak packages. Tetra Pak today operates in more than 165 markets with over 21 000 employees, and believes in responsible industry leadership, creating profitable growth in harmony with environmental sustainability and good corporate citizenship.[3] Tetra Pak is committed to running its business in an environmentally sound and sustainable manner with an Environmental Policy[4] that describes their environmental engagement at every step in the consumption and production chain.[5]

The Tetra Brik Aseptic package is very important for Tetra Pak. Last year (2004) 110817 million packages were produced by Tetra Pak. 76,2% of the packages were Tetra Brik Aseptic and next largest were the Tetra Rex with 8,9%. [6]

Bioplastics has a longer history than one might think; early 1800s experiments on bioplastics were made. Some of the experiments were more successful than others and the material was used to produce different products. The history of plastics came to a dramatical change in the beginning of 1900s when petroleum emerged. The new, synthetic plastics displaced the early bioplastics.[7] The plastics became very important in the 1940s and have since then more and more replaced other materials in a lot of different applications. The success for plastics is not only due to their good mechanical and thermal properties but their stability and durability.[8]

Plastics are not one material. Plastics are produced from polymers and additives. A polymer consists of smaller molecules, monomers, linked together in a chain. Depending on the chemistry of the monomers and how they are linked together the polymer achieves its different properties. With the additives the properties of the polymer can be further adjusted.[9]

For the last 50 years the use of plastics to provide packaging has increased. The advantages of the plastics have created a global industry providing more than 300

[1] Leander, L. 1996. p.VII
[2] www.tetrapak.com Tetra Pak 2005-02-09
[3] Ibid.
[4] The Environmental Policy is available on: www.tetrapak.com/docs/environment/EnvPolicy2004.pdf
[5] www.tetrapak.com Tetra Pak 2005-02-09
[6] ORBIS Presentations Gallery, Tetra Pak Intranet, slide number TP317
[7] Stevens, E. S. 2002
[8] Chakraborty, P. et. al. Paper. 2004.
[9] Dominic,C. et al; 2000. p. 16 ff

billion pounds per year of materials. The vast majority of these materials are based on fossil carbon, typically oil and gas, leading to increases of greenhouse gases in the atmosphere and the accumulation of plastic materials in the environment. Alternative materials based upon natural, sustainable sources that would have less impact on the environment have suffered from properties that don't measure up to the conventional polymers and higher costs.[10]

Packaging and its environmental impact have for the latest years been in focus for the public as well as for the governments. The packaging directive from EU came 1994. This has started trends like: removal of over packing, development of lean packaging alternatives and increased using of return systems.[11]

The UN climate panel consist of several hundreds of climate scientists in the world. They have from the gathered climate research and with consideration to the remaining uncertainties concluded that the global warming during the last 50 years most likely depend on the human emission of greenhouse gases. In this conclusion the scientists have considered the natural variations, from year to year and in longer cycles. It is the use of fossil fuel in the industry, for transportation, in the production of electricity and for heating that cause the increase of carbon dioxide in the atmosphere.[12] All scientists do not have exactly the same opinion in this question. Recently a new study from Swedish and Russian scientists has been published. According to the press announcement from Stockholm University they have found that natural climate changes can be bigger than one earlier thought. The study shows that it is hard to distinguish human climate impacts from the natural variations, even though the last 15 warm years best can be explained with the human impact in the calculation.[13]

According to Kjell Aleklett, professor in Physics at Uppsala University, the maximum production of oil in the world will be reached before year 2010. The exact year does different oil experts not agree on. The oil production in the North Sea reached however its maximum in year 2000. The oil production is at the same time continuing to increase in the world, especially in India and in China. Between 1993 and 2003 the oil-consumption in India and China increased with 97%.[14]

From a sustainable point of view the biomaterials are interesting[15]. Especially since consumers increasingly demand environmental friendly packages[16] as well as more convenient packages with easy open and close features on the packages[17].

1.2 Problem formulation

The problem the packaging industry now faces is the demand for more convenient packages with opening features, which means more plastics on the packages. There is also an increasing demand for a sustainable development and overall more environmental friendly packaging materials. This has led Tetra Pak and other companies' interest towards new packaging materials, the renewable biopolymers. Many questions about biopolymers remain to be answered: Do they meet the standards of the materials used today? Do they add values?

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[10] www.metabolix.com/natures%20plastic/coretechnology.html
[11] Dominic,C. et al; 2000. p. 127 ff
[12] http://naturvard.server56-web.wineasy.se/dec25WhyIsGlobalWarming.asp 2005-07-02
[13] www.insidan.su.se/pressmeddelanden.php?pm=625
[14] Eriksson, L. *Forskare varnar för oljekris* 2005. p. 20
[15] Weber, C. J. 2000. p. 11
[16] Pendegast, G. et al. 1996. p. 60
[17] www.tetrapak.com Tetra Pak Visited: 2005-03-11

1.3 Purpose

The purpose with this project is to find out typical properties of the biopolymer, polyhydroxyalkanoate (PHA) and to evaluate chemical, mechanical and barrier functions of the polymer PHA. The purpose is also to indicate if this polymer is useful in different Tetra Pak applications and define possibilities and restrictions leading to a final recommendation of what application the polymer is useful for. The main focus when it comes to Tetra Pak applications is on Tetra Brik Aseptic (TBA), caps for the TBA and Tetra Recart (TRC).

1.4 Limitations

This thesis will only consider food packaging and primary packaging. The focus will be mainly on the Tetra Brik Aseptic (TBA) and a closure for the TBA, Tetra Recart (TRC) is also included. No specific foodstuff will be considered only the package in general, since the TBA and TRC are used to pack many different products with slightly different demands on the properties of the package. When packaging material is concerned, focus will be on the polymers. Financial aspects are not included in this thesis since prices on materials are never fixed but very much negotiable, especially when the company is as big as Tetra Pak and the quantity is large. Another important reason is also that poly-hydroxi-alkanoates are not commercially available yet in the wanted quantities – which mean that there is no realistic price yet.

2 Methods

In this chapter the reader will be introduced to scientific attitudes, research approach and the research tools used in this thesis as well as research quality.

2.1 Scientific attitude

In scientific theory there are different traditions and theories in gaining knowledge:

- The ***positivism*** has its roots in philosophical discussions in foremost Germany in the beginning of the 1900s. The positivism in the science of today can be characterized with the confidence in scientific rationality and that knowledge must be empirical testable. A statement is true if it correlates with the reality. Estimations and judgments are not to be bases for facts, measuring is the way to knowledge. Criticism has been among other things that the positivism leaves some areas of research out that are not possible to objectively measure.[18]
- The ***system theory*** grew during the late 1960s as a reaction towards the positivism[19]. The system theory is an interdisciplinary field which studies relationships of systems as a whole[20]. This theory arises from the needs within research areas like ecology where numerous factors interact and none of them can be studied separately or isolated in laboratory without loosing its meaning. Tasks in the system theory analysis are for instance the system border, the structure of the system, the flow within the system and interactions between different parts.[21]
- The ***hermeneutic*** has its roots in theories in the Bible and other text interpretation. It can be seen as the knowledge of interpretation in its widest sense. The interpretation can range from decoding of conventions or symbols, understanding a message despite different disturbances like language and sickness to understanding art and architecture.[22]
- The ***phenomenology*** is sprung from a philosophy about awareness, self-awareness, awareness of something and phenomenon. In the phenomenology one has to avoid relating subjective phenomenon to physical factors or occurrences in the surrounding. The central in phenomenology is the experiences in contradiction to the positivism where everything has to be proved by testing it empirically. [23]

The system theory is the closest one to the scientific attitude used in this thesis, since a package can be seen as a system with many interdependent parts that needs to be studied in a context. As parts the package material, the packaging process, the packaged product, environmental issues and legislative issues can be seen.

2.2 Research approach

The scientific research methods can be divided into two separate types of approaches: qualitative and quantitative.

[18] Wallén, G. 1996 p. 26-28
[19] Ibid. p. 28-32
[20] http://en.wikipedia.org/wiki/Systems_theory 2005-08-06
[21] Ibid. p. 28-32
[22] Ibid. p. 33-35
[23] Ibid. p. 35-36

- In the ***qualitative*** approach the researchers' interpretation of the information is in focus.[24] This approach includes methods that contain or conclude with verbal formulations, written or spoken[25].
- The use of measuring, quantification with mathematics and statistics has characterized some methods as ***quantitative.*** To this group belongs among others experiments, tests and questionnaires i.e. methods that conclude with numerical observations or can be turned into such.[26]

The research strategy in this thesis contain both qualitative and quantitative parts.

2.3 Research Tools

This research is based on literature studies, interviews, pilot study, laboratory evaluation and SWOT-analysis. The qualitative parts of the thesis are the interviews and the pilot study, while the laboratory evaluations constitute the quantitative part. The SWOT-analysis is a model used in this thesis to structure the analysis and to better illustrate the results.

2.3.1 Literature studies

The literature collection process has mainly been based on: Searches on the Internet with help from the search engine Google. Searches have also been conducted at different databases with help from the information specialist Hanna Andersson at Tetra Pak R&D. Searches have been made on databases such as Elin, SciFinder, Caplus, Dialog and Medline. The searches have been conducted with search phrases like "packag?", "pha, polyhydroxialkanoates", "biopolymers in packaging", "biopolymer", "bio polymer", "biodegradable polymer", "package?", "overview or introduction". The patent database, Derwent, was also used. The search results have been sorted and validated from criterias like: Origin, relevance in view of the purpose of this thesis and age. Initially the search was concentrated to literature such as overviews and summaries of the research area. Later in the project phase the search was for literature in order to get a deeper understanding of the area. The literature was then reviewed on the basis of the purpose of this thesis.

2.3.2 Interviews

The scientific interview always has the purpose to give the interviewer a certain kind of information. The two persons acting in the interview have two different parts to play. The interviewer seeks the information and the respondent gives the information. Interviews can be structured or unstructured.[27]

- In a ***structured interview*** the interviewer is bound to a prepared scheme with the questions, the internal order between the questions and their formulation predefined.[28]
- The ***unstructured interview*** is free and focusing on a theme or a certain subject that is to be covered with suitable questions. This type of interview gives possibilities to use open questions for general and broad questions in the beginning and later narrowing the subject with more specific questions.[29]

[24] Holme, I. M. et al. 1991. p. 99 ff
[25] Backman, J. 1998. p. 31
[26] Backman, J. 1998. p. 31
[27] Carlsson, B. 1990. p. 80 ff
[28] Ibid.
[29] Ibid.

The interviews have been unstructured and the targeted areas were barrier materials, packaging demands, polymers used today, environmental aspects and the laboratory test methods. The informants are all persons working within Tetra Pak with for this thesis key competence. The selection has been made in agreement with my supervisor at Tetra Pak. The interviews have been conducted to get a deeper insight in some main areas.

Notes were taken during the interviews. No taping of the interviews was made since a freer form of interview with a comforting atmosphere was strived for. Taping might have a hampering effect on the informants.

2.3.3 Pilot study

The PHA materials from two different suppliers were tested in pilot-scale production. Films were extruded and caps were injection moulded. How the production went with the different materials was observed. The purpose with this pilot study was to compare the process ability of the materials from the different suppliers. Notes were taken during the study.

2.3.4 Laboratory evaluation

The materials from the two suppliers have been subjected to different laboratory testing. The tests that were conducted were based on the knowledge gathered in the literature studies as well as the consultation of Lars Sickert, the supervisor at Tetra Pak. The laboratory evaluation was made to find out the mechanical, thermal, sensorial, repulping and barrier properties. The testings were conducted by the laboratory personal at Tetra Pak with standard methods.

2.3.5 SWOT-analysis

SWOT is a method that can be used in many different contexts. The SWOT-analysis is a tool to make evaluation of internal as well as external key issues more systematic. SWOT is an abbreviation and stands for: **S**trengths, **W**eaknesses, **O**pportunities and **T**hreats. The first two variables, strengths and weaknesses, are used to evaluate the strategic capability of something. Opportunities and threats are used to summarize the key issues from the surrounding. The identified strengths can be used to take advantage of the opportunities. By discovering the weaknesses the organization becomes aware of the threats in its business surrounding. [30]

In this thesis the SWOT-analysis is used to systematically evaluate the strengths and weaknesses of the biopolymer, PHA. The opportunities and threats that the use of the biopolymer would mean to Tetra Pak are also evaluated.

2.4 Research Quality

2.4.1 Reliability

Reliability is the extent to which an experiment, test, or any measuring procedure delivers the same result on repeated trials. For example a question that at one time gives one answer and at another time gives a different answer is not a reliable question.[31]

To achieve a good reliability efforts have been made to not influence the results in any direction. By explaining the research process, the used tools, laboratory

[30] Johnson, G. et al. 2002. p. 183
[31] Bell, J. 1993. p. 64-65

methods as well as the theory and empiric chapters the intent is that the study shall be possible to replicate.

2.4.2 Validity

Validity is a measure on the success of a study to measure what the researchers set out to measure.[32] Two types of validity exists: external and internal. External validity refers to the extent to which the results of a study are generalizable or transferable. Internal validity refers to both the rigor with which the study was conducted and the extent to which the designers of a study have taken into account alternative explanations for any causal relationships they explore.[33]

In this thesis participant control has been used, which for instance means that people that have contributed with information have been able to control if the information were correctly understood. Horizontal review and criticism has also been used which means that the supervisor from Tetra Pak and the supervisor from LTH have continuously been able to give comments on the thesis.

2.4.3 Objectivity

To reach objectivity in a thesis all traces of subjectivity have to be excluded. Subjectivity can come from emotional attachment or personal favouritism. To demonstrate that a thesis is objective it is required that enough evidence is gathered to support a presented view, statement, suggestion, theory or thesis.[34]

The objectivity in this thesis is possible to question in the parts concerning Tetra Pak specific areas since the sources used have been the Tetra Pak website and all the persons who have contributed with information are Tetra Pak employees. In these areas no independent sources have been found. Since this information is of the character facts and concerning different package types, its closures and packaging machines the risk for subjectivity is estimated as small. The main parts of this thesis can be considered to hold a high standard concerning objectivity since the information is based on many different sources and from all over the world.

[32] Bell, J. 1993. p. 65
[33] http://writing.colostate.edu/references/research/relval/pop2b.cfm
[34] www.library.csi.cuny.edu/~edward/thesisstatements.htm Visited: 2005-08-06

3. Packaging

In this chapter the reader is introduced to packaging systems, its functions and the different packages within Tetra Pak and legislative issues in generally.

3.1 Packaging System

Packaging can be classified as primary, secondary and tertiary packaging with regard to the levels of packaging. A packaging system has five different categories of purposes; to hold the product directly (the primary package), to display information about the product and the handling, to protect from leakage of the content and give protection from the surrounding environment, make handling and transports easy and finally to display the product and its brand as a marketing tool.

- **The primary package** is the one the consumer usually takes home i.e. the package that is in contact with the product[35]. Its main purpose is to make the product accessible and at the same time protect and keep the properties of the product[36].
- **The secondary package** contains several primary packages. Secondary packages should make the handling of the products more effective. Sometimes it's designed to be placed directly on the shelves in the retail stores[37].
- **The tertiary package,** also called transport packaging, is used when a number of secondary packages are assembled on a pallet or a roll container[38].

Further in the thesis it's mainly the primary package that will be considered.

