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Master´s Thesis

Ilari Vahtila

THE REQUIREMENTS OF A FEASIBLE PLASTIC PACKAGING MATERIAL FOR CULTURED DAIRY PRODUCTS

Examiner: Henry Lindell, Professor of Packaging Tecgnology, LUT
Ville Leminen, Researcher of Packaging Technology, LUT

Supervisor: Outi Kaikkonen, R&D Manager, Coveris Rigid Finland Oy

ABSTRACT

Author:	Ilari Vahtila
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The objective of this Master´s Thesis was to conduct a wide scale preliminary survey regarding the package requirements of a cultured dairy package, and to compare the currently used material polystyrene to other suitable packaging materials. Polystyrene has a long history of use in dairy cups, but in recent years its price has increased significantly compared to other common packaging materials. The overall environmental effects of a package and a package material are today a part of designing a sustainable product life cycle. In addition, in certain contexts there has been discussion of the risks posed by styrene polymer for the environment and for humans. These risks are also discussed in this thesis. Polystyrene (PS) is still the most widely used material in dairy cups. In recent years, polypropylene (PP) cups have appeared in increasing numbers on market shelves. This study focuses on the differences of the suitable polymers and examines the suitability of alternative "suitable" polymers with regards to dairy packaging. Aside from focusing on the cup manufacturer, this thesis also examines its subject matter from the viewpoint of the dairy customer, as well as observing the concrete implications of material changes in the overall value chain.

It was known in advance that material permeability would be one of the determining factors and that gas transmission testing would be a significant part of the thesis. Mechanical tests were the second part of the testing process, providing information regarding package strength and protectiveness during the package's life cycle. Production efficiency, along with uninterrupted stable production, was another important factor that was taken into consideration. These two issues are sometimes neglected in similar contexts due to their self-evident nature. In addition, materials used in production may have a surprising significance to the production and efficiency. Consistent high quality is also partly based on material selection. All of the aforementioned factors have been documented and the results have been analyzed by the development team at Coveris Rigid Finland. Coveris is now calculating the total finance effects and capacities should the material changes be implemented in practice. There are many factors in favor of switching to polypropylene at the moment. The overall production costs, as well as the environmental effects of resin production are the primary influences for said switch from the converters' perspective.

ACKNOWLEDGEMENTS

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Hämeenlinna, November 2014

Ilari Vahtila

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ABBREVIATIONS

CO_2TR	Carbon dioxide transmission rate
EFSA	European Food Safety Authority
EU	European Union
EC	European Commission
EPR	Extended Producer Responsibility
GPPS	General Purpose Polystyrene
GTR	Gas Transmission Rate
HDT	Heat deflection temperature
HIPS	High Impact Polystyrene
LCA	Life Cycle Assessment
MAP	Modified Atmosphere Packaging
MFI	Melt Flow Index
MFR	Melt Flow Rate
MPET	Metallized Polyethylene Terephtalate
MVR	Melt Volume Rate
OML	Overall Migration Limit
OTR	Oxygen Transmission Rate
APET	Amorphous Polyethylene Terephtalate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
SML	Specific Migration limit
STEL	Short term Exposure Limit
TWA	Time Weighted Average
VOC	Volatile Organic Compaund

DEFINITIONS

Copolymer	when two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer
Culture	means a liquid or powder containing one or more acceptable selected micro-organisms used in the manufacturing of cultured buttermilk, sour cream, sour milk, yoghurt or any other type of fermented milk product
Fermentation	a process in which chemical changes are brought about in an organic substrate through the action of enzymes elaborated by microorganisms
Glass transition temperature	see “Melt temperature Tm”
Pasteurization	means the heat treatment, where all vegetative pathogens are destroyed and if the product concerned does not undergo further processing, the cooling thereof to below 50°C immediately after having been thus heat treated
Dairy	is a company, with the primary business of the further processing of milk
Homo polymer	a polymer which is made by linking only one type of small molecule, or monomer, together, ~~it~~ is called a homo polymer
Long-term temperature	is defined as being the maximum temperature at which plastics can be kept in hot air for 10,000 and 20,000

	hours without losing more than 50% of the initial values for their typical properties.
Melt temperature Tm	semi crystalline polymers have true melting temperatures (Tm) at which the ordered regions break up and become disordered. In contrast, the amorphous regions soften over a relatively wide temperature range (always lower than Tm) known as the glass transition (Tg). Fully amorphous polymers do not exhibit Tm, of course, but all polymers exhibit Tg. Above these temperatures, polymers are liquids. Below Tg amorphous polymers are hard and brittle.
Migration	is the transfer of a compound from the packaging material into food.
Oxygen transmission rate	is a calculated measurement of the amount of oxygen gas that, over a given period of time at a steady rate, passes through a substrate.
Permeability	is the qualification of permeate transmission, gas or vapor, through a resisting material.
Package	is the physical entity that actually contains the product.
Packaging	is the integration of the physical elements through technology to generate the package and the protection of the packaged product for the purpose of facilitating its journey to the marketplace and use by the consumer. Packaging is that combination of materials, machinery, people, and economics that together provides protection, unification, and communication.
Polymer	a polymer is a large molecule (macromolecule) composed of repeating structural units connected by covalent chemical bonds. While "polymer" in popular usage suggests "plastic", the term actually refers to a

	large class of natural and synthetic materials with a variety of properties and purposes
Raw milk	means milk that has not undergone pasteurization, sterilization or ultra-high temperature treatment
Skimmed milk	denotes milk from which the fat (cream) has been removed
Sour cream	or (cultured cream) is the product obtained from pasteurized cream that has been inoculated with a culture in order for it to develop certain microbial flora under controlled conditions
Short-term temperature	denotes the short-term peak temperature values that the plastic can withstand for a period of minutes or sometimes even hours without the plastic being damaged, taking into account the load and its duration.
Sour milk	or (cultured milk) means the product obtained from pasteurized milk that has been inoculated with a culture in order for it to develop certain microbial flora under controlled condition
Thermoplastic	is a type of plastic made from polymer resins that becomes a homogenized liquid when heated and hard when cooled. That is, it can be reheated, reshaped, and frozen repeatedly. This quality also makes thermoplastics recyclable.
Viili	finnish curd milk. Traditional stretchy finnish cultured dairy product which is fermented in package.

1 INTRODUCTION

The primary goal of this thesis is to find the limits and the window in which the manufacturer can operate - with the customers being satisfied – when both the package manufacturer and the customers want to find a new raw material for cultured dairy product packaging. First of all, it is good to go over the basics of package production, the package materials and the dairy processes which are used before the end product is on the shelves. Raw material development and changes in material prices are continuous, which provides a motivation for continuous product improvement. When considering replacing a raw material, in use for decades, the process needs to be planned out carefully. In a best case scenario, the replacement material will provide more value for both the manufacturer and the customers. The manufacturer and the customer are linked together in this sense, as the employment of a more suitable packaging material from the manufacturer will result in better and/or cheaper packages, providing the customer with an increased quality in package properties and/or a more favorable price for the consumer without the loss of profitability. The benefits of a material switch, to name a few, can include decreased material usage, better quality, better printability or a better resistance to logistics stresses. The purpose of this study is to find all primary requirements which are absolutely needed to increase the value of the package, as well as secondary requirements, which are not necessary but still give value to the package. All the effects which are linked to and result from the planned replacement of raw materials must be noted and taken into consideration, before actually supplanting one material with the other. A wide set of information regarding the requirements, as well as other relations subject to change should the material switch occur, is presented in this paper. As mentioned above, there are two major viewpoints to be considered with regards to this change, the needs of the manufacturer and the needs of the customer. Thinking further, concepts such as production efficiency, machinery investments, disposal, risks of implementation activities, changes in material or package characteristics, etc. arise.

The theory part of the thesis will demonstrate the basics of cup manufacturing and the dairy process, as well as the materials and the main characteristics which are used in dairy cups and the reasons to explore developments in this matter. The second part of this paper will introduce the research methods which were used. In the third part, all the results of this work are presented. Finally, in the fourth section, the results are discussed and conclusions are made.

1.1 Coveris (PACCOR) and the operating environment at the moment

PACCOR is one of the leading manufacturers of rigid packaging and customized packaging solutions in Europe. PACCOR has 19 factories in 13 countries, one of them being located in Hämeenlinna, Finland. The group's growth is set to continue in the future. Other factory locations are situated more South, e.g. Germany, France, Poland, Hungary and Bulgaria. Production at the Hämeenlinna site is mainly focused on dairy and fresh meat packages. Both sectors are highly competitive. (PACCOR 2013)

On the 1st of May 2013 PACCOR and four other packaging companies joined together under Exopack holdings. By the end of the year 2013 the five companies were given a shared name, Coveris. Coveris is now the world's 6th largest packaging company. Exopack, Kobush, Paragon, Britton and Paccor all have special expertise in the packaging field. Coveris, with $2.5 billion in annual sales, develops, makes and sources flexible and rigid plastic and paper packaging. *The company, with 64 plants in North America, Europe, the Middle East and China, also provides coatings for consumer and industrial markets*, stated Jack Knott, CEO of Coveris in Plastic news 18th of November 2013. He said that *Coveris now has approximately 8.600 employees.* (Plastic News 2013)

This study will focus only on dairy packages and more deeply cultured dairy products. Technologies which are used will be presented afterward in the Technologies chapter. As mentioned below, manufacturers such as PACCOR, later on Coveris, are one part of the package value chain. Every part of the chain has its own missions but also many co-operative functions and responsibilities to fulfill. The most important function of manufacturer is to give more value to the customer by selling products which are demanded. Inside the company, research and development actions aimed at better products and services in the future. The aim of this project is to find the requirements window for the cultured dairy package. Cultured products have some special features while fermenting that modify the needed requirements of the package. Those features are explained in the package requirements chapter.