3.2 Packaging functions

The packaging of food products is a challenging task and requires extra caution since food is a very complex and diverse product to pack[39]. Not only shall the package hold and protect the product from impacts and shocks, but also from biological interference of microorganisms and insects. The hygienic aspect is also very important. The sensitivity of the food is dependent of the type of food as well as the preservation method. To maintain a good quality of the product different barriers are required. When the package is in direct contact with food it also requires that the packaging material does not contaminate the food, therefore only materials with known composition are to be used.[40]

A packaging system has to include functions that contribute to make the handling more efficient in the distribution or at the consumer. A package should be adjusted to the size of the consumer demands in order to minimize food spoilage and increased turnover rates.[41] Minimizing food spoilage is important since it's not only the product that is spoiled but also all the efforts put in to produce it.[42] The size optimum varies of course from person to person so the optimized package might have to be a flexible package such as: selling by weight, portion packs in multi-pack or re-sealable packages. Since long the strive has been for low weight packages since the

[35] Saghir, M. Paper. 2004. p. 7
[36] Dominic,C. et al. 2000. p. 23ff
[37] Ibid.
[38] Saghir, M. Paper. 2004. p. 7
[39] Weber, C. J. 2000. p. 47 ff
[40] Thorén, A. et al. 2000. p. 104
[41] Ibid
[42] Saghir, M. *Lecture:* 2004-05-06

weight of the truckloads are limited. The packaging must have a good usability all through the whole value chain from package producer to end-consumer and not to forget during recycling or likewise. It should therefore be adapted to all the different conditions it will encounter during its lifecycle. The need of information varies throughout the distribution chain. The different levels in the packaging system have to provide the actors in the supply chain with certain information.[43]

The marketing functions of a package contain, to the end-user, value-adding activities. The package can fulfil the market demands in different ways, and thus contribute to a more attractive product. Other customer demands may concern ergonomics or be regulated by the law.[44]

3.3 Packages within Tetra Pak

Figure 1: Shows the different beverage cartons that Tetra Pak produce.

Tetra Pak produces a wide range of different packages see figure 1 (from left):

- **Tetra Classic** is the tetrahedral package that was introduced in 1952. The aseptic version Tetra Classic Aseptic came in 1961.
- **Tetra Wedge Aseptic** was introduced in 1997 and has a new and innovative shape. The package is based on the technology of the Tetra Brik Aseptic system.
- **Tetra Rex** is the rectangular package with a gable-shaped top. The first Tetra Rex packaging machine was installed 1966.
- **Tetra Prisma Aseptic** is the name of an eight-sided package that was commercially introduced in 1997.
- **Tetra Brik Aseptic** is a rectangular shaped aseptic package and available with a large number of different openings. There is also a Tetra Brik, i.e. a nonaseptic version that came 1963, six years before the aseptic version.
- **Tetra Fino Aseptic** is the name of the carton-based pillow-shaped package, which was introduced in 1997.
- **Tetra Top** package is a rectangular shaped package with rounded corners. Tetra Top is a reclosable package with an injection-moulded lid. It was launched in 1986.
- **Tetra Recart** is a carton packaging system, which is an alternative packaging solution for a variety of food products that are normally packed in cans or

[43] Johansson, K. et al. 1997. p. 33 ff
[44] Ibid. p 21-23

glass jars. [45] In Tetra Recart the product can be sterilized in the same way as in the traditional canning process.[46]

3.4 Legislative issues

Packaging of food is a complex task. The package serves as an important defence against external hazards. A well-known and undesirable interaction between the packaging material and the foodstuff is the migration. This problem is dealt with in the food contact material legislation. Other undesirable interactions like microbiological contamination, penetration of microorganisms, insects and rodents and collapse of packages in humid conditions are more unlikely to happen. The microbiological contamination is dealt with in the guidelines for good manufacturing practice.[47]

3.4.1 Food-Packaging regulation

All materials and articles intended to come into contact with foodstuffs are considered as food contact materials[48]. The legislation on food contact materials on EU level fulfils two essential goals: the protection of the health of the consumer and the removal of technical barriers to trade. Food contact materials should be safe and should not transfer their components (migrate) into the foodstuff in unacceptable quantities[49]. By evaluating the identity, toxicological properties and the migrating quantities during the conditions of intended use the safety of the food contact material is evaluated. [50]

Two types of migration limits have been established for plastic materials:

- The Overall Migration Limit (OML) is set on 60mg (of substances)/kg (of foodstuff). The OML applies to all substances that can migrate from food contact materials into foodstuffs.
- The Specific Migration Limit (SML) applies to individual authorised substances. This limit is based on the toxicological evaluation of the substance. The SML is generally set according to the Acceptable Daily Intake (ADI) or the Tolerable Daily Intake (TDI).

The OML and SML have been established to make sure the protection of the health of the consumer and to avoid contamination of the foodstuff.

Food contact materials are in the EU regulated by three types of directives:

- The Framework Regulation (EC) No 1935/2004. This regulation sets up general requirements for all food contact materials.[51] It is also listing all the materials to be regulated and defining principles for adding new materials.[52]
- Specific Directives that cover single groups of materials and articles are listed in the Framework Directive.
- Directives on Individual Substances or groups of substances that are used in the manufacture of materials and articles intended for food contact.

[45] www.tetrapak.com Brochure: "Tetra Pak is not a package" 2005-02-09
[46] News release 8/7-2004 www.tetrapak.com
[47] Thorén, A. et. al. 2000
[48] www.europa.eu.int/comm/food/food/chemicalsafety/foodcontact/index_en.htm
[49] www.europa.eu.int/comm/food/food/chemicalsafety/foodcontact/eu_legisl_en.htm
[50] Weber, C. J. 2000. p. 86
[51] www.europa.eu.int/comm/food/food/chemicalsafety/foodcontact/eu_legisl_en.htm
[52] Weber, C. J. 2000. p. 86

For plastics there are certain criterias in the Framework directive and in specific directives that according to Weber, C. say:

1. "Plastics must be produced by good manufacturing practice.
2. Plastics must not transfer their constituents to foodstuffs in such quantities as to constitute a health hazard.
3. Plastics must not transfer their constituents to foodstuffs in such quantities as to bring about an unacceptable change in the composition of the foodstuff (overall migration limit).
4. Plastics must not transfer constituents to foodstuffs in such quantities as to alter their sensory properties.
5. Plastics must be made from starting substances listed in the plastic directives.
6. Starting substances not listed can be used on condition that they are mixtures of approved substances, oligomers, or natural or synthetic macromolecular compounds or mixtures of the two as long as they have been produced from starting substances included in the list.
7. Authorized substances can be used only if they comply with restrictions applicable to them.
8. The substances must be "of good technical quality as regards purity requirements".
9. A symbol or the words "for food use" must accompany plastics sold to consumers that are not in contact with foods, but intended to come into contact with foods. Articles that by nature are clearly intended to come into food contact are exempted from these obligations."[53]

3.4.2 Environmental legislation

The European directive No. 94/62 states that a producer or importer of packaging is responsible for: At least 65% will be recovered, at least 45% will be recovered by material recycling and at least 15% of each packaging material will be recycled.

The requirements for compostable products are collected in a draft standard, prEN 13432. According to this, compostable products must fulfill the following criteria:

- The packaging components shall individually be completely biodegradable.
- The complete product shall disintegrate completely during a composting process.
- The addition of the product to the biowaste shall not have negative effects on the composting process nor on the quality of the final compost.[54]

[53] Weber, C. J. 2000. p. 87-88
[54] Ahvenainen, R. 2003. p. 526 f

4. Tetra Brik Aseptic & Tetra Recart

In this chapter the reader is deeper introduced to Tetra Brik Aseptic and Tetra Recart.

4.1 Tetra Brik Aseptic (TBA)

The Tetra Brik was launched in 1963 and the aseptic version came six years later[55]. A definition of Aseptic package is: "Aseptic packaging means filling a sterilised package with a sterile food under a confined hygienic environment. Shelf stability, therefore, is reached without the use of preservatives and/or refrigeration."[56] In retail stores the Euro-pallet was starting to get commonly used in the storing and transport of commodity products. The Tetra Brik was perfect for the new and revolutionizing handling system for milk, with the euro-pallet as base. The Tetra Brik was not only optimized for the pallet but also to get the best ratio packaging material to volume content. The package was also adjusted to the demands from the distributors. The high salary as well as cost-levels in the country was a driving force in the development of a automated and rational handling system instead of the at that time existing manual handling. The Tetra Brik was warmly welcomed since it was easy to buy, carry home and store in the fridge. The opening demanded a scissor and the pouring ought to be done carefully, but the good qualities of the new package were predominant. The launch of the Tetra Brik was not without difficulties, in the beginning this package kept a lot of Tetra Pak technicians awake during the nights. During the 1960s demands for more ergonomical solutions started to grow in Sweden, which the transport solutions of the Tetra Brik-systems fulfilled.[57]

With the launch of Tetra Brik Aseptic the distances in time and space were eliminated. Milk, Juice and other liquid products were now products without boundaries; they could be transported all over the world.[58] No refrigerated distribution was needed, the product safety was improved and the shelf life of the products was prolonged with the TBA. Still today no other package shape offers as high distribution efficiency trough the whole value chain, as Tetra Brik Aseptic packages does, even with openings applied. The package meets the basic convenience demands of the consumers. It is easy to store, safe and hygienic and provided at a low cost. The TBA is now offered in a wide range of different volumes and shapes. These are available with a range of openings, to suit the brand image and meet consumer requirements (see figure 2).[59]

Figure 2: Shows the development of the TBA package.

The packaging material for TBA is composed of a laminate of paperboard, polyethylene and aluminium foil of which the only material to touch the contents of

[55] www.tetrapak.com Tetra Pak Visited: 2005-03-11
[56] Bernier, L. Tetra Pak Carton Ambient www.tetrapak.com
[57] Leander, L. 1996. p. 105 ff
[58] Ibid. p. 147
[59] www.tetrapak.com Tetra Pak Visited: 2005-03-11

the package is food grade polyethylene (see figure 3). The material may be printed using flexography, rotogravure or offset lithography. It is the paper in the laminate that makes the package stiff the plastic makes the package liquid-tight, and the aluminium foil shuts light, aroma and oxygen out from disturbing the content. [60]

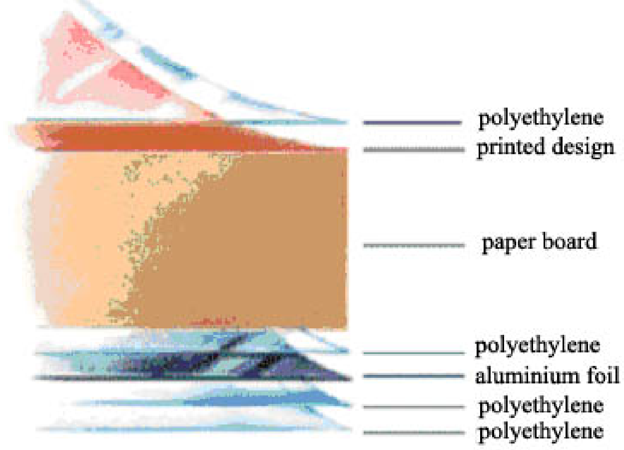


Figure 3: Shows the different layers in a TBA package from above with the outer layer first.

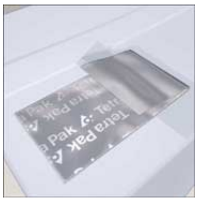
4.1.1 Openings available for TBA[61]

In the portfolio of Tetra Pak there are different types of openings available for the TBA. All the plastic openings are injection moulded[62].

Perforation

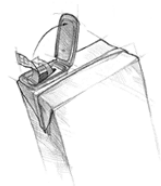
The perforation is a low cost opening that does not require any additional material. By perforating the package the consumer is able to open the package by tearing of the corner, without having to use scissors. The aluminium foil and the polyethylene layer are not perforated in order to protect the content and to maintain the barrier properties of the package.

Pull Tab



PullTab is the aluminium tab that covers the hole in the package. The Tab is applied to the package in the filling machine by a special unit. This type of opening is more complex than the perforation, since a hole is made in the packaging material before the package is filled. When the outer tab is torn away, the Inner Strip is also removed as this polyethylene layer is sealed to the aluminium tab. The PullTab is available for all TBA sizes.

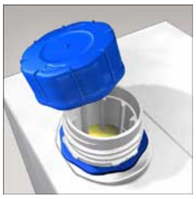
ReCap



The ReCap is a flat flip cap that makes the package recloseable but not reclosable. The ReCap is made of polypropylene. The ReCap is glued on to Pull Tab packages by hot melt.

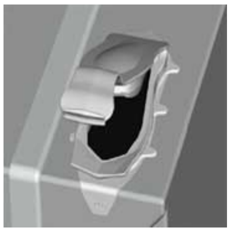
[60] www.tetrapak.com Tetra Pak Visited: 2005-03-11
[61] www.tetrapak.com Tetra Pak Visited: 2005-03-08
[62] Sickert Lars Tetra Pak R&D Spring 2005

StreamCap



The StreamCap is a new screw cap that is available also for some of the TBA packages. The StreamCap can be opened in one operation and is very tight when it is re-closed. This cap has a ring that indicates if the package has been opened. The hole in the package is pre-punched during the converting process. The aluminium and polyethylene is kept intact. When the cap is twisted for the first time to open the package, a small set of plastic teeth cut and then push away the pre-laminated membrane. The StreamCap is made of PE. After the package has been opened the first time the re-sealability helps to preserve the taste, it also allows the package to be turned upside down and shaken.

FlexiCap



FlexiCap is a low-cost re-closable opening available also for some TBA. This is a flip-cap opening, which is applied to the package using the technology of direct injection moulding. Packages with this opening are available exclusively for UHT milk. This opening offers the consumers a package opened in one operation with good pouring and re-closing performance, tamper evidence. The pouring from this opening is guided by the v-shaped hole.

ReCap3

ReCap3 is a modern designed re-closeable opening. When the consumers tear off the tab, sharp cutting teeth ensure its clean and effortless removal. ReCap3 is providing a good control when pouring and it also limits product residues. The special design makes the lid stay open while pouring. This opening device consists of a flip-cap and a PullTab. The cap is made of polypropylene (PP) and has a new design as compared to previous ReCap.

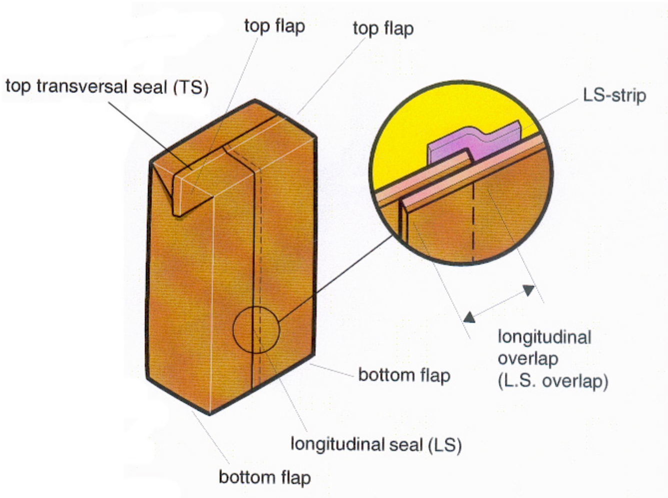
SlimCap

The SlimCap is the newest opening innovation for TBA. SlimCap consists of a screw cap and a ring-pull, both made entirely of HDPE material, and a standard PullTab opening, made of aluminum. The ring pull is attached to the PullTab. The main function with the adding of SlimCaps is convenience for the consumers. The SlimCap makes the package easy to open, it also contribute to make the pouring easier to control and more accurate. The cap makes the package completely reclosable which protects the product and it also makes the storing and handling after it has been opened easier. The package is still highly competitive when it comes to distribution efficiency and environmental profile. The TBA with closure still maintains its good space/shelf-efficiency, which it's famous for. The opening process for a SlimCap is divided into two steps fist; by unscrewing the cap two little plastic wings breaks that function as a tamper evidence, secondly you pull a plastic ring that opens the PullTab.

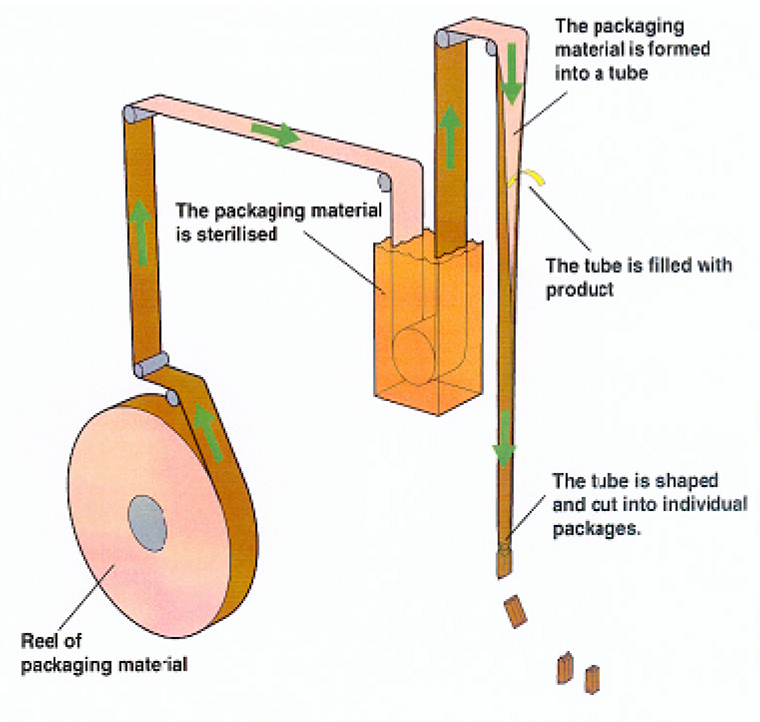
Straw hole

The straw hole is punched in the package in the converting plant and a straw is applied to the package in the packaging line. Various types of straws are available.

4.1.2 Filling machine for TBA



The packaging material comes on reels to the filling machine. A strip of laminated plastic (LS-strip) is applied along the inside of the packaging material. Only half of the strip is sealed to this edge of the packaging material. The other half is sealed to the other edge when the packaging material is formed into a tube. This strip is covering the seal on the inside of the package to prevent product from soaking the edge of the paperboard of the longitudinal seal. The material is then sterilized in a peroxide bath. After the peroxide bath the material is dried with heated air. The material is then formed into a tube and the tube is filled with the product. In a TBA there are three different seals. First the packaging material is formed to a tube and sealed longitudinal. After the filling the bottom and top is transversally sealed below the level of product in the tube. This sealing is made by induction heating. The aluminium layer in the packaging material is used to heat and melt the polymer. After the transversal sealing the tube is cut into separate packages. Last comes the sealing where the TBA gets its final shape. The flaps in both the bottom and top are held down when folded by a seal made with hot air. The outer polymer coating is melted and pressed against the sides and the bottom of the package. When the polymer is cooled the flaps are sealed.[63]



[63] Training Document Basic Course TBA

4.2 Tetra Recart (TRC)

Tetra Recart is a carton package that can be used to pack wet shelf-stable products of any size. Products like rice, beans, tomatoes and pet food are examples that can be packed in Tetra Recart. This package makes it possible for Tetra Pak to offer a packaging solution for food that has traditionally been packed in cans and glass jars. The material used in the Tetra Recart allows the product in the package to be sterilized in the same way as the traditional canning process.[64]

The Tetra Recart delivers benefits along the whole value chain. The consumers get a lightweight package that is easy to carry home and easy to pour from and easy to reseal.[65] A benefit compared to the can is the easy opening that doesn't require any tool and does not present any sharp edge.[66] When the TRC is empty it takes little space in the bin and fits in the existing waste recycling system for carton packaging. The TRC is 30-40% more economical in use of shelf place and offers an unrivalled handling efficiency, which is very important for the retailers and distributors.[67]

Special packaging material and new forming and sealing technology have made this package possible.[68] The packaging material in Tetra Recart is of the same kind of laminar structure as the one used in the TBA but modified to cope with retorting.[69] The Tetra Recart is a carton package that can be taken through a retorting process where both the package and the product get commercially sterile at the same time. The big difference with the materials in the Tetra Recart compared to other beverage cartons is that the carton board is moisture-resistant and that the used polymers are heat-resistant.[70] The material in the TRC is of a laminar structure. Today ethyl-vinyl-alcohol (EVOH) and aluminium are used as barrier materials.[71] The material used in the package is recyclable and complies with Food and Drug Administration (FDA) and United States Department of Agriculture (USDA) standards.[72] The first product to be packaged in a Tetra Recart was launched in 2003.[73]

4.2.1 Openings available for TRC

The only available opening for the Tetra Recart is the Tetra Recart perforation. The perforation makes the package easy to open and is one of the things contributing to the convenience the TRC offers. The opening of a Tetra Recart does not require any tools. To open the package one has to unfold the top and tear along the laser made perforation (see figure 4).[74]

[64] News release 8/7-2004 www.tetrapak.com
[65] News release 6/4-2005 www.tetrapak.com
[66] News release 8/7-2004 www.tetrapak.com
[67] News release 6/4-2005 www.tetrapak.com
[68] Ibid.
[69] Sickert, L. 2005-06-29
[70] Tetra Recart… Brochure from www.tetrapak.com
[71] Kjellstrand, M. 2005-04-20
[72] News release 8/7-2004 www.tetrapak.com
[73] News release 6/4-2005 www.tetrapak.com
[74] www.tetrapak.com

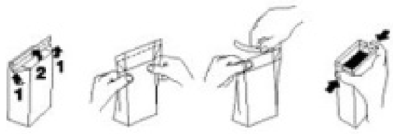
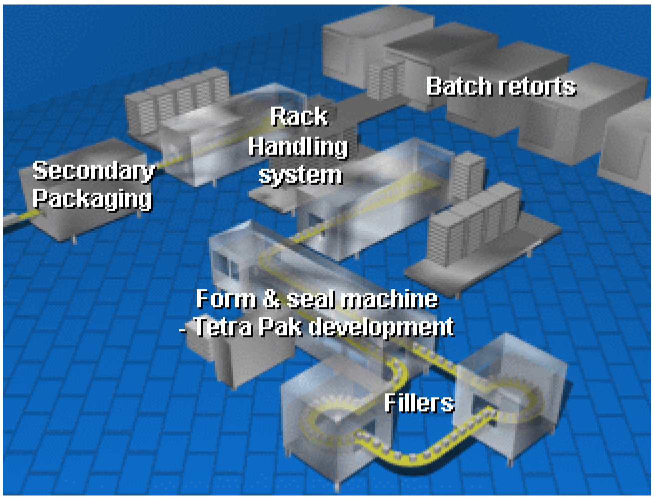


Figure 4: Illustrates the opening procedure for a Tetra Recart[75].

4.2.2 Filling machine for TRC



The cartons arrive in boxes to the Tetra Recart line. They are manually placed in the Automatic Carton Loader, which automatically feed them into the Form & Seal Machine (FSM). When the packages have been top sealed with Induction Heating they leave the FSM to be filled in an external filler. In the filler the packages are bottom filled with product i.e. the package is upside down when filled. When filled, the package returns to the FSM where they are sealed in the bottom with induction heating. The filled and sealed packages are fed into the Final Folder Unit where the top- and bottom flaps are folded and sealed with hot air.[76] There is a need for sterilization of the packages and its content before the packages can be packed for distribution. The sterilization in the TRC system is based on batch retorts, which sterilise the package and the content at the same time.[77]

4.3 Material converting processes

When it comes to material converting processes only injection moulding and extrusion coating are relevant for this study and thus the only ones included in this chapter. Injection moulding is a process usable to produce for instance caps for the TBA and the extrusion coating is used to produce laminar structures like the ones used as packaging material in the TBA and TRC.

When producing a part one has to consider that there are a lot of different aspects that together shape the final result. Important aspects are: function, resistance for environmental impact (heat, mechanical forces, friction, voltage, chemicals), material, batch size, converting process and cost.[78]

4.3.1 Injection moulding

Injection moulding is the dominating method for producing plastic parts. During the process very high pressures are used from 20 up to 100 MPa or even higher. The parts produced can achieve a surface roughness ranging from rough to very fine (even so

[75] www.tetrapak.com
[76] http://tetrarecart.tetrapak.com/Departments/EquipmentDevelopmentSupply/Technical%20Training/TRC-MD-010.pdf Visited: 2005-06-07
[77] http://tetrarecart.tetrapak.com Visited: 2005-06-08
[78] www.plastinformation.com/Informationsmaterial/infomaterial_index.html Visited: 2005-02-18

fine it measures up to optical quality). The shapes produced with this method can be simple to very complex. [79]

The Injection moulding machine consists of three different main components; the injection unit, the mould and the clamping system. The injection unit prepares the plastic melt. The melt is then transferred via the injection unit to the mould. The mould is opened and closed with the clamping system. The moulding process is divided into five different steps:[80]

1. *Plasticizing*: The plastic is heated and melted.
2. *Injection*: The melted plastic is forced, with pressure, into the mould.
3. *Afterfilling*: The after filling is due to compensate for decrease in volume of melt during solidification and to prevent backflow of melt.
4. *Cooling*: The plastic in the mould is cooled until its rigid enough to be ejected.
5. *Moulded-part release*: The mould is opened, the part is ejected and the mould is closed.

4.3.2 Extrusion coating

When extrusion coating, the extruded film is rolled onto the surface of a desirable material that can be film, foil, paper or a laminate.[81] The molten polymer is then cooled to form a continuous coating[82]. The extrusion coating process is schematically described in figure 5. This process is normally working at a speed over 10m/s; some processes are designed to work up to 15m/s. When coating paper the highest speeds are generally reached. [83]

The extruder is supplied with plastic in granulate. The granulate is heated into a low viscosity mass when fed through a heat cylinder by a rotating screw. The melted plastic is then to be pressed trough a nozzle of which the shape of the profile is decided and thereby also the shape of the produced product. The pressure used in this process range from 1 to 5 MPa. [84]

Corona is a surface treating method to increase the surface energy of films, foils, paper and polymers. One purpose of the treating is to increase the adhesion of coatings.[85]

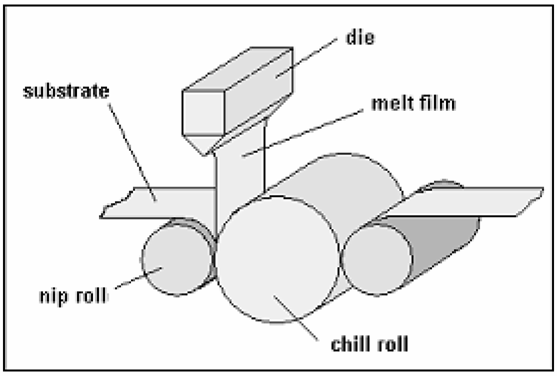


Figure 5: Describes schematically the extrusion coating process[86]

[79] www.plastinformation.com/Informationsmaterial/infomaterial_index.html Visited: 2005-02-18
[80] Rosato, D. et al. 2000.
[81] Glyde, B. 1990. p. 40
[82] www.pac-it.org.nz/booklet/glossary/
[83] Osborn, K. R. et al. 1992. p. 101 f
[84] www.plastinformation.com/Informationsmaterial/infomaterial_index.html Visited: 2005-02-18
[85] www.enerconind.com/treating/resources/basics.html Enercon Visited 2005-05-17
[86] Toft, N. Tetra Pak R&D Power Point presentation Chalmers 2005-02-07

5. Demands

In this chapter the reader is deeper introduced to the different demands that occur for TBA and TRC along the value chain.

5.1 Packaging Demands

Different demands on a package occur during the whole value chain. The material converting and filling process adds other important demands on the packaging material[87]. Both thermal and mechanical properties of the packaging material are important for the processing of the packaging material but also for the use[88].

The demands on the package can be divided into three main groups: Barrier functions, grip stiffness and integrity. These three groups of demands can in turn be derived to demands on the packaging material and in turn certain demands on the polymer.[89]

5.1.1 Barriers

A barrier is according to the Institute of Food Technologists defined as: "A layer of material designed to prevent migration of unwanted elements into a package."[90] Depending on which product that is packed different needs of barriers against gases, light, aromatic substances, moisture and microorganisms occur[91]. Oxygen that migrates into a package can give changes in nutritional value trough deterioration of fatty acids, amino acids or vitamins. It can also cause development of off-flavors and discoloring components. Light can accelerate chemical processes like denaturation of proteins and destruction of light sensitive vitamins. Odour can cause taste changes of the packed product. Changes in consistency can be caused by moisture. Microorganisms cause changes of the product.[92]

Different packaging materials have different properties concerning barrier functions, i.e. the materials have different permeability for different substances. The permeability is dependent on the surrounding pressure, temperature and concentration. To achieve wanted properties materials with specific wanted qualities are combined.[93] The barrier demands on the package depend on the product, which it is ought to pack. When it comes to barrier functions in laminar packaging material the different materials have different tasks.[94]

The thinnest layer of aluminium foil in the packaging is a complete barrier and prevents the loss of valuable aromas and protects contents against light, oxygen, moisture and contamination. Aluminium foil is used as a barrier in TBA. It is the crystalline structure of the aluminium that provides a high performance barrier even at thicknesses under 6.5µm. It is non-reactive except to substances of high acidity or alkalinity, it is also non-absorbent and proof against grease, oil, water and other liquids. Aluminium foil is safe for use in contact with food. It is also tasteless and odour-free. The metal is light, strong and very flexible and can be easily deformed to a large degree without loosing its barrier integrity. It can be easily laminated with

[87] Toft, N. 2005-06-01
[88] Weber, C. J. 2000. p. 30
[89] Toft N. Spring 2005
[90] www.ift.org/cms/?pid=1000419#pack 2005-06-03
[91] Thorén, A. et al. 2000. p. 104
[92] Jönson, G. et al. 2001. p. 43 f
[93] Thorén, A. et al. 2000. p. 104
[94] Toft, N. 2005-06-01

other materials. The foil enables significant reductions in thickness of other substrates in the laminar packaging material. It can be heated to high temperatures without distorting or melting which is ideal for autoclaving and heat-sealing processes. Aluminium foil has a high thermal conductivity, which reduces the energy required for sealing and sterilisation.[95] The aluminum layer with its good conductivity is necessary for sealing with induction heating[96].