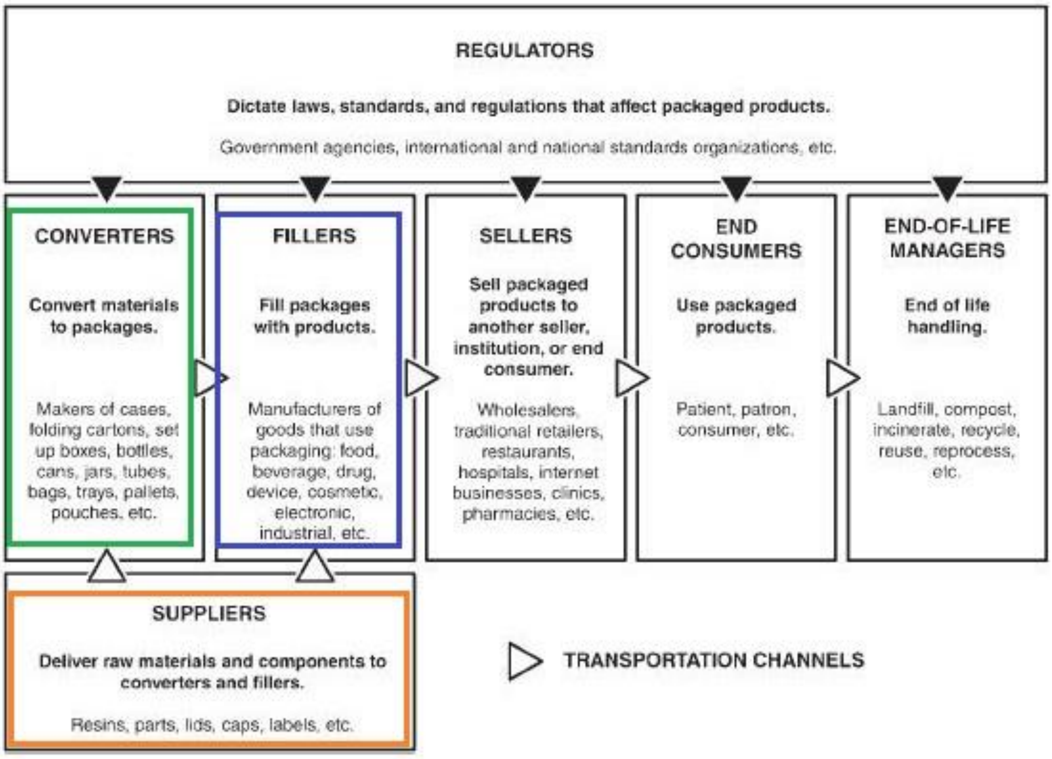


Figure 1 The package value chain through all the phases. Paccor, as well as one step before and after are colored. Green) cup manufacturer, Blue) dairy, Orange) raw material manufacturer. (Yam 2009)

Feedback in the chain is a necessary part of learning and developing. Information sharing and knowledge improvement are the basis of development. Cooperation between the players of the chain boosts development activities. Suppliers as material manufacturers usually get feedback from converters functioning as cup or lid manufacturers. The feedback given to converters is primarily provided by fillers and sellers, but indirectly also by end consumers. Sellers are in this case retailers and distributors. The main role of the end user is to vote by individual shopping behavior. After critical mistakes of early phases the end user can give straight feedback to the seller or filler.

1.1.1 Sustainability issues

The environmental impact of package

Susan Selke from the Michigan School of Packaging wrote in her article in the Encyclopedia of packaging that*:"Increasingly, packaging designers, manufacturers, and users are paying attention to the environmental impacts of packaging. This is being driven by a combination of pressure from consumers and from regulators and the desire of business and industry to engage in responsible corporate citizenship".* This trend is, and in the future will be even more, important. Based on current knowledge, the best way to assess environmental impacts is Life cycle assessment, LCA. The target is to analyze an entire package system during its life, from the raw material production to the end of the cycle. Comparison of material performance is a good method for determining the quality of a packaging concept, as well as where the largest amount of environmental impact lies in the package life cycle. Normally the impacts are divided to a few distinct categories, such as solid waste, energy consumption and pollution. These topics are discussed at more length further on in this chapter. (Siracusa 2012)

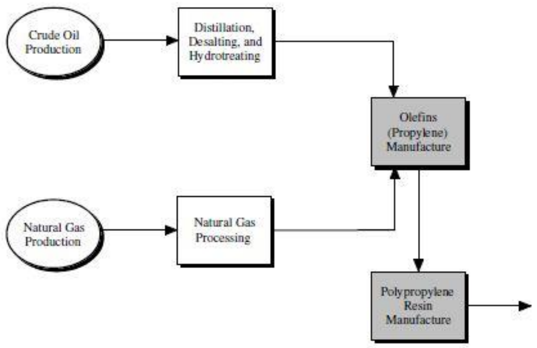
Primary food packages, and especially dairy packages, are almost always "use and throwaway"- packages. Some cups can be used as drinking cups after their primary purpose is served, but this is not common. LCA is calculated by using times per product, so all the environmental effects will be calculated to the damage from a single use.

Contribution of environmental issues is the obligation of a responsible company. A company can use their advanced knowledge of environmental issues for their competitive advantage. EUROPEN, The European Organization for Packaging and the Environment, has summarized topics which have opened steps to responsible actions. The main steps for how a product should be designed and function are listed below: (EUROPEN 2013)

- be designed holistically with the product to optimise overall environmental performance
- **be made from responsibly sourced materials**
- be designed to be effective and safe throughout its life cycle
- meet market criteria for performance and cost
- meet consumer choice and expectations
- be recovered efficiently after use

(EUROPEN 2013)

The sentence “be made from responsibility sourced materials” in the list above is the primary target of this study. Environmental effects from materials occur mainly from the raw material usage of polymer, resin production, polymer production, product production, water consumption, energy consumption and transportation between every step of production. Some of the polymers have a more difficult structure and need many different raw materials or higher temperatures in resin production. Longer transportation routes increase fuel consumption. Thus all these reasons increase the carbon footprint of the material and the final product. The processes of a few common package polymers, such as PP, PS and PET are diagrammed below in figure 2. The phases of resin productions and package life of PLA, PET and PS trays is illustrated in figure 3. (Madival Santosh & Co 2009) a.



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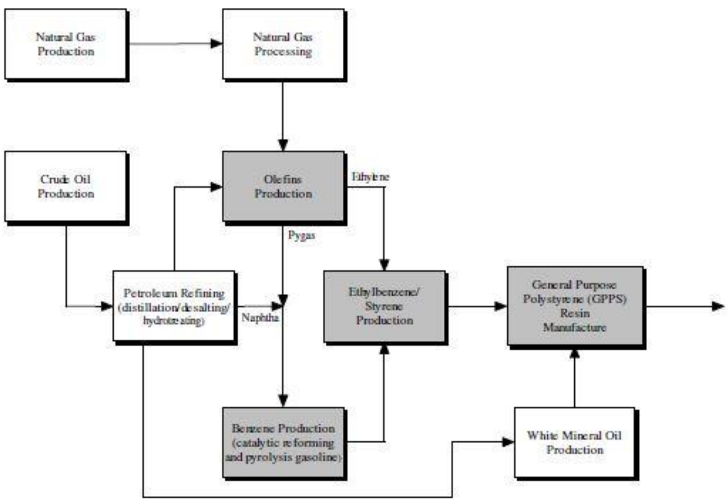

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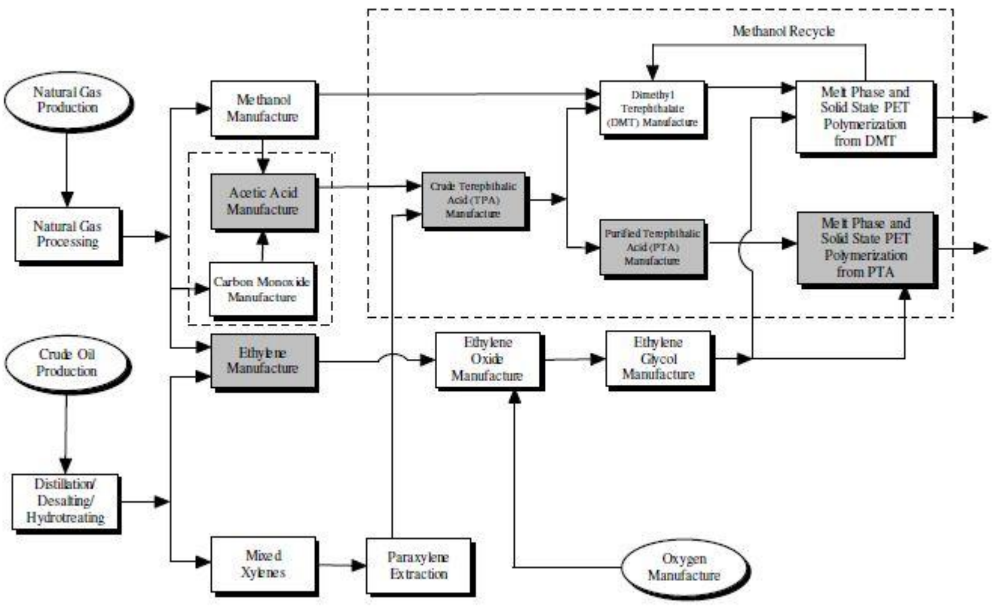

Figure 2 The process diagrams of most common cup materials. PET process is the most complicated process. a) PP, b) PS and c) PET. (Franklin Associates 2011)