EVOH and PVOH are two standard commercial polymer barrier materials. Ethylene-vinyl alcohol (EVOH) is a hydrolysed copolymer of ethylene and vinyl acetate[97]. DuPont produces EVOH under the trade name Elvanol. This is a water-soluble synthetic polymer. EVOH is a versatile polymer that offers a good resistance to oil, grease and solvents. It also offers high tensile strength, flexibility, and high oxygen barrier.[98] Also Kuraray produces EVOH but under the name EVAL, their films provide high barrier properties to oxygen and other gases and to flavor and aroma permeation. The films also offer a very good resistance to oil and organic solvents. It also has a good UV-resistance. The surface can easily be printed on without any special treatment and without any loss of the barrier properties. EVOH is a thermoplastic with a very good processability. It can easily be processed with conventional thermoplastic converting equipment. EVOH fulfill the requirements for materials in food contact. The material is also fully recyclable and multilayer structures containing EVOH can be recovered or reused.[99]

Polyvinyl alcohol (PVOH) is a polymer of vinyl alcohol. Polyvinyl alcohols are produced by polymerization of vinyl acetate. The produced polyvinyl acetate is then undergoing alcoholysis.[100] Mowiol and Kuraray Poval are trade names for polyvinyl alcohols produced by Kuraray. The grades are available as colorless granules or powders. PVOH can be used in a manifold of applications and is non-toxic. It has approvals for a variety of applications for instance as components of paper and paperboard in contact with aqueous and fatty/ dry food.[101] The physical properties of PVOH, such as the strength, water solubility; gas permeability and thermal characteristics vary with the degree of crystallinity, which is dependent on the degree of hydrolysis and the average molecular weight of the polymer.[102]

5.1.2 Grip stiffness

When it comes to the grip stiffness of the package it is the bending force on the packaging material and the E-modulus of the polymer that are considered. If the E-modulus of the polymer is high, it gives a good contribute to the stiffness of the package, it can even make it possible for thinner carton board in the laminate. The grip stiffness is needed to facilitate the handling of the package through the whole value chain.[103]

[95] www.alufoil.org/eng/alufoil_158.html Visited: 2005-06-02
[96] Training Document Basic Course TBA
[97] Brandrup, J.et al. 1999.
[98] www.dupont.com/industrial-polymers/elvanol/pdsprint/elvanol_usage.html Visited: 2005-05-30
[99] www.eval.be
[100] Mowiol Polyvinyl Alcohol. 1999.
[101] www.kuraray-am.com/pvoh-pvb/faqs.html#Anchor-What-23240
[102] www.azom.com/details.asp?ArticleID=266#_Poly(vinyl_alcohol) Visited: 2005-05-30
[103] Toft N. 2005-06-01

5.1.3 Integrity

To make an aseptic package it is important that the package is tight. This leads to demands like a high breaking strain in the polymer to avoid crack propagation into the polymer, when folding the packaging material. Mechanical properties like elongation at break, stress at break and impact strength are important properties of the polymer.[104]

5.2 Converting demands

For a polymer to be useful as a laminate in a packaging material it has to be processable in foremost extrusion coating. The outer polymer on the packaging laminate also has to be printable since there has at least to be a date on the package[105]. In laminar packaging material adhesion between the different layers is very important.[106] Adhesion, thermostability, rehology, and oxidative stability are the demands on the polymer material[107].

5.3 Filling machine demands

A packaging material used in a normal TBA filling-line has to be able to put a cap on. The different caps are applied with different methods and have thus different demands on the packaging material. The material also has to withstand the sterilization process which is a peroxide bath. The laminar longitudinal strip has to be able to put onto the inside of the packaging material. It has to be sealable with induction heating or ultrasound for the longitudinal and transversal seals. It also has to be able to seal with hot air to seal the flaps to the package[108]. For materials used in packaging laminates for Tetra Recart they also have to be retortable[109]. This means following demands on the polymer: Elasticity, water barrier, acid/basic stability, sealability and peroxide resistance[110].

5.4 Summary of the demands

When the packaging, converting and filling machine demands are considered the following properties are important for a polymer used in a beverage carton like TBA or TRC:

- Barriers –Gases, water vapour & light
- E-modulus
- Strain at break
- Stress at break
- Impact strength
- Adhesion
- Thermostability
- Rehology
- Oxidative stability
- acid/basic stability
- Sealability
- Peroxide resistance
- Retorting (only for TRC)

[104] Toft, N. 2005-06-01
[105] Sickert, L. Spring 2005
[106] Training Document Basic Course TBA
[107] Sickert, L. Spring 2005
[108] Training Document Basic Course TBA
[109] http://tetrarecart.tetrapak.com Tetra Pak Visited: 2005-06-08
[110] Sickert, L. Spring 2005

Not all of these properties will be further dealt with in this thesis. The properties that are tested in this thesis has been selected together with the supervisor at Tetra Pak. The properties selected for testing are chosen on their ability to give a broad picture of the materials possibility to be used in a Tetra Pak application the selection is also based on what tests the polymer laboratory has been able to assist with and the time frame of the thesis.

The barrier properties against oxygen and water vapour are the only barrier properties to be investigated, or rather the transmission rate of oxygen (OTR) and water vapour (WVTR), since they are very important barrier properties when it comes to food-packaging and can serve as important indicators on the materials suitability for use in a Tetra Pak application.

The E-modulus is the slope of the stress-strain graph in the linear area. The linear area however does not exist for polymers, in real life, since they are viscoelastic i.e. there is always a deformation of the material. The E-modulus for different materials is however in the same order as the storage modulus for the same materials, the value is however not necessary the same for E-modulus and storage modulus. The E-modulus or rather the storage modulus is measured since it is an important property of the polymer for the grip stiffness.

The adhesion between the PHA materials and carton board is tested, since the adhesion is a decisive property for a polymer to be used in a laminar package material.

The rheology of the materials is investigated since it contributes with important information about the molecular structure of the material and is thus important knowledge when for instance the material is extruded.

For a polymer to be usable in a Tetra Recart the ability to withstand a retorting process is a decisive property.

Impact strength, thermostability, oxidative stability, acid and basic stability, sealability and peroxide resistance are left to future investigations.

6. Polymers

The materials used today are presented as well as a short biopolymer overview that includes the more or less potential materials for the production of TBA and TRC in the future.

6.1 Polymers used today

In the TBA package and in closures for the TBA the only polymers used today are polypropylene, polyethylene and high-density-polyethylene.

6.1.1 Polypropylene (PP)

Polypropylene is used in closures like ReCap and ReCap3[111]. Polypropylene (see table 1) is a partly crystalline thermoplastic with a high fatigue resistance[112]. A thermoplastic material can be melted and shaped more than once[113]. PP is getting brittle in temperatures below -20^{o}C. The PP is deteriorated by UV-light. The PP is stiffer than HDPE and maintains its mechanical properties better at high temperatures than HDPE. The mechanical and electrical properties are kept even in water. PP is suitable for injection moulding, hot forming, blow forming and extrusion.[114]

Properties	PP
T_g (glass transition temp.)	-20 – (-10) ^{o}C
T_m (melt temp.)	160-175 ^{o}C
ρ (density)	900-910 kg/m^3
Color	white, transparent
Strain at break	12 -600%
Stress at break	31-41 MPa

Table 1: The properties of PP [115].

The WG341C from Borealis is used as a layer in TRC. The WG341C is a blend of PP standard grade with about 30% PE to gain a good processability.[116] WG341C is developed specially for extrusion coating and coextrusion coating applications at high speed. Paper and board coated with WG341C receive a high grease and temperature resistance. They can even be submerged into boiling water for a period of time without deteriorating. This material can be processed on lines designed for LDPE. The WG341C fulfil the requirements for food contact. [117]

6.1.2 Polyethylene (PE)

Polyethylene is used in caps and in some of the layers in the laminar package material used in the TBA[118]. Polyethylene (see table 2) is also a partly crystalline thermoplastic. The PE can be used in contact with food.[119] PE possesses a lot of positive properties. It is waterproof, enables sealing of the package, possible to apply

[111] www.tetrapak.com
[112] Klason, C. et al. 1995. p. 113-114
[113] Training Document Basic Course TBA
[114] Klason, C. et al. 1995. p. 113-114
[115] Klason, C. et. al. 1995 and www.maropolymeronline.com and www.boedeker.com
[116] Sjölin, R. Spring 2005
[117] www.borealisgroup.com/public/customer/data_sheets/Data_sheets.jsp Visited: 2005-05-19
[118] www.tetrapak.com Tetra Pak
[119] Klason, C. et al. 1995. p. 110-112

in thin layers, transparent and thus does not affect the printed design on the carton board. PE is also chemically resistant which means that it does not react with other substances. Some negative properties are that it does not resist much heat or cold, it is fat-soluble and a poor oxygen barrier.[120] The PE is difficult to print on without surface treatment. The mechanical properties are highly temperature dependent. .[121]

The polyethylene is divided into two density groups: Low-density-polyethylene (LDPE) and high-density-polyethylene (HDPE). LDPE and HDPE are suitable for blow forming, hot forming, injection moulding, extrusion and rotation moulding.[122] Tetra Pak mainly uses LDPE[123].

Properties	**LDPE**	**HDPE**
T_g	-120 – (-25) °C	-120°C
T_m	98-125 °C	115-140 °C
ρ	0,910-0,940	0,940-0,965
Color	White, transparent	white, transparent
Strain at break	100- 650%	10-1200%
Stress at break	8-30 MPa	22 – 31 MPa

Table 2: The properties of PE[124].

6.2 Overview Biopolymers

Biopolymers are the name for biodegradable polymers whose parts are derived entirely or almost entirely from renewable raw materials.[125] There are different types of biodegradable polymers, biopolymers, produced by different companies around the world. Biopolymers are growing fast, the consumption 2003 was the double referred to the consumption 2001. IBAW sees biopolymers as a great contributor in achieving sustainable development.[126] IBAW is an organisation networking in the fields of biobased materials, especially biodegradable polymers[127]. IBAW stands for Interessengemeinschaft Biologisch Abbaubare Werkstoffe[128] or International Biodegradable Polymers Association in English[129].

6.2.1 Starch based polymers

Starch based polymers are thermoplastic materials that are based on starch. They are biodegradable and incinerable. The densities of starch-based polymers are higher than most conventional thermoplastics and also higher than most biopolymers. The high densities are decreasing their price competitiveness on volume basis. The oxygen and carbon dioxide barriers are moderately good but the sensitiveness to moisture and water contact and high water vapour permeability limits the possible packaging applications for the material.[130] Mater-Bi is a starch-based polymer produced by the

[120] Training Document Basic Course TBA
[121] Klason, C. et al. 1995. p. 110-112
[122] Ibid.
[123] Training Document Basic Course TBA
[124] Klason, C. et. al. 1995 and www.maropolymeronline.com
[125] Stevens, E. S. 2002. p. 104
[126] www.ibaw.org
[127] www.biomatnet.org/secure/Other/S1396.htm Visited: 2005-07-29
[128] www.ibaw.org/deu/seiten/home_frameset.html Visited: 2005-07-29
[129] www.ibaw.org/ Visited: 2005-07-29
[130] Crank, M. et al. 2004. p. 13-18

Italian company Novamont[131]. It is made from the renewable material, non-genetically modified starch in maize and is available in granular form, with different formulations[132]. Mater-Bi can be processed with the same processes as conventional polymers with a similar output. The polymer can be printed on with normal ink and printing methods. It can also be coloured in bulk, using biodegradable master-batches. Mater-Bi can be sterilized using gamma rays.[133] The permeability to water vapour of films made of Mater-Bi is much greater than of PE. Mater-Bi is completely biodegradable in different environments; in composting, in the soil in fresh and in salt water.[134]

6.2.2 Polylactic acid (PLA)

PLA is derived from lactic acid in renewable resources such as potatoes, corn, wheat or sugar beets[135]. Sugars are processed from the starch[136]. The lactic acid is extracted by fermentation of the sugars, by lactobacillus[137]. PLA is considered to have a large potential since it can be produced in large scale at a rather low cost. Today PLA is the only biopolymer that is produced in large scale.[138] NatureWorks LLC is producing corn-based PLA[139] named NatureWorks PLA[140].

PLA is water resistant and can only withstand temperatures up to 55 degrees C. It is mostly used for production of different types of packages[141]. PLA has a good odour and flavour barrier and a high resistance to oil, grease and moisture. This makes the PLA suitable for packaging applications for viscous oily liquids. The PLA is also considered to be well suited for packaging of dry products and short shelf-life products. The poor oxygen, carbon oxygen and water barrier makes it unsuitable for packaging carbonated beverages and other liquids.[142]

PLA can be copolymerised with other material in order to be either rigid or flexible. PLA can be made with different mechanical properties in order to be appropriate for different manufacturing processes such as injection moulding, sheet extrusion, blow moulding, thermoforming, film forming, fibre spinning[143] and extrusion [144]. PLA is a non-volatile, odourless polymer and is classified as GRAS (generally recognized as safe) by the Food and Drug Administration in the US[145].

The polymer is made from 100% renewable resources. It is fully compostable in commercial composting facilities.[146] Since the PLA has to be hydrolysed at elevated temperatures (>85°C) before it can biodegrate, it will not be able to degrade in garden composts. Under normal use and storage conditions the PLA is rather stable.[147] PLA can be converted back to monomers, which then can be turned into

[131] *Fakta om biopolymerer…* www.plastinformation.com/Informationsmaterial/infomaterial_index.html
[132] Crank, M. et al. 2004.
[133] www.biogroupusa.com/mater_bi.htm
[134] Crank, M. et al. 2004.
[135] *Fakta om biopolymerer…* www.plastinformation.com/Informationsmaterial/infomaterial_index.html
[136] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-11
[137] Ahvenainen, P. 2003 p. 521 f
[138] *Fakta om biopolymerer…* www.plastinformation.com/Informationsmaterial/infomaterial_index.html
[139] www.natureworksllc.com/corporate/nw_pack_food.asp Visited: 2005-02-10
[140] www.foodproductiondaily.com/news/printNewsBis.asp?id=57598 Visited: 2005-02-21
[141] *Fakta om biopolymerer…* www.plastinformation.com/Informationsmaterial/infomaterial_index.html
[142] Crank, M. et al. 2004. p. 31
[143] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-11
[144] Ahvenainen, P. 2003 p. 521 f
[145] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-11
[146] Ibid.
[147] Crank, M. et al. 2004. p. 31

new polymers. PLA biodegrades into water, carbon dioxide and organic material.[148] Today the main obstacles for PLA are the lack of a composting infrastructure in the European, Japanese and US markets and the price of the raw material [149].

6.2.3 Polyhydroxyalkanoates (PHA)

Just as PLA, Polyhydroxyalkanoates are produced via fermentation of renewable feedstock. The fermentation of carbon substrate is a process that's taking place within the microorganism.[150] PHA is a family of renewable polyesters[151]. Polyhydroxybutyrate (PHB) is the most common in the PHA family[152]. There are about 250 known organisms that produce PHA, but only a few of them can produce PHA at a high concentration. More than 90 different monomers from different organisms have been found to be potential PHA building blocks.[153] The composition of the PHA is dependent on the carbon source and the microorganism[154]. The material can be either thermoplastic or elastomeric, with melting points ranging from 40 to 180°C[155]. PHA have low water vapour permeability, close to the one of LDPE, this is of special interest when food packaging is concerned.[156] The PHA will be further described in chapter 8.