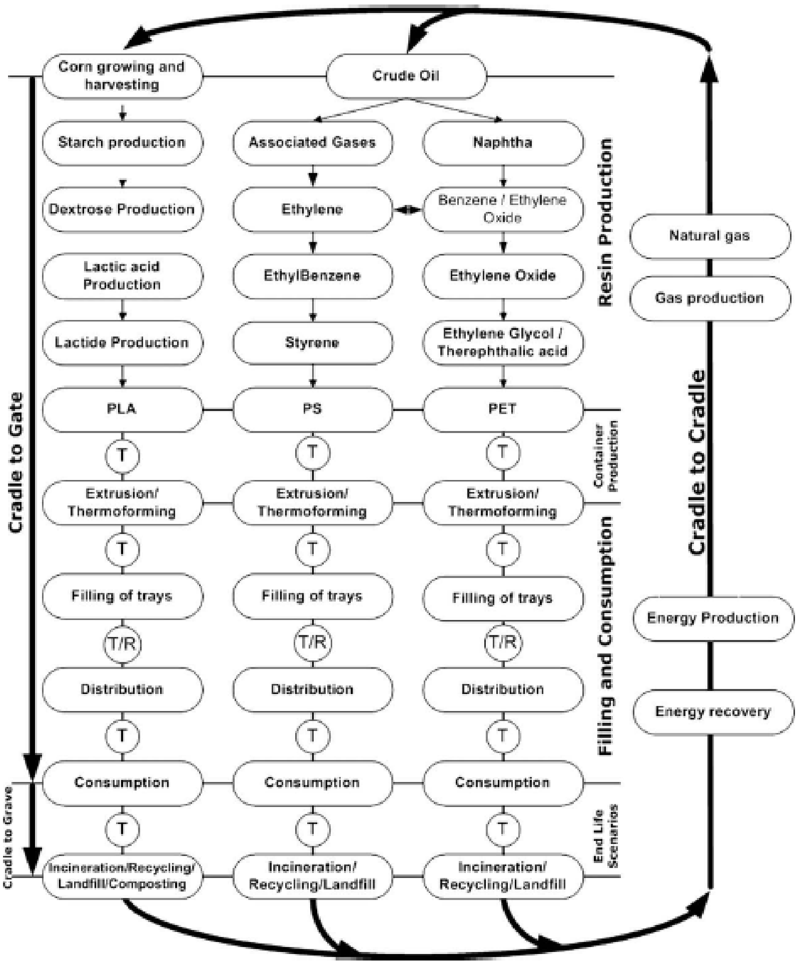

Figure 3 Resin production and main phases of package life cycle. (Madival Santosh & Co 2009)

When comparing these package materials, energy consumption and emission values are often used. Various studies are available but the results of studies are in agreement. The results depend on which part of the production is focused upon, what the transportation types are, as well as on distances and other uncertainties. Some of the raw material is easier to granulate, but in contrast the converting is more complicated or harmful to environment. If critical phases are left outside of the analysis, the results will differ between studies. Some of the studies concentrate only on carbon footprints but there are also studies which calculate greenhouse gas emissions. GHG, *Greenhouse gases are trace gases in the lower atmosphere that trap heat through a natural process called the "greenhouse effect."*(Office of Energy Efficiency & Renewable Energy). Greenhouse gases are divided into two categories: Naturally occurring, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and manmade gases, such as perfluorocarbons (PFCs), Hydrofluorocarbons (HFCs) and Sulphur hexafluoride

(SF_6). (Office of Energy Efficiency & Renewable Energy, 2014). Emission calculation is one part of environmental management, and it makes emission reduction more relevant and efficient.

The material data in tables 1-7 provide very compact information about energy consumption and emissions. In this context, PP and PET resin is made by using less energy than with PS. The carbon emissions and GHGs of PS resin production are also higher than those of PP resin. On the other hand, polystyrene converting has a smaller effect on GHGs than polypropylene or polyethylene terephtalate. The reason for this is not clear due to the lack of documentation. The author's educated guess is that higher energy consumption is due to material characteristics, as shown later in this chapter. Still the largest impact to the energy consumption and emission management resulted from resin production and transportation distances, if the latter were longer. The results of these studies are not comparable among themselves. (Franklin Associates 2011, Keoleian G. 2012)

Table 1 A summary of Total energy and GHG emissions of plastic products. (Keoleian G. 2012)

Material	Total Energy mmBTU/ton	%	GHG emissions g/ton	%
PP	70152	110 %	2248634	117 %
PET	63626	100 %	2959275	153 %
PS	74809	118 %	1930118	100 %

Table 2 A summary of total energy, GHG and carbon emissions of resin production from the extraction and refining of crude oil and natural gas to production of final resin. (Keoleian G. 2012)

Material	Total Energy		CO_2		VOC,CO,CO_2		GHG	
	mmBTU/ton	%	g/ton	%	g/ton	%	g/ton	%
PP	62628	113 %	1272575	100 %	1283580	100 %	1614654	100 %
PET	55563	100 %	2053513	161 %	2074463	162 %	2314689	143 %
GPPS	76221	137 %	2288062	180 %	2305028	180 %	2638958	163 %
HIPS	76892	138 %	2277184	179 %	2294091	179 %	2633028	163 %

Table 3 A summary of Energy consumption, Carbon emission and waste of 1000kg cradle to resin production. (Franklin Associates 2011)

	Energy		CO_2 + CO		Waste	
Material	GJ	%	Kg	%	kg	%
PP	76	110 %	73	100 %	41	124 %
PET	69	100 %	300	411 %	33	100 %
GPPS	94	136 %	330	452 %	42	127 %
HIPS	95	138 %	313	429 %	45	136 %

Table 4 Total and partial CO2 emissions of Strawberry package production and transportation. (Madival Santosh & Co 2009)

TOTAL CO_2	PLA 735 Kg	%/Total %	PET 763 Kg	%/Total %	PS 730 kg	%/Total %
Resin prod.	60	8 %	65	9 %	70	10 %
Extrusion	15	2 %	16	2 %	12	2 %
Thermoforming	22	3 %	24	3 %	18	2 %
Electricity prod.	3	0 %	4	1 %	3	0 %
Transport Res-Man	28,7	4 %	50,2	7 %	31,7	4 %
Transport Man-Fill	41,8	6 %	39,3	5 %	30,1	4 %
Transport Fill-Reta	564	77 %	565	74 %	565	77 %

Table 5 Total and partial energy consumption of Strawberry package production and transportation. (Madival Santosh & Co 2009)

TOTAL Energy	PLA 13400 MJ	%/TOTAL %	PET 14000 MJ	%/TOTAL %	PS 13500 MJ	%/TOTAL %
Resin prod.	991	7 %	2412	17 %	2400	18 %
Extrusion	283	2 %	303	2 %	231	2 %
Thermoforming	476	4 %	508	4 %	389	3 %
Electricity prod.	41	0 %	54	0 %	42	0 %
Transport Res-Man	477	4 %	837	6 %	528	4 %
Transport Man-Fill	697	5 %	655	5 %	501	4 %
Transport Fill-Reta	9416	70 %	9440	67 %	9410	70 %

Table 6 A comparison of polymer properties which affect processing temperatures and transportation emissions. Density, specific heat, temperature difference, heat of fusion and temperature which is needed in thermoforming process can be found below. (Madival Santosh & Co 2009)

Polymer	ρ, kg m^{-3}	cp, J kg^{-1} K^{-1}	ΔT, K		ΔH_f, kJ kg^{-1}	Heat required, MJ
			T_{tf}, K	T_{sheet}, K		
PLA	1246	503	383	294	27.03	0.21
PET	1370	568	435	294	34.00	0.31
PS	1052	697	455	204	0.00	0.30

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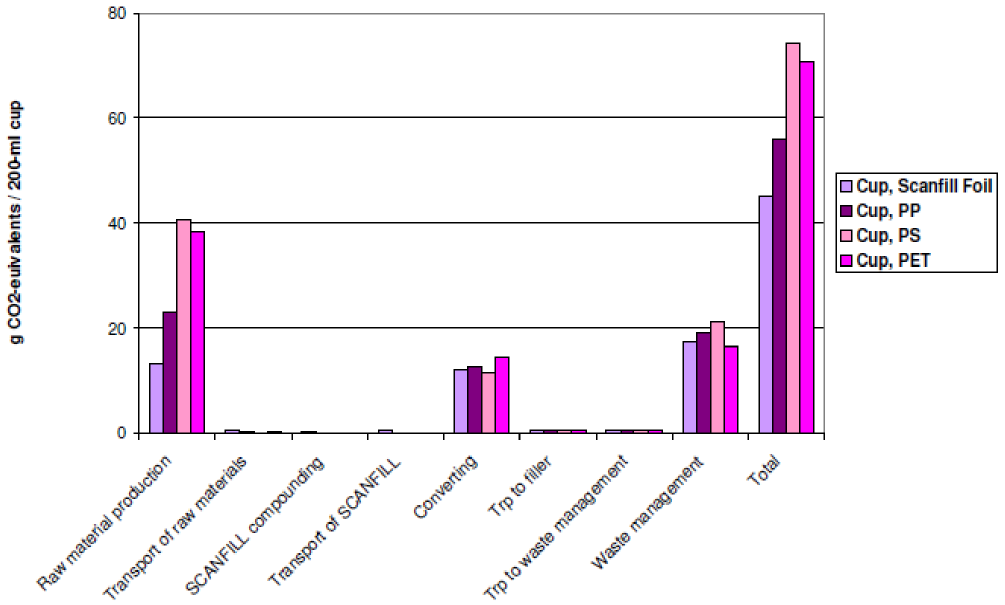