6.2.4 Other biopolymers

There are other types of biopolymers: Cellulose polymers are produced from wood pulp, which result in for instance cellophane. This is a rather expensive packaging material but with good characteristics and is used for instance in packaging of wrapping paper for candy and tobacco. Protein based polymers are derived from gluten, soya and gelatine. This type of polymers is used for production of medical devices with special requirements. Combination polymers are a group of polymers where a normal synthetic polymer is mixed with 5-10% starch based polymer in order to achieve wanted rate of compost ability. [157]

[148] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-11
[149] Ahvenainen, P. 2003. p. 521
[150] Crank, M. et al. 2004.
[151] www.bpiworld.org/Files/Article/ArtXRU8ov.pdf
[152] Weber, C. J. 2000. p. 25-26
[153] Chakraborty, P. et. al. Paper 2004
[154] Weber, C. J. 2000.p. 25-26
[155] www.designinsite.dk/htmsider/m0955.htm
[156] Weber, C. J. 2000. p. 25-26
[157] *Fakta om biopolymerer…* www.plastinformation.com/Informationsmaterial/infomaterial_index.html

7. Environmental aspects

In this chapter the reader is deeper introduced to sustainability, the different recovery methods both in general and the ones used for beverage cartons like TBA and TRC. The reader will also be introduced to Life cycle Assessment (LCA).

7.1 Sustainable development

The Brundtland Commission defines sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs", in the report Our Common Future 1987. According to this report the sustainable development is based on three dimensions: environmental, economical and social.[158]

The environmental aspect is often an important factor when choosing packaging system. Consumers are increasingly demanding more environmentally friendly packaging but the pressure for environmental friendly packaging is also coming from EU directives.[159] The environmental impact of a package is very much based on the material of the package. Different materials use different amount of energy in production and in the recycling process. In Sweden the packaging industry was one of the first businesses that got a "producer responsibility". This means that the producer has the physical and the economical responsibility for the product even after it's been consumed. The purpose is that the environmental cost should be calculated and taken into consideration as early as in the product-developing phase. The aim with "producer responsibility" is to drive the development to more environmental thinking.[160]

7.2 Recovery methods in general

There are different methods to recover used packages: reuse, recycling, incineration, composting and landfilling[161]. Both recycling and composting aims to recover the material in the packages while incineration can be an energy recovery method[162]. The recovery methods can be placed in a hierarchy, where some methods are more preferable than others. The environmental impacts of waste are not just limited to their disposal. The processing, manufacture and transport of materials use energy and resources and thus create pollution before they end up as waste. To reduce waste is regarded as the best option in the waste hierarchy. The reduction of waste is including: cutting down on throwaway products and excess packaging as well as only buying what is needed.[163] Independent of what recovery method that is used, three major components are required in order for the method to function. There must be a consistent and reliably source of recycled material and methods for processing the recycled material into a suitable form for reuse. Last but not least a market for the reprocessed material must exist.[164]

[158] www.unido.org/en/doc/3563 Visited: 2005-04-12
[159] Pendegrast, G. et al. 1996. p. 60
[160] Dominic,C. et al; 2000. p. 131-133
[161] Jönsson, G. et al. 2001. p. 98-99
[162] Dominic, C. et al. 2000.
[163] www.wasteonline.org.uk/resources/Education/WorkatWasteatSchool_files/page2.html
[164] Selke, S. E. M. 1990.

7.2.1 Reuse

When a package is reused, the original package is reused without alterations. Normally only cleaning is needed[165]. Reusing is more energy efficient than recycling, since no extra energy or raw materials are required to get a second use[166]. The reuse of a package extends its life and prevents the purchase of new ones[167].

7.2.2 Recycling

Recycling is primarily concerning material recycling. Paper, aluminium and glass have well established recycling facilities, while plastics still have few compared to the need[168]. There are about 50 different groups of plastics, with hundreds of different varieties. All the types are recyclable. It is when the materials are mixed that they are difficult to recycle.[169] The recycling method can be divided into two types a primary and a secondary one. The primary recycling is a closed loop, when recycled products are used to make the same or similar products, for instance when glass bottles become new glass bottles. The primary one is regarded as having a higher value than the secondary. The secondary recycling is when the material is used to produce new products with less strict specifications.[170] The use of recycled material in packages has increased which has led to an increased attention to the safety of these materials. When the safety of recycled packaging material is evaluated there are three main aspects: the source of the materials, the nature of the process and the conditions of use. [171] Recycling reduces the amount of waste to be landfilled or incinerated and the need of energy. Although recycling reduces the need for virgin raw material it can never replace the whole need. That's why it's very important to reuse materials as much as possible before recycling them.[172]

7.2.3 Incineration

When waste is incinerated it can be done with or without energy recovery. The heat from the incineration can be used to generate energy[173]. Incineration is a oxidative degradation of waste at a high temperature. The main advantage is that the process reduces the volumes of waste.[174] Although the modern incinerators are constructed so they can produce energy for heat and/or power and to minimise the resultant air pollution there still remains concerns with this method. Some of the concerns are the production of dioxide emissions from incineration as well as the remaining waste, ash and other materials. The remains from the incineration are often landfilled and are a concentrated end product, often more toxic than the original waste. The incinerators are also extremely costly to build.[175]

[165] Jönsson, G. et al. 2001. p. 98-99
[166] www.raceagainstwaste.com
[167] www.wasteonline.org.uk/resources/Education/WorkatWasteatSchool_files/page2.html
[168] Jönsson, G. et al. 2001 p. 98-99
[169] www.raceagainstwaste.com
[170] Selke, S. E. M. 1990.
[171] Risch S. J. 2000. p. 104
[172] www.wasteonline.org.uk/resources/Education/WorkatWasteatSchool_files/page2.html
[173] Ibid.
[174] www.colebrand.com/wastinc.htm
[175] www.wasteonline.org.uk/resources/Education/WorkatWasteatSchool_files/page2.html

7.2.4 Landfill

When decomposing organic waste in landfills, biogas can be drawn off and used to provide energy. Environmental concerns with landfilling are for instance the risk for leakage of chemicals and other substances into water and surroundings. Finding new sites to landfill is hard and as sites fill up, waste has to be transported longer distances, increasing pollution from carbon dioxide emissions. The methods for landfilling have been developed and modern landfill sites can now be capped and lined to prevent leakage.[176]

7.2.5 Industrial composting

A package is compostable when it can be biodegraded in a compost process. To claim compostability it must have been demonstrated that it can be biodegraded and disintegrated in a compost system, and completes its biodegredation during the end use of the compost.[177] Biodegradation is the degradation caused by biological activity, especially enzyme action, leading to significant change of chemical structure of material with no time limit[178]. The European Directive on packaging and packaging waste has been driven and speeded up the process for getting specific standards on compostability[179]. A package is considered to be compostable if all of its components have individually been qualified as compostable.[180]

7.3 Recovery methods for beverage cartons

After use the Tetra Brik Aseptic and the Tetra Recart can go through all waste management options: It can be recycled to recover the component materials or the energy that the packages contain can be recovered in municipal incinerators or in industrial plants. Trials have shown that cartons can also fit into composting programs. If there are no other appropriate recovery options available, the packages can safely go to landfills.[181]

Tetra Pak believes in an integrated waste management system where each of these alternatives has an important role to play. Which waste management method that is best depends on local conditions like transport distances, collection systems, markets for recycled products, existing waste management infrastructure, legislation and costs. Since these conditions vary a lot in different countries, flexibility in choosing an optimal combination of waste management options is important.[182]

The most common way to recycle used beverage cartons like TBA and TRC is to recover the fibres at paper mills using hydrapulpers. In this process the baled cartons are sent to paper mills for recycling, were the cartons are dropped into a hydrapulper filled with water. The mixture is agitated for 15-30 minutes to separate the fibres from the polyethylene. A hydrapulper recovers more than 90% of the fibres in beverage cartons. The last step is when the recovered fibres are used for making new paper products like kitchen towels, printing paper, paper bags and tissue paper.[183] In the recycling the packaging material is separated into fibres and polyaluminium

[176] www.wasteonline.org.uk/resources/Education/WorkatWasteatSchool_files/page2.html
[177] www.refuse.ca/www.refuse.ca/BioBag.htm
[178] Ibid.
[179] Weber, C. J. 2000.
[180] Ibid.
[181] www.tetrapak.com
[182] www.tetrapak.com
[183] www.tetrapak.com

(polyethylene and aluminium).[184] Today the energy in the polyaluminium is recovered by incineration[185]. Few solutions have been in place for recycling the polyaluminium until recently, when a new process was developed in Brazil. This process is based on plasma technology. The polyaluminium is heated up to a very high temperature until it turns to paraffin wax (the polyethylene) and pure aluminium with hardly any emissions. The loop is closed when the aluminium is concerned since the supplier of the aluminium foil will use the recycled aluminium to produce new foil.[186]

Life Cycle Assessment (LCA) have shown that energy recovery can be a good complement to recycling from an environmental perspective. TBA, TRC and other beverage cartons are valuable sources of fuel in modern incinerators with energy recovery. The cartons are made primarily from renewable resources and are rich in energy.[187] The cartons cause no dangerous by-products when incinerated[188]. An interesting comparison is that one ton of beverage cartons contains as much energy as half a ton of oil.[189]

It is only the paper fraction of the beverage carton that can be composted. The polyethylene and the aluminium have to be removed from the final composting in a separation process.[190]

The TRC is passing trough the recycling process together with TBA and other beverage cartons without any problems. When making products from the rest-material, when the fibres are removed and recycled, one can choose different ways. One is to make pellets from the material and from that make new products. Another way is to press the material and let heat melt the poleolefins together in its new shape.[191]

7.4 Life Cycle Assessment (LCA)

Life Cycle Assessment is a tool used to evaluate the potential environmental impact, caused by a product, material or service during its whole lifecycle. Environmental impact usually includes acidification and eutrophication caused by discharges in water, air and land. Waste and the usage of natural resources is also included in the analysis[192]. The LCA is built up by three main stages: inventory analysis, impact assessment, and improvement assessment. "Cradle-to-grave" analysis is commonly used to describe the LCA.[193] The method for LCA has been standardized under the ISO 14040 series[194]. The use of LCA helps companies and governments in deciding whether a certain material, product or service is appropriate[195].

[184] www.tetrapak.com Visited: 2005-04-12
[185] Nyström, T. 2005-04-28
[186] www.tetrapak.com Visited: 2005-04-12
[187] www.tetrapak.com *What happens to…*
[188] Nyström, T. 2005-04-28
[189] www.tetrapak.com *What happens to…*
[190] Ibid.
[191] Nyström, T. 2005-04-28
[192] www.plastkretsen.se/aktuellt/cit_gua_rapportsammanfattn.pdf
[193] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-28
[194] www.Nnfcc.co.uk/library/producereport/download.cfm?id=56
[195] http://edis.ifas.ufl.edu/BODY_AE210 Visited: 2005-02-28

8. Poly-Hydroxi-Alkanoates (PHA)

In this chapter the reader will be introduced to poly-hydroxi-alkanoates and three different suppliers.

8.1 The properties of PHA

Polyhydroxialkanoates are a family of bio-based polyesters that are produced by fermentation of carbon substrate within the microorganism. [196] Over 120 of monomer units with different (R)-pending group have been found (see figure 6).[197]

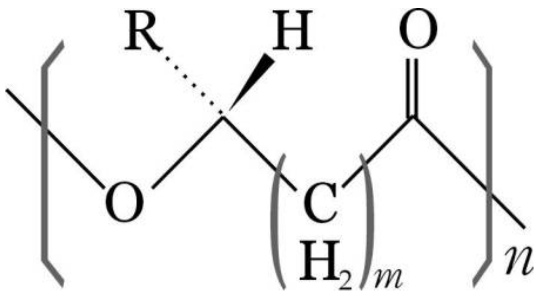


Figure 6: Describes the chemical structure of the PHA molecule in general[198].

The PHA serves as energy reserve material and accumulates as granules within the cells. PHA has a semi crystalline structure with a crystallinity ranging from 40% to 80%.[199] The PHA range from brittle to flexible and elastic, depending on side chain length of hydroxyalkanoates[200]. The PHA family consist of both homopolymers and copolymers.[201] A homopolymer is a polymer where the molecular chain is composed of a great many identical molecules. The copolymer is made up of different types of molecules randomly connected along the chain. Homopolymers are more compact than copolymers; they also have a higher melting point, better stability, greater flexural strength and greater surface hardness.[202]

The most common member of the PHA family is the homopolymer poly-3-hydroxybutyrate (PHB). PHB belongs to the short chain length PHA with monomers containing 4-5 carbon atoms. Copolymers of PHA containing short chain length monomers such as 3-hydroxybutyrate (HB) and medium chain length (6-16 carbon atoms) 3-hydroxyhexanoate (HHx) have dramatically improved mechanical properties compared to PHB.[203] The copolymers of PHA vary in type and in proportion of monomers. Poly-3-hydroxybutyrate – co-3-hydroxyvalerate is one example and is going under the trade name Biopol.[204] The US Food and Drug Administration (FDA) have approved Biopol, the PHA produced by Monsanto as food contact material. Other types of PHA have (2003) not been approved food applications yet.[205]

[196] Crank, M. et al. 2004. p. 56-57
[197] http://mbel.kaist.ac.kr/research/phas.htm Visited: 2005-08-06
[198] Ibid.
[199] Crank, M. et al. 2004. p. 56-57
[200] Chen, G., et. al. No5 2000. pp.389-396
[201] Crank, M. et al. 2004. p. 56-57
[202] www.deutsches-kunststoff-museum.de/optimal/eplast02.htm
[203] Chen, G., et. al. No5 2000. pp.389-396
[204] Crank, M. et al. 2004. p. 57
[205] Ahvenainen, R. 2003. p. 523

PHAs are fully biodegradable in both aerobic and anaerobic conditions[206]. The PHAs are completely biodegraded by microbial enzymes to water and carbon dioxide[207]. If composting conditions are not fulfilled the polymers remain intact for years[208].

8.1.1 Poly-3-hydroxybutyrate [P(3HB)]

P(3HB) or PHB has melting point 180°C and good thermoplastic properties. It can be processed as classic thermoplastics. Articles made by PHB can be autoclaved. The possible applications are however limited since the polymer is fairly stiff and brittle[209] due to its high cristallinity[210]. The PHB is water insoluble and rather resistant to hydrolytic degradation. It also possesses a good resistance to solvents. The resistance to oils and fats is good as well as the resistance to UV. The resistance to acids and bases is on the contrary poor. The material has low oxygen permeability and compared to other biopolymers it also has low water vapor permeability.[211]

8.1.2 Copolymers

Copolymers of HB and 3-hydroxyvalerate [P(3HB-co-3HV)] have better mechanical properties compared to PHB. Copolymers of HB and 3-hydroxyhexanoate [P(3HB-co-3HHx)] improve the mechanical properties even further. [212] The copolymer P(3HB-co-3HV) has lower cristallinity than the PHB.[213] The cristallinity is depending on the monomer ratio and ranges from 39% to 69%.[214] The mechanical properties are also improved compared to the PHB. The stiffness and brittleness are lower and the tensile strength and toughness are increased. The material is still fully biodegradable.[215]

8.2 Handling of PHA

The PHA is a group of new materials and that is why it's not yet known by the Occupational and environmental medicine institute of Lund University[216]. A new material always means uncertainties but according to the material safety datasheet (MSD) from the suppliers there is nothing that indicates any greater safety risks with handling the PHAs compared to the polymers used today[217].