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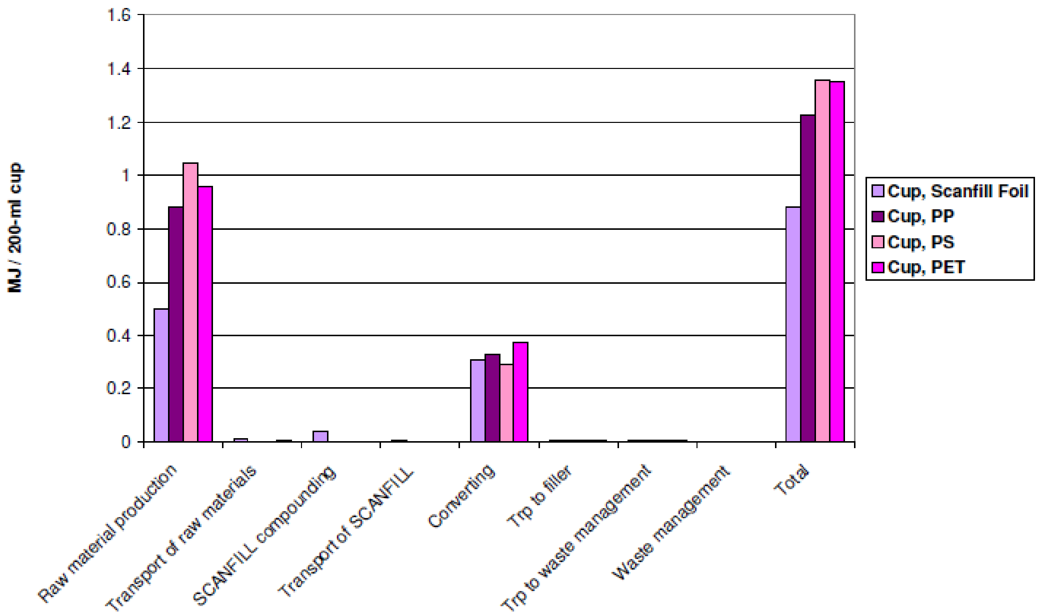


Figure 4 A comparison of CO_2 total emissions a) and energy consumption b) between a traditional dairy cup material and filled polypropylene. (Widheden A. 2009)

Bob Hope, the Material Technology manager of Coveris group stated that PP has 30% less kgC per ton than PS. The PS value is 799kgC and PP 562 kgC per ton. Based on this knowledge, every 10% of PS replaced with PP results in the carbon impact reduction of 42.2 kgC per ton. These numbers take into account chemical composition and production methods. (Bob Hope 2013)

Source data has been collected from different sources and alternative modelling approaches. Long distances and emission sensitive transportation modes between the supplier and producer increase the subtotal emission of PET. PS has the lowest total emission out of the three polymers. PLA and PET usually need a drying unit before extruding. To the filler company and to end user, it may look like PP is the greenest polymer out of the four but the greenest end product appears to be polystyrene. Polystyrene production is ideal in many ways for thermoforming. (Madival Santosh & Co 2009).

Figure 4 presents the results of the LCA of plastic cups. Filled material seems to be the most environmentally friendly in terms of CO_2 emissions. In this survey, as in others, polystyrene resin takes the biggest share of resin production. Like the other aforementioned studies, polystyrene is again the greenest material to convert. Converting still accounts for only a small part of total emissions, thus the total emissions of PS are the highest. Polypropylene seems to be the most emission friendly, with filling emissions reduced even more. Transportation emissions are at a very low stage out of the total amount in this study, compared to Santosh’s research. Global sourcing provides possibilities for centralizing purchases, resulting in savings. Cost savings and the most environmentally friendly choice are often mutually exclusive so you need to pick one of the two. The inversely proportional situation makes the choice more difficult, but the world´s thinking atmosphere is greener today compared to earlier times. Sustainable business can see the possibilities behind short term cost and use green issues for long term goals. Widheden´s research use much shorter distances in her study, so the use of domestic materials is assumed. This research was conducted for Polykemi, the producer of filled PP material. (Widheden A. 2009)

The density of the polymer increases the weight of a specific volume of polymer, but on the other hand it may enable loading more weight in cargo in same volume. A good filling rate for a transportation unit reduces emissions per specific unit but fuel consumption is higher with a heavier load. Normally, the higher density also provides more strength to the material and the package. The emissions per product may be reduced through this. Referring to the studies discussed, the most critical phases for reducing emissions and energy consumption are raw material production, converting, and transporting if distances are longer. Converter's possibilities for reducing emissions and energy consumption include material changes, optimized production methods and sustainable sourcing methods.

The EU regulates its member states and further on companies which are working with food and food packages. Decisions are passed either by the Commission alone or jointly by the EU Council and the European Parliament. Decisions are based on the technical knowledge of support experts and side groups. Regulations are addressed to every member state while directives are addressed to national authorities who proceed with further actions. Regulations are legally binding in all states directly after a regulation is passed, without national implementation actions. Directives assign the targets of member states, and thus countries need to find a way to achieve targets during a given period of time. In addition, national legislation needs to be mended to meet the directive targets. Authorities find the best way to do this with special processes in the legislation of a specific country. In figure 5 three levels of decision making are depicted. (European Commission 2013)

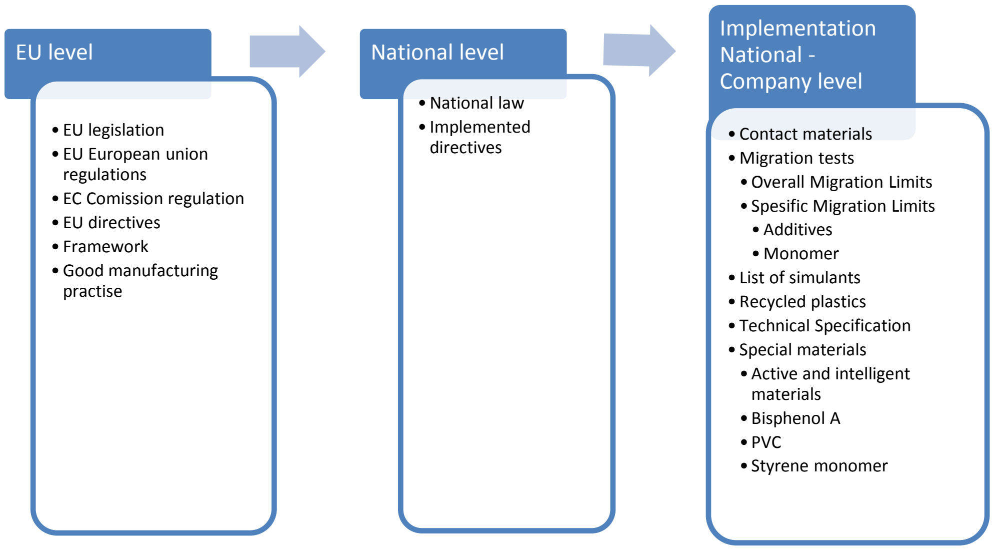


Figure 5 A simplified illustration of the EU legislation process and implementation activities.

A specific directive needs to pass a four-step route before adoption. First, the Commission service make a draft, secondly the Scientific Committee for food makes the decisions in view of public health. After those two steps, the Advisory Committee on Foodstuff consults with consumers, industrial, labour, commercial and agricultural parties. Finally the Scientific Committee on the Food chain and Animal health adopt the new Commission directive if no obstacles occurred. (European Commission 2003)

Increasing legislative demand will enter a new age at the beginning of the year 2016 when the new law of waste (646/2011) will be fully implemented. Old practice is allowed until May 2015. The new law is based on EU directive 94/62/EY. Changes in the new law obligate all fillers and importers to create a separate collection system for packages. The target is to have more efficiency in priority order recycling. The old practice is called partial manufacturer responsibility, in which the city council have responsibility for recycling, but the new law will set full manufacturer responsibility or extended producer responsibility (EPR). (Levinen 2013)

Costs from recycling networks will be transferred to the product prices. The changes may result in increased price competition for fillers, which may reflect on converters too. Figure 6 helps to understand the lifecycle of a package. The circular shape means that with recycling, the raw material can be used again for a new product.

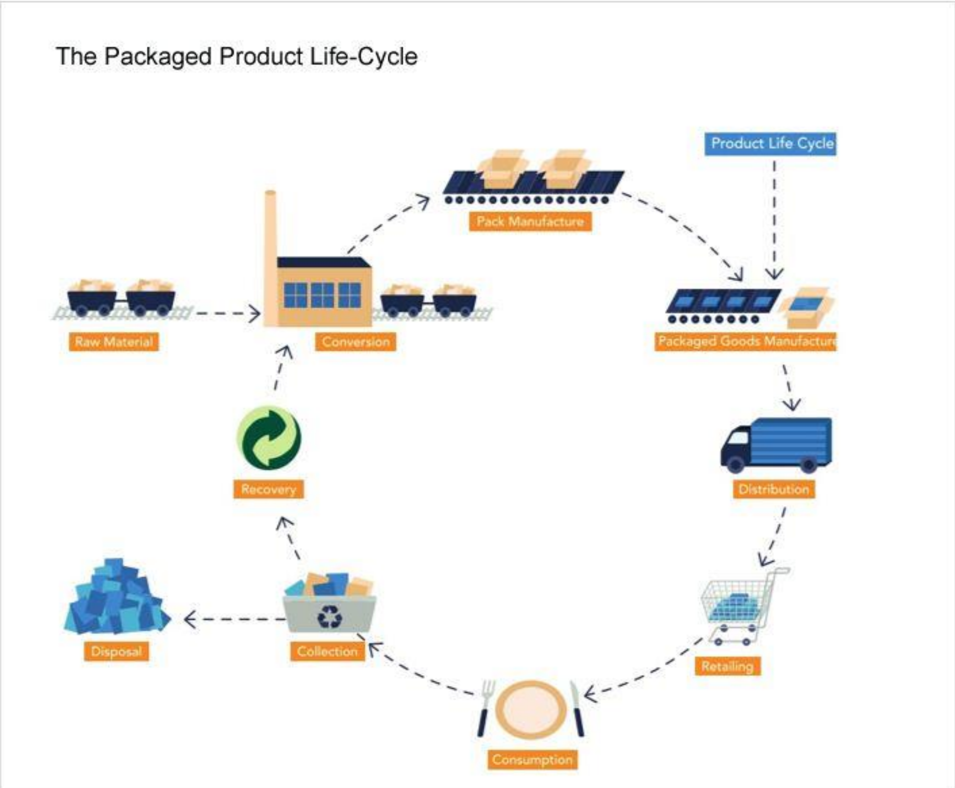


Figure 6 The product life-cycle of a food package and food. (EUROPEN 2013)

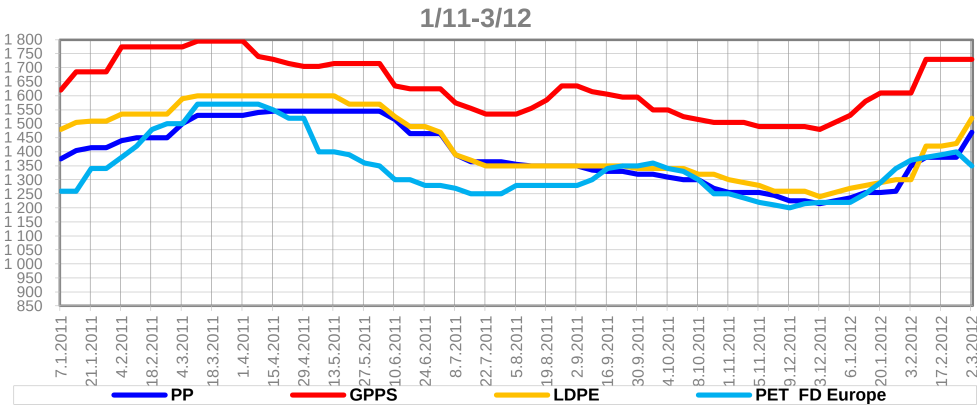
The most important phase in the plastic cycle in recycling terms is collection, and it should be an intelligent collection. There are a wide scale of different plastics which could be used in the most optimal way if the plastics were correctly sorted. Sorted plastics could be used for new products which allow recycled raw materials. Too often the problem is unsorted waste which is also dirty. This kind of plastic waste is impossible or unprofitable to use as raw material. In these cases, the best choice is often energy recovery. The major challenge is to build a collecting system which enables sorting and which is still easy enough for consumers. This requires changing public opinion and also a well-working collection system. One way to develop the life cycle and decrease waste per product lifetime is to produce reusable products. The package can be used again, if it is good enough or if it can be more than a package. Coca- Cola is trying to launch a 2nd life boom (figure 7). They are selling add-on caps which give a second life to the empty bottle. The idea is great but its effect may be more image boosting than actual reuse increasing. In any case, Coca-Cola wants to show that they are interested in finding greener ways, at least in a marketing sense (Coca-Cola 2014). At the moment in the dairy cup industry, material optimizing, and material saving are the long term trends. Multilayer structures and high quality decorations are of high value today in some products. Sometimes multilayer structures can enable light weight, but they also make recycling more difficult. The overall effects of the life cycle should always be kept in mind.

Figure 7. Coca-Cola 2nd life example. Reuseable and functional caps can be used as a pen sharpener, a bubble maker, a whistle cap or even a watergun. Special caps sold separately. (Coca-Cola)

1.1.2 Financial issues

The price of polystyrene has increased in recent times. The trend is more increasing than that of, for example, polypropylene, which is widely used in food packages. The figures 8 A-B below illustrate that PS and PP prices have been relatively close during the profile time frame, but recently the gap has expanded. In early 2012, the gap between PS and PP was about 200€ per ton, that is, about 20%, but in early 2014 the gap has expanded to 600€ and 40% per ton. Prices are based on the ICIS database, which is updated weekly. The database provides a clear picture regarding the trends of material prices. Depending on the supplier and volume, the price may waver up and down. In this case, such price changes contribute only to a small variance in the numbers. Under the new name Coveris, and with larger volumes, price tendering is easier. The real reason behind the ascendant trend is the law of supply and demand. The worldwide usage of PS is decreasing and the price of benzene, butadiene and other ingredients of polystyrene is increasing. The North American sales of PS have dropped approximately 5% in the first half of 2012, compared to the first half of 2011, as stated by the Senior reporter of Plastic News Frank Esposito in the article “Polystyrene and PET prices rise in August”. The trend has continued to this day with PS - however not with PET - after the publication of the article on the 13th of September 2012. The PET price today is quite competitive. Production issues are increasing the total costs of companies. Material price is a contributing factor but there are also energy costs and production costs that vary depending on the material. Production costs are further explored in a chapter concerning production.

a.



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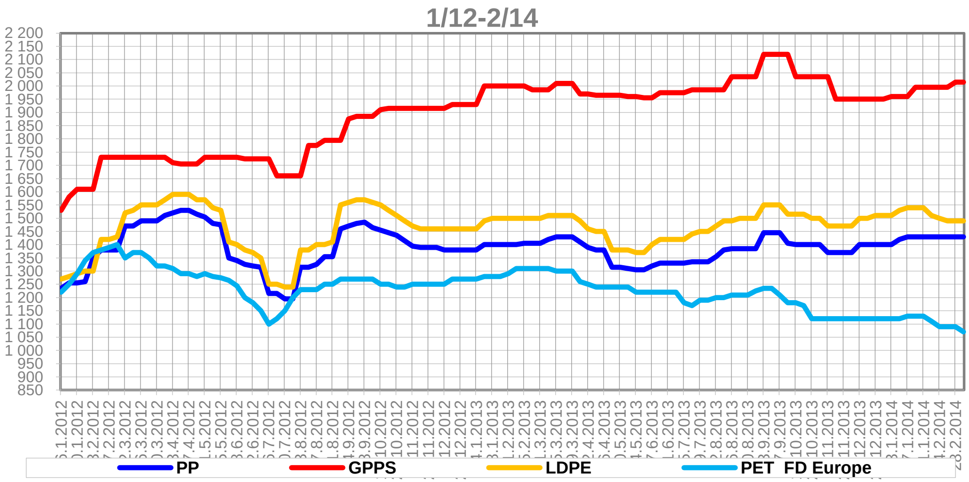


Figure 8 Material price charts a) January 2011 – March 2012 (up) and b) January 2012 - February 2014 (down). The price increase of polystyrene has been the highest during recent years, with the gap to the other materials expanding. (ICIS 2014)

1.1.3 Production issues

The converter's point of view

The characteristics of a material have a huge impact on the processing of dairy cups. The properties of the material used are always optimized to meet the needs of the product. The chosen material is a compromise if all the needs are taken into account. Nevertheless, it should be the best compromise possible when considering the priorities of the product life cycle.

A different material has a high probability to change almost everything in the later process flow. The biggest changes can include material handling system modification, material drying system purchasing, extruder purchasing, layout modification, new mold designing and purchasing and setting different process parameters, to name a few. A lower cycle time will result in a lack of capacity, resulting in new machine investments and in the worst case a bigger production hall. New thermoforming machines are luckily more efficient than older. The new material is of course a challenge when first employed, thus it takes time to get used to it. These topics are discussed later in more detail.

The filler's point of view

This chapter will examine the most important cup properties which fillers normally expect from a cup. For fillers and consumers product durability throughout the packaging line and life cycle is important. Sometimes packaging lines have higher requirements than end users. During transportation a package needs to be stiff enough to carry loads and withstand impacts. This is one factor which is tested in this study. Top load tests provide information about a package with regards to how much load a cup can carry. The second important factor is correct dimensions, and roundness. Wrong shrinkage, which is typically the result of incorrect temperature control during the converting process, may lead to unwanted dimensional errors, such as ovality or a wrong volume in the package. Tolerances of filling pockets are qualified and a package with wrong dimensions may not fit into the pocket. In the practical section of this work the differences in the shrinkages of different materials are tested. The material is one of the most dramatic factors affecting the shrinkage rate.

The concave bottom of a cup, “Bubble bottoms”, may lead to errors in packaging lines if the package begins to rotate in its place. The centrum of the bottom should usually be straight and not the lowest point of the bottom. Rims around the bottom are typically the lowest point of cup and carry the load when the cup cannot rotate easily. A concave bottom is often the result of thickness varying and due to this temperature differences across the cup. High differences may cause partially smaller shrinkage and the part with lowest shrinkage rate will be wider than other parts. A round shape will concave due to this effect.

1.2 Technology

COVERIS Rigid Finland is primarily focused on thermoforming technology. Thermoforming is one of the most productive process methods for producing cups, trays and lids for the dairy industry. Plastic sheets, which are formed later to cups and trays, are also made in Hämeenlinna. This paper focuses only on dairy cups (an example in figure 9).

Decoration is a process step after cup manufacturing that is not included in the core issues of this work. The aim of this work is to concentrate on the issues that affect permeability or mechanical cup properties. Decoration methods are primarily concerned with visual effects on the package, but there is one exception. The Duosmart carton sleeve is a layer which gives strength to packages in which it is used. This special case is not included in the main focus of this work.