8.3 The production of PHA

Polyhydroxyalkanoates are accumulated by many bacterial species in the form of intracellular granules as reserves of carbon and energy.[218] There are a lot of different types of PHA but only few of these are seriously investigated and produced or are

[206] Crank, M. et al. 2004. p. 62
[207] Chakraborty, P. et. al. Paper. 2004
[208] Crank, M. et al. 2004. p. 62
[209] Crank, M. et al. 2004. p. 60ff
[210] Chen, G. et. al. No 3 2001. pp. 193-199
[211] Crank, M. et al. 2004. p. 60ff
[212] Chen, G., et. al. No5 2000. pp.389-396
[213] Crank, M. et al. 2004. p. 60
[214] Volova, T. 2004. p. 99
[215] Crank, M. et al. 2004. p. 60
[216] Albin, M. Occupational and environmental medicine, Lund University. June and July 2005
[217] Sickert, L. Tetra Pak R&D. 2005-07-12
[218] http://aem.asm.org/cgi/content/abstract/65/4/1524 Visited: 2005-06-15

planned to be produced in industrial scale[219]. More than 300 different microorganisms are known to synthesise PHAs but only a limited number of bacteria has been used for production of PHAs[220].

The production of PHA produced by bacterial fermentation consists of three main steps: fermentation, isolation and purification. The fermentation vessel is filled with mineral medium and inoculated with seed ferment that contains the bacteria or microbe. The carbon source is fed at various rates until the growth of the cells and the accumulation of the PHA is complete. The fermentation takes 38-48 hours to complete.

The isolation and purification of the PHA is made with hot solvent. The residual cell debris is in solid state and can be removed with a solid-liquid separation process. The remaining solvent contains dissolved PHA. The PHA is then precipitated by adding a non-solvent and recovered by a solid-liquid separation process. It is then washed with solvent to enhance the quality and dried under vacuum and moderate temperatures.[221]

During the last years it has become possible to produce recombinant strains as more efficient producers of biopolymers. There are two possible ways of engineering efficient producers of biosynthetic PHA, capable of utilizing many different types of carbon sources. One way is to introduce substrate-utilizing genes into PHA synthesizing bacterial strains to broaden their trophic potential. The second way is to introduce genes of PHA synthesis into fast-growing microorganisms incapable of PHA synthesis but with broad organotrophic potential.[222]

The production technology to produce PHA directly in crops is driven by the strive to reduce production costs. Oil-producing crops such as sunflower and corn have been bred to accumulate these oils at high level. The potential of an agricultural PHA production system is enormous if one were able to replace the oil with PHA.[223] The production takes place in specific plant tissues, such as leaves or seeds driven by photosynthesis using only carbon dioxide and water as raw materials. Unfortunately all these attempts have so far been lacking an economic defendability. Metabolix however states that they are making progress with their metabolic engineering to produce PHA with high yields directly in industrial crop plants.

The type of feedstock that is used vary depending on the wanted grade of the product and what microorganism that is used in the fermentation. Important carbon sources today are:

- **Carbohydrates:** glucose, fructose and sucrose.
- **Alcohols:** methanol and glycerol.
- **Alkanes:** hexane to dodecane
- **Organic acids:** butyrate and upwards

In EU the dominating source is beet sugar and in the US, corn. Palm kernel and soybean oil are also used with some microorganisms.[224] The cost of the carbon source is giving a strong impact on the overall production cost of the PHA. This is why it's

[219] Volova, T. 2004. p. 51
[220] Ibid. p. 36
[221] Crank, M. et al. 2004. p. 59
[222] Volova, T. 2004. p. 44
[223] Ibid. p. 48
[224] Crank, M. et al. 2004. p. 59-60

important to find inexpensive substrates for the PHA production.[225] Possible carbon sources in the future are:[226]

- **Carbohydrates:** Molasses, starch and whey hydrolysates (maltose), lactose from whey, cellulose hydrolysates.
- **Alcohols:** Wastes from biodiesel production: methanol plus glycerol, methanol
- **Fats and oils:** lipids from plant and animal wastes.
- **Organic acids:** lactic acid from the diary industry.

8.4 Different potential suppliers

8.4.1 Metabolix

Metabolix was founded in 1992 and is an American company[227] that employs about 30 people. The employees at Metabolix are a very interdisciplinary team with competences as: molecular biologists, chemists, chemical engineers, and polymer scientists and technologists. Metabolix is a private company.[228]

The PHA from Metabolix is derived from sunlight, carbon dioxide and water through the process of photosynthesis. PHA is a sustainable, renewable alternative to petroleum-based products. It is very versatile material and can be used to make a wide range of products.[229]

8.4.2 BioMatera

BioMatera was founded in 1998 and is a Canadian company. The research and development within BioMatera began in the middle of 1999. It started with a collaboration of the Biotechnology Research Institute (BRI)/National Research Council (NRC). Today BioMatera employs fourteen people, of which several biopolymer and fermentation specialists. This company has since its foundation been doing research and working for a commercial development of new biomaterials. BioMatera was one of the first companies to focus on the development of PHA. The mission of BioMatera is: "To become a leader in the research, development and commercialisation of innovative biopolymer materials used for value-added industrial, cosmetic and cosmeceutical applications."[230] The PHA from BioMatera is produced by fermentation of renewable resources.[231]

8.4.3 Nodax

Procter & Gambles brands are touching over 2 billion consumers every day over the world. The brands are ranging from Pringles, potato chips to Swiffer, cleaning products. P&G has a clear vision for the future with environmental sustainability including; reduced CO_2 emissions, use of biobased feedstock, reduced landfill accumulation, renewable energy and composting.[232] In March 2004 P&G Chemicals and Kaneka Corporation of Osaka, Japan joined together in a joint development for

[225] Volova, T. 2004. p. 52
[226] Crank, M. et al. 2004. p. 59-60
[227] www.metabolix.com/biotechnology%20foundation/structurespace.html Visited: 2005-02-15
[228] www.metabolix.com/resources/faq.html Visited: 2005-02-28
[229] www.metabolix.com/sustainable%20solutions/sustainablesolutions.html Visited: 2005-02-15
[230] www.biomatera.com Visited: 2005-02-28
[231] Written information from BioMatera
[232] PPT Presentation from meeting with Nodax 2005-02-24

the completion of research and development leading to the commercialisation of NODAX™ H, poly (3-hydroyxbutyrate-co-3-hydroxyhexanoate) (PHBH). Kaneka Corporation is a leading global manufacturer of plastics, resins, synthetic fibres and chemicals.[233] PHBH will be the first PHA biopolymer in the Nodax family (see table 3) to be commercialised.[234]

Nodax is a biodegradable polymer produced by fermentation of renewable feedstock's such as: sugars, starches or oils.[235] The most feed materials are low-cost or come from waste streams[236]. PHA is then extracted in mechanical and chemical processes.[237]

PHA	R-group
PHBHx	$-CH_3$, $-CH_2\,CH_2\,CH_3$
PHBO	$-CH_3$, $-(CH_2)_4\,CH_3$
PHBD	$-CH_3$, $-(CH_2)_6\,CH_3$
Etc	

Table 3: The Nodax family[238].

The biopolymers in the Nodax-family can be blended with other polymers including the NatureWorks PLA. If the blending ratio is 5-10% Nodax in PLA, the ductility, degradability, hydrophobicity, and barrier properties will be improved and the blend will also become heat sealable. If the blending is 10-20% PLA into Nodax the processability and tensile strength will be improved. The optimum blend is dependent on the application. [239]

Nodax has good oxygen and odour barrier properties. The surface properties are well suited for printing and wicking. The material can be moulded or converted into films, fibres and nonwoven fabrics.[240]

Unfortunately Nodax has been excluded from further analysing in this thesis since they haven't been able to deliver any sample.

233 www.nodax.com/kaneka_pgchemicals.htm Visited: 2005-02-25
234 www.nodax.com/nodax_extras/Modern%20Plastics.doc Visited: 2005-02-25
235 PPT Presentation from meeting with Nodax 2005-02-24
236 www.nodax.com/nodax_extras/Modern%20Plastics%20-%20December.doc Visited 2005-02-25
237 PPT Presentation from meeting with Nodax 2005-02-24
238 www.nodax.com/ICBP-Nov_2003.pdf Visited: 2005-02-25
239 www.nodax.com/nodax_extras/Modern%20Plastics.doc Visited 2005-02-25
240 Ibid.

9. Pilot production

In this chapter the PHA from the different producers will be tested and validated.

9.1 Injection moulding

The injection moulding were made with an "Arburg allrounder 270 90 350".

9.1.1 Supplier A

The purpose with the injection moulding test were to try if it's possible to make simple caps with no screw thread. The trials were made with a non-temperate mould. No shape stability was received, the caps stuck to the tool and were soft and rubber like. Very slowly the caps got harder. Trials were made to make the tool warm (around 60°C) in order to achieve a faster crystallisation, but with no success. The tool cooled faster than expected which resulted in an order of a tool with heating possibilities.

9.1.2 Supplier B

Unfortunately no material was received to make the injection-moulding test with. But from supplier B injection moulded samples, dog-bone and straight shaped, where received. The injection moulding where made at 160°C and with two different mould temperatures 50°C and 80°C.

9.2 Extrusion

For the extrusion a Rheomex 252 were used with a standard metering screw 3:1, 200mm die and coating unit. The extrusion was made with two different web-material: Film sample on PET, 36µm from DuPont and Paper "A1" on inside of 80mN CLC/C Duplex from Stora Enso. The extrusion tests were easy to start up and worked very well with the materials from both suppliers. From supplier A two different grades of the biopolymer were extruded into films. Two different temperatures were used on the chillroll, 65 and 45°C. Two different grades of the biopolymer from supplier B were also extruded into films with two different chillroll temperatures, 60 and 80°C. Before the extrusion the polymers from supplier B were dried at 100°C for 4 hours. The high temperatures on the chillroll were set to avoid sticking and to speed up crystallization in the polymer.

9.2.1 Extrusion of films

The polymers were extruded as films first. The results from this are presented in table 4 for the different thickness and chillroll temperatures.

		Supplier A		Supplier B	
Thick-ness	Chillroll Temp.	Grade A	Grade B	Grade A	Grade B
100 µm	45°C	Rather nice, some gels	Rather nice, some gels	--	--
	60-65°C	Rather nice, some gels	Rather nice, some gels	Rather nice	--
	80°C	--	--	Rather nice	Rather nice but rather many small particles & very small holes.
50 µm	60-65°C	Rather nice, some gels	Rather nice, some gels	--	--
	80°C	--	--	Variation in thickness especially at the edges & some small inhomogeneous areas in the film	Rather nice but some very small particles & some gels or unmolten particles
<50 µm	60°C	Rather nice when 30µm some gels. When <30µm big edge waving.	--	--	--
	80°C	--	--	Big variations in thickness, small unhomolten areas & big holes	Big variation in thickness & very small particles & some gels or unmolten particles

Table 4: Compilation of comments on the different samples during pilot extrusion of films.

The films were all varying in thickness, some more than others. The extrusion was performed at different speeds in order to achieve different thickness of the film. There were generally more disturbances in the thinner films, and the problems with holes also came when the speed was increased. The biopolymers from supplier A were better coping with increased speed compared to the ones from supplier B. Since the processing problems occurred when the films were getting thinner there is a problem to solve since it's the thin films that's of interest in the production lines. This indicates that these materials are not able to process in the same way as PE and that there is a need of redesign or completely new processing equipment.

9.2.2 Extrusion on paperboard

The polymers were then extruded on paperboard. The results are presented in table 5 for the different thicknesses and chillroll temperatures.

		Supplier A		Supplier B	
Thick-ness	Chillroll Temp.	Grade A	Grade B	Grade A	Grade B
100 µm	45°C	--	Rather nice	--	--
	65°C	--	Rather nice	--	--
	80°C	--	--	Rather nice	Rather nice
50 µm	45°C	Too much sticking, and much too "soft" polymer.	A lot of small defects	--	--
	65°C	A lot of small defects	A lot of small defects	--	--
	80°C	--	--	Rather nice	Rather nice

Table 5: Compilation of comments on the different samples during pilot extrusion on paperboard.

The pilot production of thick (100 µm) films went very well but when the speed was increased the problems started to occur for the biopolymers from supplier A. Maybe the extrusion of the thinner films on paperboard requires higher temperatures than the temperatures used for the extrusion of films on PET. The carton is much thicker than the film used above and it also contains some moisture which has a cooling impact. This has to be compensated for with a higher chillroll temperature in order to give the polymer enough time to crystallize.

9.3 Summary from Pilot production

When injection-moulding PHA the tool has to be tempered in order to get a faster crystallisation, which means that it can't be processed as the polymers used today where a cold tool is used.

When extruding PHA films problems occur when the films are getting thinner and it is the thin films that are of interest in the production lines. The tests indicate that these materials are not able to process in the same way as PE and that there is a need of redesign or completely new processing equipment. The testing to extrude films on carton shows problems with the thinner films which indicates that the PHA needs longer time to crystallize. This might be solved by giving the polymer a higher crystallization speed with using a higher chillroll temperature to compensate for the chilling impact from the carton material.

The whole pilot production shows that the PHA requires changes in the process in order to be used. A big difference is the slow crystallization that is speeded by warm chillrolls when extruded and warm tools when injection moulded.

10. Laboratory testing

In this chapter the reader is introduced to the different laboratory analyze methods. The results from the same are presented for the PHA from the two different producers.

10.1 Material properties

To conclude whether the material is suitable for an application or not knowledge about the properties of the material is of great importance. Therefore the material properties were evaluated in laboratory testings with different methods and equiptment.

10.1.1 The methods

Different tests were used to evaluate the properties of the materials. The conducted tests were: Rheology, DSC, DMA, adhesion, tensile test, OTR, WVTR, off-flavor and retorting. The methods used for each test are described under each test.

10.1.1.1 Rheology

Rheology is the science that deals with the way materials deform when forces are applied to them[241]. When it comes to polymers rheological behavior is controlled directly by molecular structure, crystallinity, cross-linking and polydispersity. Rheology bridges the gap between molecular structure, processability and its ultimate performance properties.[242] The flow behaviour is important in many industrial processes. It is always a good idea to characterize polymers used in a process and identify important process parameters.[243]

In the evaluation of the rheological properties, the sample is put between two plates.[244] On one of the plates a periodic deformation is applied which causes a periodic response in the sample. The response may be lag or lead the deformation. The phase lag (delta, tan delta) is a direct measurement of the ratio of the viscous to elastic contribution to the overall response in the sample. By using the phase lag and the magnitude of the response, the signal can be decomposed into the in phase and 90° out of phase components.

- The ***in phase*** represents the elastic response. From this the storage modulus (G') can be determined. The storage modulus or elastic modulus is a measure of a sample's ability to store energy.
- ***90° out of phase*** represents the viscous response. From this information the loss modulus (G") can be determined, which is a measure of the sample's ability to dissipate energy.
- The ratio of the G'' to the G' is called ***tan delta***, and represents the damping properties of the sample.[245]

A controlled stress rheometer, StressTech from Reologica Instruments, was used for the rheological analysis.