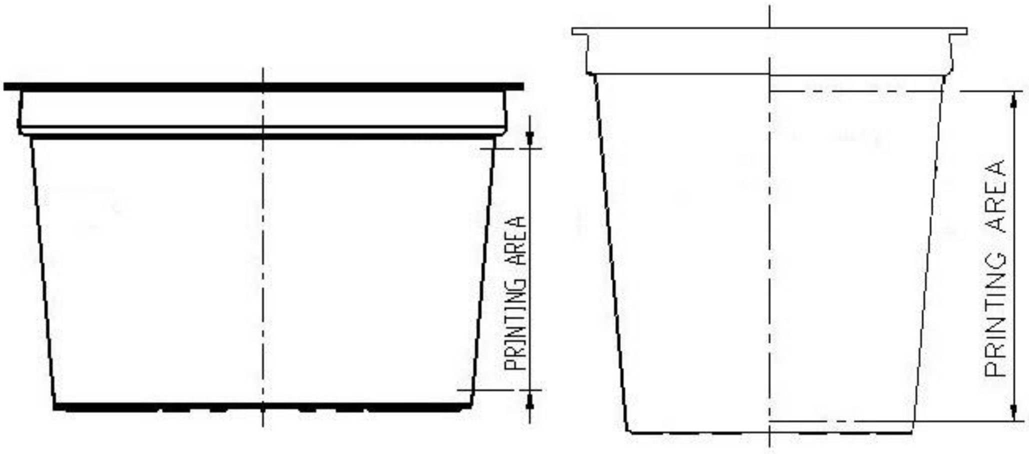


Figure 9 A few popular service dairy cup types in Finland, lower cup (left) and deeper cup (right). (Product catalogue of Coveris)

1.2.1 Sheet extrusion

Extrusion is a process where plastic granulates are melted by fraction and heating, then melt pressed through a flat die. An extruded high quality sheet provides the possibility of success in further process steps. The aim of extrusion is to get homogenous material from the die at a right thickness and right temperature. The material flow has to be equal for the entire width of the die. Wrong parameters can destroy polymer structure and reduce the features of the polymer. Thermoplastic materials such as polystyrene and polypropylene, have memory as long as they are not melted again. This also means that the quality of the sheet will remain consistent at each stage of the process. Orientation, crystallization rate and dimension stability are highly dependent on sheet quality. One of the most important actions in sheet extrusion is the cooling process. A sheet should cool down in as symmetric fashion as possible. A deeper analysis of process parameters is left out of this study. An extrusion machine is shown in figure 10 below. This kind of machine is necessary when the sheet for cups is needed. Assembly may vary according to manufacturing needs. There can be, for example, more screws when multilayer structures or a higher capacity are possible.

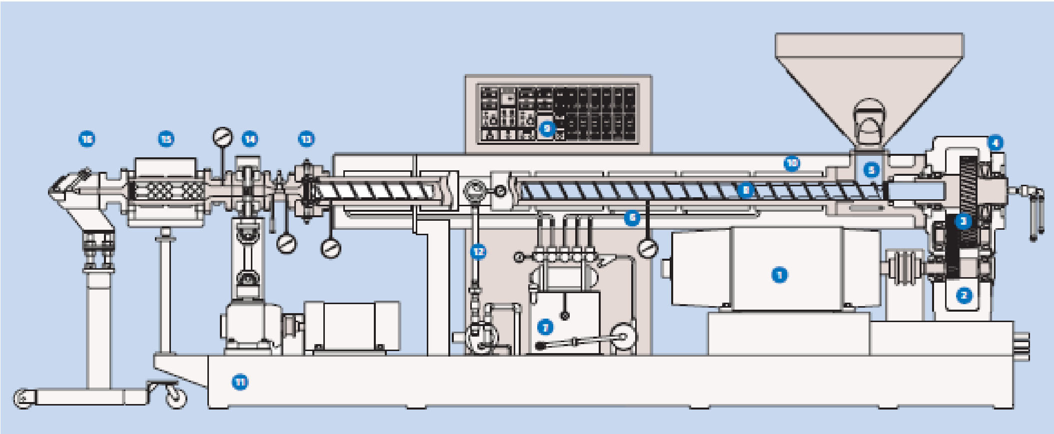


Figure 10 A polymer extruder and its most important parts. 1-4. Motor and transmission, 6-7. Heating and cooling equipment,8, Screw, 10. Cylinder, 12. Venting channel, 13. Screen changer, 14. Gear pump, 15. Static mixer and 16. Die (Lyondell 2013)

1.2.2 Thermoforming

Thermoforming is a process in which a 3D-product is formed out of a plastic sheet. In this case the sheet is heated to the required temperature, the product is formed by plug and air pressure, then cooled down to the rigid shape by a cooled mold and finally cut and stacked. Thermoforming machine is shown in figure 11. Pressure thermoforming is typically used when the depth of the product and the draw ratio is low (see figure 12). Plug stretching is used to help material stretching if the depth is higher. Mechanical force is a more stable way to elongate a high viscous plastic material compared to non-touching air pressure. The mechanical plug cools down that part of the product which is in direct contact with it. The plug can damage the material by scratching. The plug base radius strongly defines the thickness of the cup's base. The bigger the radius of the plug is, the smaller is the resulting initial contact area, and thinner the base of the cup. A bigger radius increases the need of pressure stretching after plug stretching in the corners and this will make walls thinner near the bottom. Optimized wall thicknesses depend on the product. Better top load is achieved with a thicker side wall and a stronger material. The stretching of the material strengthens the wall in the direction of elongation. Material orientation is directed more towards the direction of stretch during elongation. The aim is to get equal wall thickness, that is, thickness distribution. More on this can be found in Thermoforming – A Practical guide. (Illig A. 2001)

Amorphous materials normally have a smaller shrinkage rate. An amorphous material such as polystyrene or poly lactic acid has a lower shrinkage rate compared to partly crystalline materials, e.g. polypropylene. Tool dimensions are calculated by using earlier knowledge of the design. Negative angles have to be smaller and other dimensions need to be closer to the end product dimensions in low shrinkage materials. (Illig A. 2001)

The most critical material parameters in thermoforming are:

- Stiffness, Hardness, Flexibility, Impact strength

  (Tensile strength, Elastic modulus, Izod, Shore D)

- The material factor for heating and cooling time

  (Thermal conductivity, Specific heat, Heat capacity)

- Forming temperature and temperature range

  (Melting point, Crystallization temperature, Degradability temperature)

- Density

  (Mass of package, Price of package, Permeation characters)

- Shrinkage%

  (Dimensional accuracy, mold detail requirements)

- Printability

  (Surface tension, purity, thickness distribution)

Figure 11 A thermoforming machine. The heated sheet is formed and cut in the mold section and products are stacked and transferred to the belt. The film strip is wound to the grinder and blown back to use. (Gabler)

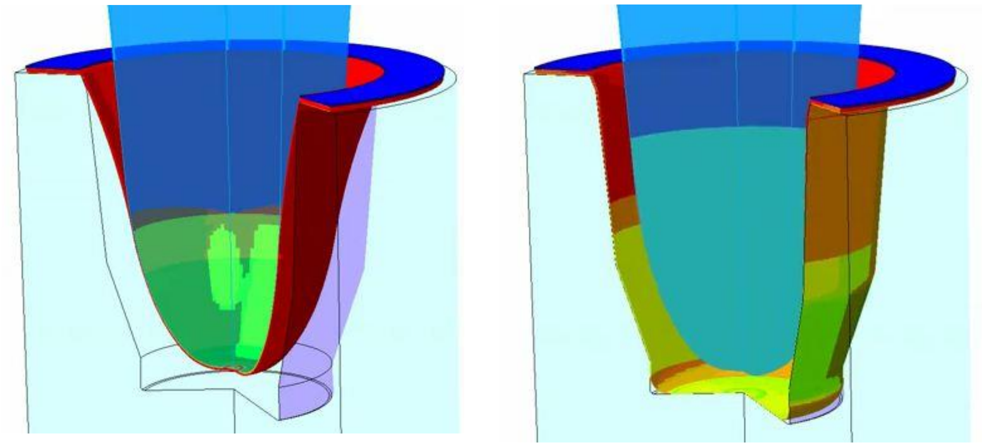


Figure 12 The mechanical plug assisted thermoforming principle by using plug and air pressure. The stretching process has two phases, first by plug (left) and then by pressurized air (right). (Queen's University 2011)

This chapter will focus on critical characteristics and consider their effects as well as the reasons for said effects. In the thermoforming process, the material has many properties which are important to understand while processing. Material moisture absorption may affect the pre-drying need if the material is humidity sensitive. Drying needs energy and higher energy consumption always increases production costs. A material which is formed should be heated to the correct temperature window. For amorphous materials this temperature is always above the glass transition point. For partially crystallized materials it is normally a few degrees below the melt point. It is typical that PP, for example, has its forming range between 150-160 C°, but the optimal forming range can be even narrower. The melt point is dependent on the material producing process where the material gets its characteristics. Copolymerization and the molecular weight of polymer change the melting point. Polystyrene (PS) does not have a critical melting point. Amorphous materials have a wide softening area, wherein the material slowly loses its strength. PS forming range is about 120- 160 C°, a wider area is possible but not necessary. A higher forming temperature increases the need for heating energy and a narrower forming range will make forming more challenging. Good melt strength makes forming easier and decreases sag problems. In reality, the process optimizing must be made more carefully, and in spite of this small changes in the surrounding environment or material can result in the poor quality of a product. The most important characteristics of thermoplastics while heating before forming are the heating period, expansion, strength of material at forming temperature, temperature range and temperature gradient across material thickness. If the material has no strength at the forming temperature, it is more difficult to handle and it can drop down on the heating units and burn. The temperature gradient indicates the extent of the difference between the surface layer and the core layer. It is impossible to get the layers to the same temperature because heaters work more effectively on the surface (see figure 13). The bigger the thermal condition value is the smaller the difference between the surface and core temperature is. (Illig 2001)

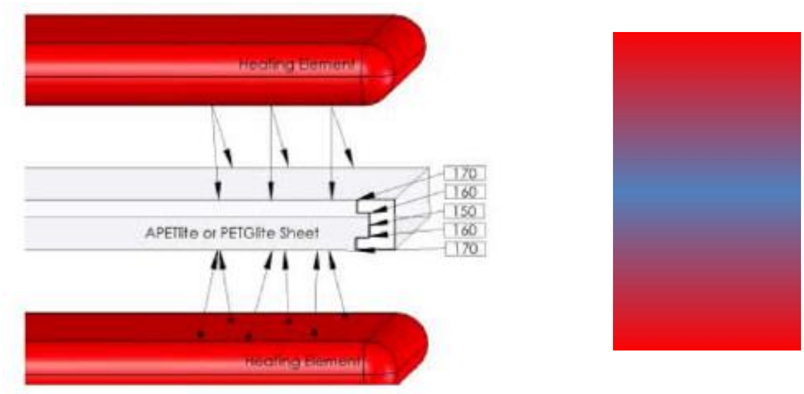


Figure 13 The heating of a plastic sheet. Surfaces are always warmer than the core. The higher the thermal conductivity of the material and the thinner the sheet, the faster the core warming and the lower the difference are. (Foamalite 2014)

PS has a relatively low shrinkage compared to other competitive materials. Partly crystallized materials, such as PP, have a three or four time higher shrinkage rate. Higher shrinkage can have an increased effect on dimensional instability, the oval shape of the cup or on the rising of the seaming surface. These unwanted phenomena occur if the production cycle time is optimized too close to the critical point of risk production stage. Mold parts are designed and machined with a known shrinkage rate. Thus, the same mold is impossible to use with different materials if the shrinkage rates differ too much. In the case of PP versus PS, PP shrinkage is about 1.5 -2% and PS about 0.5%.