[241] Poster at the Tetra Pak R&D Laboratory in Lund
[242] www.atsrheosystems.com/PDF%20files/Polymer%20Paper.pdf
[243] Manuscript… from laboratory personnel at Tetra Pak R&D
[244] Lindborg, K. Spring 2005
[245] www.atsrheosystems.com/PDF%20files/Polymer%20Paper.pdf

10.1.1.2 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) measures temperatures and heat flows associated with thermal transitions in a material. Properties that can be measured are glass transitions, "cold" crystallization, phase changes, melting, crystallization, product stability, and oxidative stability.[246] It is the difference between the heat flows to a sample and a reference pan that are exposed to the same temperature program that is measured. The transmitted energy corresponds to an equal change in enthalpy of the sample. [247]

Thermal analysis was made on the samples with a MDSC 2920 from TA Instruments. The samples were heated with 10°C/min from 35° to 300°C and then crystallised and cooled to 35°C with a cooling rate of 10 °C/min. During the second heating using 10°C/min until 300°C melt temperatures and heat of fusion were determined.[248]

Polymers have a memory; that's why processing temperature has an impact on the melt temperature. During the first melt the memory from the processing erased. Since the same method is used, the results from different materials, from the second melt, can be compared with one another. This is why the determination of melt temperatures and heat of fusion is made on the second heating.[249]

10.1.1.3 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) measures the mechanical properties of materials as a function of time, temperature, and frequency[250]. The modulus (stiffness) and damping (energy dissipation) properties of the material are analysed as they are deformed under periodic stress. During the DMA a sinusoidal stress is applied to the material and the resulting sinusoidal strain is measured.[251] DMA made over a wide range of time and temperature can provide a fingerprint of the molecular relaxations and ultimate properties in the part.[252]

The DMA was made with a DMA 2980 from TA Instruments in a multifrequency mode at a constant frequency 1Hz and the amplitude 20µm. The measurements were performed with a temperature ramp from 35 to 140˚C.

10.1.1.4 Adhesion

The adhesion between the extruded biopolymer and the carton (80mN CLC/C Duplex from Stora Enso) was tested with method number 10. An Instron 4502 was used with 100N load cell with a crosshead rate of 100 mm/min for the test. The specimens were rectangular shaped, 20 mm width and the test angle was 180°.[253]

[246] www.tainst.com/product.asp?n=1&id=10
[247] Manuscript… from laboratory personnel at Tetra Pak R&D
[248] Nae, D. & Lindborg, K. Analysis Report (2005)
[249] Lindborg, K. 2005-05-19
[250] www.tainst.com/product.asp?n=1&id=12
[251] Brochure: *DMA 2980..* www.tainst.com Visited: 2005-05-19
[252] www.atsrheosystems.com/PDF%20files/Polymer%20Paper.pdf
[253] Nae, D. Tensile Test Report (2005)

10.1.1.5 Tensile test

With this test the tensile properties of plastic in dog-bone shaped specimens are defined. The test is made under defined conditions (converting process, temperature, humidity) and machine speed, to achieve comparable results. This test gives information about the tensile properties for control and specification of plastic materials. This information is also useful for qualitative characterization purposes and for research and development. The tensile strength as well as the percent elongation are measured.[254] In this tensile test (method no 36) an Instron 4502 was used with a 100N load cell and a crosshead rate of 200mm/min. The extension was recorded with a video camera.[255]

10.1.1.6 Oxygen transmission rate (OTR)

In Oxygen Transmission Rate (OTR) testing it is the quantity of oxygen passing through a unit area per unit time that is measured (see figure 7). The OTR can be measured on flat films, as well as flexible and rigid packages. The testing can be performed under a range of relative humidity conditions at a range of temperatures.[256]

The OTR was in this thesis measured with an Ox-tran 2/20H on plane film samples at 23°C with different humidity, 50%RH and 80%RH[257]. In the test the samples of the films were cut into six-cornered pieces (width 91mm, length 172mm). The samples were taken from parts of the film where few or none disruptions were found. They were then one and one mounted between two chambers.[258] During the testing, one side of the film was exposed to the test gas. As it permeated through the sample material, the carrier gas, nitrogen sweeped the opposite side of the film and transported the transmitted oxygen to the coulometric sensor. [259] The sensor read how much oxygen there were in the nitrogen gas, i.e. O_2GTR.[260] This value was reported as a transmission rate[261]. The test gas was air-21%O_2 at 0,21 atm and the carrier gas was nitrogen (99% nitrogen, 1% hydrogen.[262] The unit is cc oxygen/m²/24h.

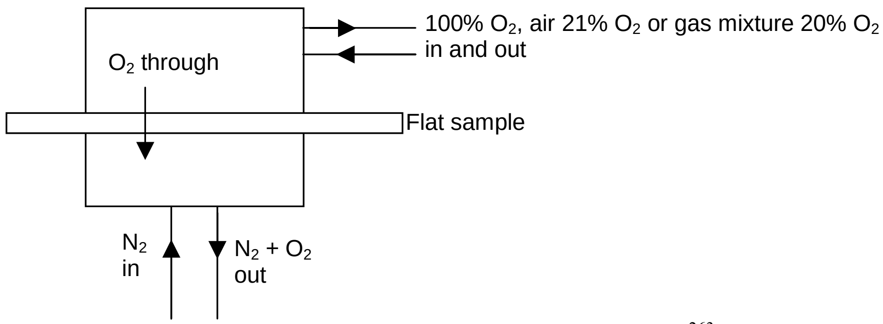


Figure 7: OTR measurement on flat samples.[263]

[254] Manuscript… from laboratory personnel at Tetra Pak R&D
[255] Nae, D. & Lindborg, K. Analysis Report (2005)
[256] Tetra Pak Intranet
[257] Dahlberg, L. Analysis report (2005)
[258] Tetra Pak Test method for transmission rate
[259] www.impactanalytical.com/otransrate.html
[260] Tetra Pak Test method for transmission rate
[261] www.impactanalytical.com/otransrate.html
[262] Tetra Pak Test method for transmission rate
[263] Manuscript… from laboratory personnel at Tetra Pak R&D

10.1.1.7 Water vapour transmission rate (WVTR)

Water Vapour Transmission Rate (WVTR) measures the ability to transport moisture through a material of known thickness. WVTR is measured in grams per square meter (g/m^2) over a 24 hours period.[264]

10.1.1.8 Sensory evaluation

The perceived off-flavour in water was tested in a method where 12g of the material, here film, was cut into 2 cm stripes and put into 2000 ml carbon filtered tap water and was stored in 23° for 1 day[265]. This water was sensory evaluated by an experienced test panel.[266]

10.1.1.9 Retorting

Extruded films from the two suppliers were put through a retorting process. The films were in two –three layers put in normal stationary, film pockets and hung in the normal retorting carriage. The retorting process was at 128°C and lasted for 55 min before it was cooled down.

10.1.2 Test results

The results from the different tests are presented under each test together with comments, using the above described methods.

10.1.2.1 Rheology

The slope tells us about the distribution in molecular weight in the material (see figure 8). The slope is greater and thus also the distribution in LDPE than in the other four materials. In the other four materials the distribution of molecular weight is very small. This will cause for instance neck-in when extruded, which also was the case when they were extruded.

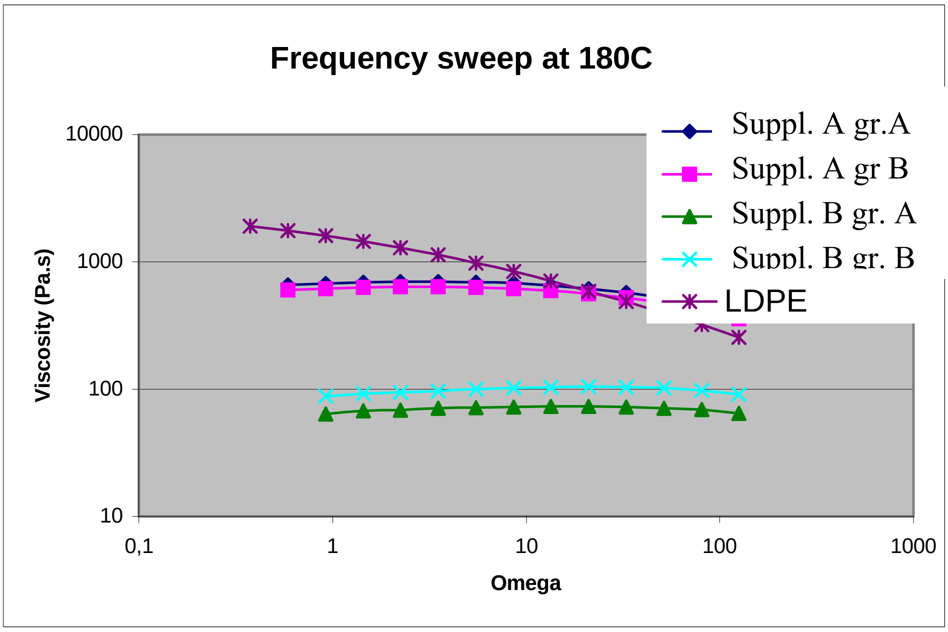


Figure 8: Shows the results from the rehological test.

[264] www.biobags.co.uk/technical/wvtr.html
[265] Bengtsson, A-C. Sensory Analysis report (2005)
[266] http://151.183.8.67/products/corporatestandard/corporatestandard/InternCS/PM/PM9600/PM961720.pdf

10.1.2.2 Differential Scanning Calorimeter (DSC)

The DSC measurements are made to define a suitable temperature area for processing[267]. From the DSC measuring the melt temperature (Tm) and the heat flow rate (ΔH) from the second melt is listed in table 6. Two different melt temperatures for a sample indicate that the sample may consist of two different materials that melt at different temperatures. The heat flow rate is important to know for instance when extruding or sealing the material, so that enough energy is added to melt the material.[268]

Sample: (chillroll temp.)	**Tm (°C)**	**Total ΔH (J/g)**
Supplier A grade A (65°C)	Tm_1 144,87 Tm_2 167,15	56,59
Supplier A grade A (45°C)	Tm_1 144,01 Tm_2 166,33	52,29
Supplier A grade B (65°C)	Tm_1 158,97 Tm_2 171,18	71,43
Supplier A grade B (45°C)	Tm_1 159,85 Tm_2 172,05	73,72
Supplier B grade A (60°C)	Tm_1 151,52 Tm_2 163,45	73,10
Supplier B grade A (80°C)	Tm_1 151,67 Tm_2 163,48	71,29
Supplier B grade B (80°C)	Tm_1 152,16 Tm_2 162,97	66,79
Ref: LD270	Tm 108,65	115,1
Ref: WG341C	Tm_1 109,88 Tm_2 163,89	108,5

Table 6: Shows the results from DSC.

Normally high heat flow rates lead to a good adhesion and vice versa. In this case the adhesion is fairly high although the low heat flow rate. This may depend on the fact that the chillroll was warm and thus the temperature was higher at the nip.

[267] Sickert, L. Spring 2005
[268] Lindborg, K. 2005-05-19

10.1.2.3 Dynamic Mechanical Analysis (DMA)

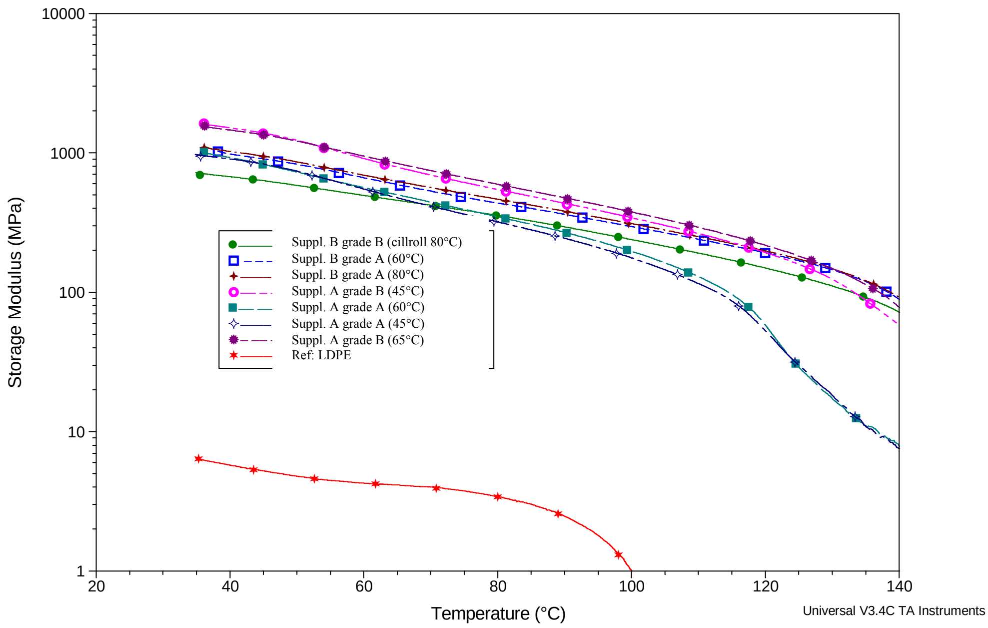


Figure 9: Shows the results from the measuring of storage modulus in the DMA test.

The results from the DMA are presented in figure 9. The graph in figure 9 tells us about the storage modulus, all the tested PHA samples are much stiffer than the reference material LDPE. The samples of same grade processed with different chillroll temperature tell us that the chillroll temperature has none or very little influence on the storage modulus.

10.1.2.4 Adhesion

The adhesion for films extruded on carton with different temperatures on the chillroll was tested (see table 7). All the samples from supplier A were treated with corona set on 2000Ws/m^2. The samples from supplier B were extruded both with and without corona treating. On the samples with corona, it was set on 2500Ws/m^2.

Test material	**Mean value** (N/m)	**Std** (N/m)	**max value** (N/m)	**min value** (N/m)
1. supplier A grade A, 50 µm 65 ° C	**42**	5*	49	35
2. supplier A grade B, 100 µm, 65 ° C	**133**	8	144	118
3. supplier A grade B, 100 µm, 45 ° C	**131**	8	145	124
4. supplier B - grade A 100µm, 80° C without	**77**	5	85	71
5. supplier B grade A 100µm, 80° C with	**75**	7	91	66
6. supplier B grade B 100µm, 80° C without	**60**	4	65	50
7. supplier B grade B 100µm, 80° C with	**55**	7*	65	46

* high standard deviation (coefficient of variation > 10%)

Table 7: Results from adhesion testing of the PHA from supplier A and B.

Sample number one is only having the half thickness compared to the other ones; this might be the answer to why it's having such a low mean value on the adhesion compared to sample number two and three.

Since only 6 to 8 specimens were tested of each material there is no statistical difference in adhesion between number four and five or between number six and seven. The interesting thing is however that both number five and seven are corona treated to improve the adhesion, which have had none or maybe even reversed effect. To be able to statistically prove an actual difference in adhesion between sample number four and five it would require testing of 100 specimens and the difference between number six and seven would take 20 specimens since this difference is greater. [269]

The values are all much lower than the accepted limit-values. At R&D values at about 300N/m are accepted and in the factory values around 200N/m.[270]

10.1.2.5 Tensile test

In the tensile test stress and strain at break were measured. 6 to 8 strips were tested of each sample. The results show that both the biopolymers from supplier A as well as from supplier B possessed a strain at break very much lower than the reference material WG341C. As a comparison it can be mentioned that the strain at break (mean value) for the reference was 808% and for the biopolymers ranging from 5,6 to 10,8%. Literature values tell us that the strain at break for LDPE is ranging from 100 to 650%[271]. This means that the elongation is much lower for the PHA samples both when compared to WG341C and LDPE. When it comes to stress at break the biopolymers are more similar to the reference material and to LDPE. The stress at break for the biopolymers ranged from 21,5 to 36,4 MPa. The higher values were found on the biopolymers from supplier A. The reference material had a stress at break at 41,7 Mpa. Literature values for LDPE ranges from 8 to 30 MPa[272]. The stress at break indicates how strong the material is and how much force one can apply before it breaks.

10.1.2.6 Oxygen transmission rate (OTR)

The OTR was measured on the material from supplier A and from supplier B. The results are shown in table 8. All the samples were about 100µm thick. Sample one and two from supplier A have been extruded with a chillroll temperature of 65°C and sample three 45°C. From supplier B both sample number one and two have been extruded with a chillroll temperature of 80°C. The OTR results from the laboratory were recalculated into $cc \cdot mm/m^2/24h \cdot atm$ by multiplying with the factor 0,476 to achieve comparability with the reference values found in the literature[273].

[269] Lindgren, R. E-mail and telephone contact 2005-05-23
[270] Nae, D. Mail-contact Spring 2005
[271] www.maropolymeronline.com/Properties/LDPE.asp#Tensile%20Strength%20at%20Break Visited: 2005-06-29
[272] Ibid.
[273] Berlin, M. Spring 2005

	1. supplier A grade A, 100 µm,	2. supplier A grade B, 100 µm,	3. supplier A grade B, 100 µm,	1. supplier B grade A 100µm	2. Supplier B grade B 100µm
OTR-Plane sample at 23°C-50% RH-21% O2 (cc/m²/24h)	13,005	10,235	9,685	41,000	74,800
$cc \cdot mm/m^2/24h \cdot atm$	6,190	4,872	4,610	19,516	35,605
OTR-Plane sample at 23°C-80% RH-21% O2 (cc/m²/24h)	16,225	12,005	11,760	42,500	74,850
$cc \cdot mm/m^2/24h \cdot atm$	7,723	5,714	5,598	20,230	35,629

Table 8: Results from OTR testing on PHA from supplier A and B.

	EVOH (EVAL EF-F)		PVOH
20°C-65% RH $cc \cdot mm/m^2/24h \cdot atm$	0,01	24°C-0% RH $cc \cdot mm/m^2/24h \cdot atm$	0,02
20°C-85% RH $cc \cdot mm/m^2/24h \cdot atm$	0,03	24°C-75% RH $cc \cdot mm/m^2/24h \cdot atm$	0,09

Table 9: Reference values for the barrier materials EVOH and PVOH found in literature.[274]

	LDPE
24°C $cc \cdot mm/m^2/24h \cdot atm$	98-138

Table 10: Reference values for LDPE found in literature.[275]

The oxygen barrier properties for the tested PHA are better for the material from supplier A than from supplier B. An interesting thing is that the transmission rate doesn't change much when the humidity increases. The transmission rate for the PHA is much higher than for the barrier materials used today (EVOH and PVOH) i.e. the barrier properties are better for the EVOH and PVOH (see table 9). The transmission rate for the PHA is however much lower than for the LDPE (see table 10).

All films have a limit when it comes to processing really thin films. An interesting thought is that barrier materials like EVOH and PVOH have such a high barrier function that it's most likely one produce films with overcapacity when it comes to barrier properties. Maybe it would be more efficient to choose a material with somewhat lower barrier properties that with needed thickness have the necessary barrier properties and maybe the material also can contribute to the stability of the package.

10.1.2.7 Water vapour transmission rate (WVTR)

No WVTR tests were made on the materials in this thesis since the waiting time to these tests is longer than this project. No values were found in the literature on the WVTR for PHA.

10.1.2.8 Sensory evaluation

The sensory evaluation was made on two different days, due to differences in delivery time from the suppliers. The evaluation of the PHA from supplier A is shown in table 11. Sample 2 is statistically significantly higher in off-flavour level than sample

[274] Massey, L. 1995. p. 238 (EVOH) and p. 288 (PVOH)
[275] Ibid. p. 159 (LDPE)

number 1. Some comments received from the panel about the taste were: some "paper/board" and a few single odd comments e.g. "burnt, pharmaceuticals, bath ball" for both samples.

1. Supplier A grade A	30
2. Supplier A grade B	39

Table 11: Results from sensory evaluation of the PHA from supplier A.

The results from the evaluation of the material from Supplier B are presented in table 12. Comments from the panel on samples were many "chemical related" and some "plastic, paper/board".

1. Supplier B grade A	50
2. Supplier B grade B	62

Table 12: Results from sensory evaluation of the PHA from supplier B.

The comments "paper/board" are not likely to cause any troubles but the other ones might cause unpleasant off-flavour. Sample number one from supplier A might, according to Ann-Christin Bengtsson at Material analysis, be possible to use in a package where some product and not water is packed. A package used to pack a product rich in flavour is less sensitive then a package used to pack water when it comes to off-flavour. Fatty products may however dissolve some unwanted flavours. When the results are compared to TBA material they are very much too high in off-flavour. TBA is somewhere half way to very weak in off-flavour i.e. around nine. For TRC the results are somewhere between very weak and average i.e. around 33. This means that sample number one from supplier B is about the same level in off-flavour as the material used in TRC. Actions that can be taken to decrease the off-flavour are to lower the process temperature, add additives and/or minimising the air gap in the process.

10.1.2.9 Retorting

From supplier A films from two different grades were tested in the retorting process. Both of the grades are sealing with themselves i.e. the different layers in the plastic pocket are sticking on to each other. The properties are somewhat changing to become more brittle. From supplier B films from two different grades were tested in the retorting process. Both the films had dramatically changed properties during the retorting process. The material was falling into pieces. In agreement with personal at the polymer laboratory at Tetra Pak R&D it was decided as useless to conduct any testing of elongation to break on the retorted films. This resulted in that the original idea, to test the elongation to break on the films both before and after the retorting process in order to compare the results, was not followed.

10.1.3 Summary from Laboratory testing of Material properties

The Rheology tells us that the distribution of molecular weight is very small for the tested PHA samples compared to LDPE. This will cause for instance neck-in when extruded, which also was the case when they were extruded.

DSC results tell us that all of the tested PHA samples have two different melt temperatures which may indicate that the materials consist of two different materials or grades that melt at different temperatures. The melt temperatures from the DSC are

important to define a suitable process temperature and the heat flow rate is important when sealing or extruding the material so enough energy is added to the material.
For the PHA samples, especially the second grade from supplier A (grade B), the adhesion is high (even though it's below the recommended values to be used in production) although the low heat flow rate. This can be dependent on the fact the chillroll was warm and thus the temperature was higher at the nip.

The results from the DMA tell us about the storage modulus, all the tested PHA samples are much stiffer than the reference material LDPE.

All of the tested PHA possess much lower values on the adhesion to carton board than the accepted limit-values.

In the tensile test stress and strain at break were measured. Both the biopolymers from supplier A as well as from supplier B possess a strain at break very much lower than the reference material WG341C and LDPE. This means that the elongation is much lower for the PHA samples. When it comes to stress at break the biopolymers are more similar to the reference material and to LDPE. The stress at break indicates how strong the material is and how much force one can apply before it breaks.

The oxygen barrier properties for the PHA are a little better for the material from supplier A than from supplier B. None of the transmission rates changed much when the humidity increased. The transmission rate for the PHA is much higher than for the barrier materials EVOH and PVOH i.e. the barrier properties are better for the barrier materials. The oxygen barrier is however much better for the PHA than for the LDPE.

The Sensory evaluation shows that the PHA samples are much higher in off-flavour than the material used in TBA. Sample number one from supplier A is in the same area as the material used for TRC and it is the only one that might be possible to use in off-flavour consideration. This sample would however only be able to use in packages for products other than water.

Both of the grades from supplier A are sealing with themselves during retorting. The properties are also changing to become more brittle. Both the films from supplier B experienced dramatically changing in properties during the retorting process. The material was falling into pieces. None of the tested PHA grades are suitable for retorting.

The laboratory testing indicates that most of the properties of the tested PHA materials, both from supplier A and from supplier B, are in need of improvement to match the materials used today and to measure up to the standards.

10.2 Recycling properties

The recycling property of the material is important when evaluating and comparing the materials. It's most common that the fibres in the beverage cartons are recovered in a hydrapulper. This led the focus on recycling properties to the recovery of the fibres. The test method used is similar to the real repulping process but in very small scale. This test was performed to get an indication of the repulping properties when using the biopolymer.

10.2.1 Test method

The recycling properties of the films extruded on board and a reference material (TBA) were tested in a repulping test as following. 20 grams of the material, cut in 50 x 50 mm pieces, were put into a modified "kitchen blender" together with 750 ml water at 40°C. The rotor is running for 60 seconds and after that the resulting mass is visually evaluated.

10.2.2 Test results

All of the materials below are based on 80mN CLC duplex, carton board, in order to achieve a comparable result. In appendix 2 photos on the resulting flakes are found. The material used in a standard TBA was used as a reference. When the resulting mass after the test where evaluated, it was found that the layers with LDPE, AL and LDPE where still in 50 x 50 mm pieces and separated from the fibres. The LDPE from the surface of the material was also free from fibres and also still in 50 x 50 mm pieces.

From **Supplier A** films, extruded on board were tested. The A and B represent two different grades of the biopolymer.

A. The polymer film is broken into smaller pieces during the process. This indicates that the material is more brittle than the LDPE in the reference material. The fact that the polymer is broken into smaller pieces would, if used, demand an increased rate of screening and cleaning in order to separate the fibres.
B. The other grade is broken into even smaller and thorny pieces than the first one. A little amount of fibres is sticking onto the polymer.

Two different grades (A and B) of the biopolymer from **Supplier B** extruded on board were tested:

A. Also this film is broken into small pieces. But with this sample the fibres seems to stick onto the polymer, to a greater extent than the sample before.
B. In this sample the polymer is clearly better than the others (excluding the reference) on enduring the test in whole pieces. Still some of the polymer sheets are broken into smaller pieces, although not as small as the other samples. A little amount of fibres is sticking onto the polymer.

10.2.3 Summary from Laboratory testing of Recycling properties

All materials pulp readily and no flakes of fibre could visibly be noticed. The breakdown of the polymers into smaller pieces indicates that the polymers are more brittle than LDPE and this could be an issue in the recycling of paper. However, the nature of this test is purely indicative and as the pulping action is much more aggressive in a small pulper than in industrial scale. It might be so that the polymers can show a different result in industrial scale. The next step in evaluating the polymers would be to evaluate the polymers in a minipulper. This will give quantitative results on fibre yields and a better understanding on the brittleness of the polymers.

11. SWOT

The conclusions of this thesis will be summarized with a SWOT analysis.

11.1 Strengths

A big benefit with the PHA is that they are completely biodegradable materials and formed from renewable resources. Another great benefit with the PHAs is that they are not dependent on the oil price or the access to oil. The vision to use wastewater in the future production is even more improving its environmental status. The making of a LCA of the PHAs is left to future investigations.

The tests show that the transmission rates do hardly change when the humidity increases. It also show that the transmission rate for the PHA is much higher than for the barrier materials like EVOH and PVOH i.e. the barrier properties are better for the barrier materials, but the oxygen barrier is however much better for the PHA than for the LDPE. So the barrier properties of the tested materials can both be a strength and a weakness depending on the reference. The fact that the oxygen barrier properties are not particularly sensitive to changes in humidity is an interesting outcome of the tests and can be a benefit for the material.

The recycling tests showed that all the materials pulp readily and no flakes of fibre could visibly be noticed. One weakness is that the polymers were broken into smaller pieces, which could be an issue in the recycling of paper. The brittleness of the materials is contributing to the small pieces.

11.2 Weakness

A big difference with the PHAs compared to the materials used today is their slow crystallization. This is a weakness for the PHA since they require warm chill rolls when extruded and warm tools when injection moulded in order to speed up the crystallisation and thereby to be able to process. A question that is left to future investigations to answer is if the high temperatures that the PHAs require are possible to have in the production?

The mechanical properties of the tested PHAs show some weaknesses with the materials, for instance that the material is very stiff. This has to be improved in order for the material to be able to use as a laminate in the laminar packaging material. It also has to be improved when it comes to off-flavor in order to be possible to use in a TBA material. One of the materials is maybe possible to use in a TRC material, when only the off-flavor is considered. The tested materials are not suitable for retorting since they experienced dramatical changes in their properties to become brittle and fall into pieces during the process. Thus the tested materials are in need of a great improvement in order to be able to use in packaging materials for TRC.

The approval for use of PHAs in food contact is essential for its use as packaging material for Tetra Pak, without this approval the material looses its value for food packaging applications.

11.3 Opportunities

The use of PHA in packaging solutions could improve the environmental profile of Tetra Pak and thus give competitive advantages. This factor is increasing in importance along with the increasing environmental awareness among the consumers. The economical potential with PHA is increasing as the price of oil increases. Since the access to oil is limited, the opportunity for Tetra Pak is greater the sooner they can find a replacement material that is totally based on renewable materials, like PHA.

11.4 Threats

Since there today is no company producing PHA in large scale there are risks but also potentials with cooperation and optimising of the biopolymer to suite Tetra Pak applications. Another aspect that has to be dealt with in further investigations is the price. Today nobody knows how high the price for PHA will be in the future but one thing is sure, the price today for the small scale produced PHA is far from the price that Tetra Pak would get if they were to use it in full scale.

If gene modified organisms are used for the production of the PHAs it might be harmful for the Tetra Pak goodwill since there is a quite strong opinion against the GMO and the risks are still unknown.

12. Conclusion and Recommendations

The conclusions and recommendations of this thesis will be presented to the reader in this chapter.

12.1 Conclusion

The Poly-hydroxi-alkanoates possess some good and needed properties compared to other biopolymers. But still there are properties needed to be improved and they are still not as easy to process as the materials used today. The use of the tested materials does not seem possible, today, in applications like TBA and TRC material or caps. For use in any of the applications the process lines need to be redesigned for the PHAs with for instance warm chill rolls and warm tools in the injection moulding. But as time goes and the experience of these materials increases, the processing equipment and the processing may be possible to optimise for this new materials, as the process has been optimised for PE and PP today.

To be able to use the tested PHAs in a TBA material, it cannot be as brittle as today, not have such a high off-flavour, and must have an improved adhesion. To be able to replace one of the barrier materials in the TBA it also must have improved oxygen barrier properties. To be useful in a TRC application the material must not have such high standards as the TBA material in off-flavour but it has to be able to withstand a retorting process, and therefore needs extra improvements.

12.2 Recommendations

The recommended next step, with consideration to the result of this thesis, is to contact the potential suppliers; Metabolix and BioMatera in order to discuss the result of the laboratory testing and the possibilities to make improvements. If the discussions with Metabolix and BioMatera are successful and new and improved materials are processed I suggest further testing of the material. If it does not result in a new modified PHA grade I suggest further research to find other potential suppliers.

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APPENDIX 1 "Photos from Recycling test"

Photos taken during the recycling test.

Reference: LDPE	
Supplier A - material grade A	
Supplier A - material grade B	
Supplier B - material grade A	

APPENDIX 1 "Photos from Recycling test"

Supplier B - material grade B