A material change from polystyrene to polypropylene means a lower production speed due to the thermal properties of polypropylene. New machinery with a new mold helps to increase efficiency in the future. Investment in a new mold is very expensive so the customer base for the products depend on it as well as the payback time should be certain. It is calculated that new generation machines can radically decrease the cycle time and provide 40% (PP) to 50% (PS) better production efficiency due to novel innovations such as a new cooling system. The running speed of polystyrene is 17 to 25% faster than PP depending on machine generation, as stated by Grzegorz Lasicki, Plant Director of Coveris Rigid Poland. Gaps between materials are smaller with new generation machines (see figure 14). (Grzegorz Lasicki 2014)

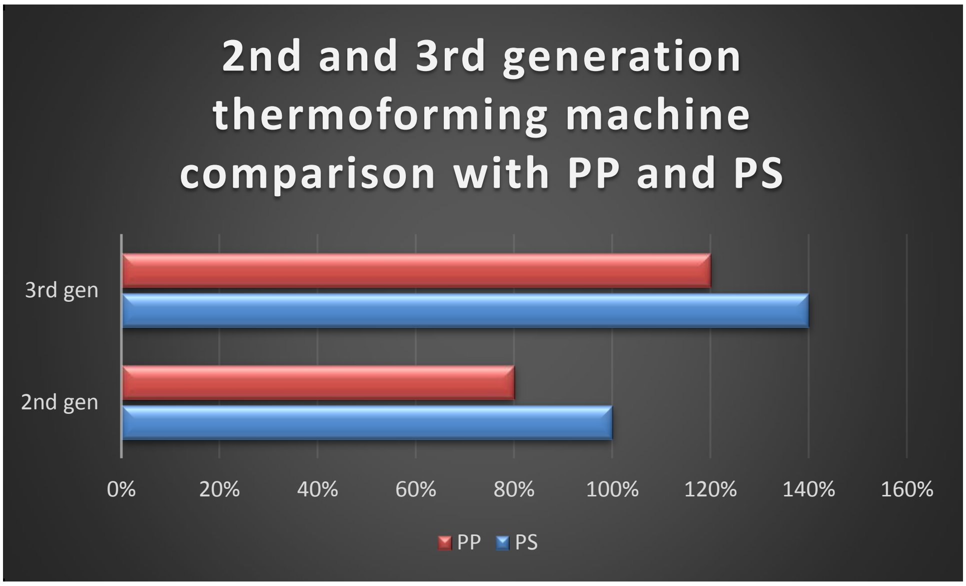


Figure 14 A faster cycle time with a new generation machine. The polystyrene thermoforming cycle time is crucially faster than that of polypropylene but new innovations lower the gap.

Equal wall thickness is a result of many factors, such as plug speed, air pressure, friction between plug, material, shape of plug, sheet thickness, temperature of material, mold temperature. These factors and their timing affect the end product. The sheet quality should be as required. Sheet production and quality are further explored in a dedicated chapter further on. In summary, the ideal material should be easy to form with a low forming temperature. The material should have good flow characteristics and thermal strength, high impact strength and low shrinkage on cooling. Environmental issues and the price of processing, including energy, may sometimes be more emphasized than the optimal characteristics of a material. (Illig 2001)

1.2.3 Lid

The lid is a component of a dairy package. When features such as gas transmissions are studied, all parts of the package must be taken into account. Even if Coveris Finland do not produce any lids for fermented dairy products, they need to understand the effects of lids to the end product. This entails close relationships with the customers and other suppliers. A list of various fillers' expectations of packages can be found below:

- Protection
    - Mechanical stress
        - Compression load
        - Impact forces
        - External and internal pressure
    - Chemical stress
        - Acids – Lactic acid
        - Gas permeation – O_2, CO_2
        - Organoleptic barrier
- Attraction
    - Shape of lid
    - Printability
        - Surface quality (roughness)
        - Gloss and Shiny
    - Decoration
- Smooth production
    - Perforation
    - Free of static charge
    - Flatness
    - Stiffness
- Usability
    - Seam
        - Open force - tight seam
        - Openability in one piece, non- rupture
        - Slippery vs. tacky
- Recyclability
- Image of material
- Price versus properties

Usually the lid material in dairy products is printed aluminum, but recently customers have moved toward metalized plastic lids. Metalized plastic lids are designed to offer better print quality, tear resistance, usability and characteristics with regards to environmental issues. In general, marketing teams want increasingly attractive package solutions, but production units face material difficulties and deal with the resulting problems first hand. Currently in many cases the aluminum lids have a larger parameter window and better seaming results. The development of MPET lid seaming is continuing on. (Toikkanen K. 2013, Bergengren T. 2013)

1.2.4 Packaging material

Polystyrene in general

Polystyrene is one of the most widely used plastics in the world and has applications in many different fields, such as packaging, the automobile industry, construction, electronics, furniture, and house ware. Over the years, polystyrene grades have been developed to meet the different needs of applications. PS is based on the styrene monomer and as figure 15 shows, the polystyrene molecule has an aromatic ring, which largely provides the characteristics of the polymer. The ring provides chain displacement which makes the molecule more brittle and stiff. The production of polystyrene is illustrated in figure 16. General purpose polystyrene, GPPS, is the original - and widely used - amorphous polymer, also known as crystal clear polystyrene. GPPS is hard, stiff, brittle, transparent, and dimensionally stable. GPPS is a very suitable material for the surface layer of a plastic sheet. It gives a glossy surface which is a good base for printing. The other commonly used polystyrene is high impact polystyrene, HIPS, which is actually a copolymer with rubbery substances. Brittleness in packages is usually avoided, when high impact grade is used for better impact resistance. Transparency and stiffness of the material decrease, when rubbery monomers are added. Butylene monomers are commonly added when high impact and puncture resistance are needed. Impact and puncture resistance are extremely important when the cup is carried home. The most common copolymer is butadiene-styrene. High impact polystyrene has about seven times better impact strength and half of the tensile strength of styrene homopolymer. Its softening point and hardness are lower. (Ravve 2012)

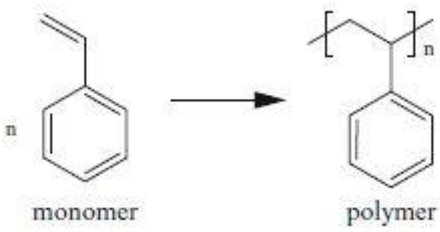


Figure 15 Styrene monomer (left) and Polystyrene (right). In polymer, the double bond is opened and monomers are fixed together. (Principles of polymer chemistry)

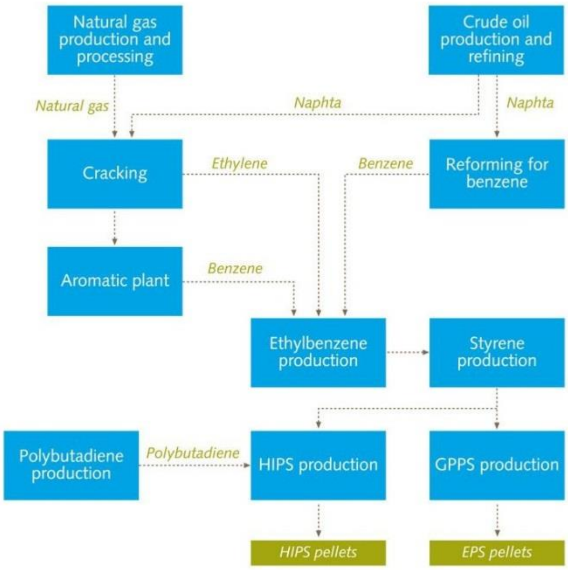


Figure 16 The production of HIPS, GPPS and EPS granulate. (PSPC 2013)

A styrene monomer might be harmful, if its concentration is more than 20 ppm. Worst situations arise from the production of reinforced plastic or polyester resin production, as some contents measured from these exceed set limits. The small amount of styrene monomer in extrusion and thermoforming production can be removed with a good exhaust system. Styrene monomer may cause irritation if exposure is prolonged or short-term styrene content is above the defined limits. Studies have shown that short-term exposure to styrene vapor may cause mild irritation such as headache, dizziness and fatigue, dermatitis. A concentration at around 100 ppm will cause definite irritation, such as slower reaction times, reduced manual dexterity, impaired co-ordination and balance will occur at 200-500 ppm and severe irritation at over 500 ppm. It has been reported that long-term exposure may affect the central nervous system, slow down reaction times, damage genetic material or be carcinogenic for humans. (WorkSafe Western Australia Commission 1996)

Measurements in polystyrene converters’ plants in Finland show that levels of styrene monomer content in air are low. Exposure standards for styrene monomer, short term exposure limit (STEL) and time weighted average (TWA) are clearly above the converters’ values. Values are measured in extrusion and injection molding companies in Finland. The STEL and TWA limits of the Finnish Institution of Occupational Health (FIOH) are 100 ppm/15min and 20 ppm/8h. A survey by the FIOH reveals that the average styrene amount during converting is about 2-3 % of the Finnish TWA limits (20 ppm). The limits are defined separately in different countries, and TWA limits vary between 20- 100 ppm. The Occupational Safety & Safety Administration limit is 50 ppm. According to the EU Dangerous Substances Directive the health effects of styrene are classified as “Harmful by inhalation” and “Irritant to skin and eyes”. (Työterveyslaitos 2014)

PS compared to other materials

For a long time, polystyrene’s many advantages have been impossible to achieve with other materials at the same price. The stiffness, transparency, and safe food contact properties with a reasonable price have created a competitive advantage for polystyrene. PS is also easily modified and this makes it suitable to many applications. For thermoforming companies, the excellent thermal properties of polystyrene provide relatively low forming temperatures, a fast processing cycle and therefore lower production costs and efficiency. (Cardarelli 2008; Ravve 2012)

In this study, polystyrene is the reference material as it is the material in use at the moment. Polypropylene referred to often in this thesis for comparing polymer properties, because polypropylene is one of the competitors of polystyrene. PP has a higher thermal stability and impact strength than PS. Both GPPS and PP homopolymer need additives if the product is used in temperatures below 0 °C. APET has recently increased its market share in the packaging field and is one of the major food package materials used. The origin of this thesis stems from the need for a material which has relatively weak barrier properties. It is known that the APET polymer has high barrier properties and thus APET was left out of these tests. APET has very good stiffness, transparency, and a small shrinkage rate but it also has a high gas barrier, and requires a relatively high melting temperature and a drying unit before melting. The use of APET requires practice and knowledge of production in order to produce high quality sheets efficiently.

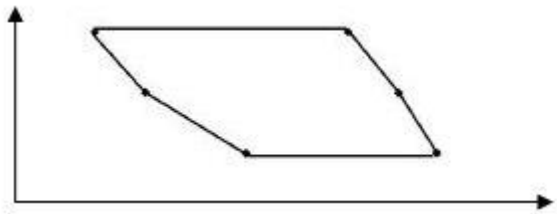
Poly (lactic acid), PLA, is a bio-based material, and its properties are quite close to those of polystyrene. It is stiff, transparent, and normally amorphous. Its forming window is also wide. Dairy packages are already made out of PLA in Europe. The bio-based raw material is in principle a good thing, but the source of PLA is typically corn. Hence PLA requires corn fields to cultivate raw material for packages. 1 kg PLA production demands 2.5 kg corn based on the article, PLA: Critical analysis. (Kingsland C.) PLA is not an oil based material like most other hydro-carbon based plastics are. PLA is also compostable in specific composting environments. Commercial composting needs concentrated composting facilities or a distributed system to achieve a correct composting environment for PLA. (Madival Santosh & Co 2009)

Polymer properties related formability

The melt flow index describes how viscous the material is at a specific shear rate. In the MFI test method, the shear rate is low, but it still provides information on material characteristics. The forming of higher MFI material requires less temperature or pressure than that of a lower MFI material. Because the lowest and the highest forming temperatures are limited by material characteristics, a high MFI material has a narrower process window than a low MFI material. Figures 17 a-c below show clearly how the processing window changes as MFI changes. By using nucleating agents, the processing window can be widened.

A = Low MFI

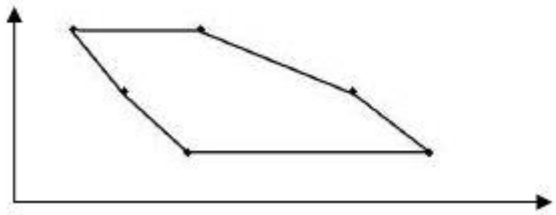
Pressure



Temperature

B = Middle MFI

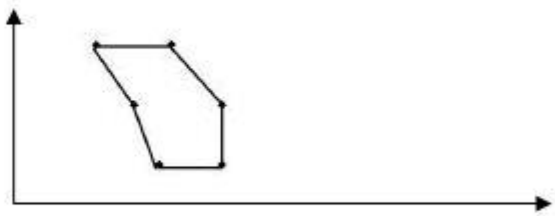
Pressure



Temperature

C = High MFI

Pressure



Temperature

Figure 17 Processing windows of three different MFI materials. High MFI means a narrower processing window but it enables forming at a lower temperature and pressure. Values are for illustrative purposes only. Vertical = Temperature, Horizontal = Pressure. (INEOS)

In Principles of Polymer Chemisty, it is stated that *the physical properties of polymers are also related to their molecular weights. Melt viscosity, hot strength, solvent resistance, and overall toughness increase with molecular size*. **Molecular weight distribution**, MWD, describes the proportional numbers of different weight molecules. Molecule chain length and chemical structure increase the weight of the chain. The higher the molecule weight, the higher the softening point is. There are also other parameters which affect the characteristics of a polymer´s thermal properties. A low MFI material is easier to melt and needs a lower amount of heat to become formable. A high molecular weight usually influences the mechanical properties of the polymer and makes material forming harder. The polymeric dispersity of material is a ratio between the weight average molecular weight Mw and the number average molecular weight Mn. The higher the ratio, the wider the dispersity. (Ravve 2012)

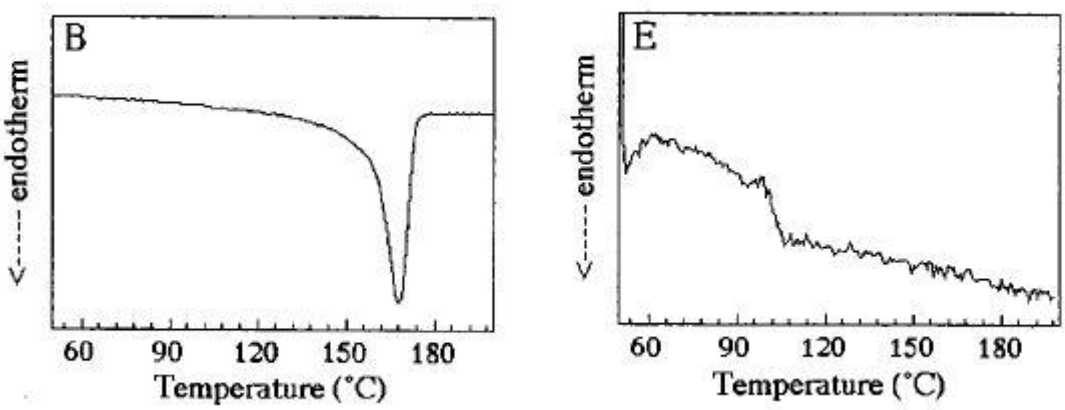


Figure 18 DSC curves of PP (right) and PS (left). PS does not have a critical melting point but PP does. The PP melting point is approximately 163 C°. PS glass transition range is between 95-110 C°. (Mannivan A. & Seehra M.S.)

Forming temperature is dependent on material properties. Figures 18, 19 and 20 show that amorphous and crystalline materials behave very differently. As James Throne has stated, PP viscosity does not change radically at the glass transition temperature, but at the melt temperature, however, it does. It is still possible to form it at a lower temperature but this requires faster movements and more forming force. PS viscosity changes rapidly after Tg and the optimal forming temperature is quite close to it.

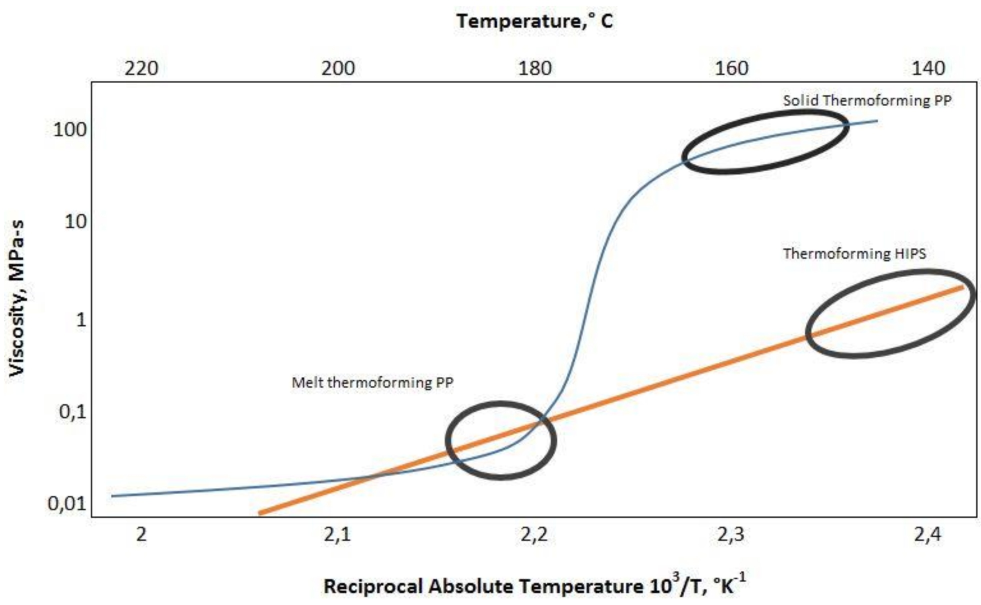


Figure 19 The viscosity of polymers when the temperature increases. Polypropylene viscosity changes radically when temperature reaches the melting point. Styrene has an almost linear softening after its crytallization area. (Throne J. 2013)

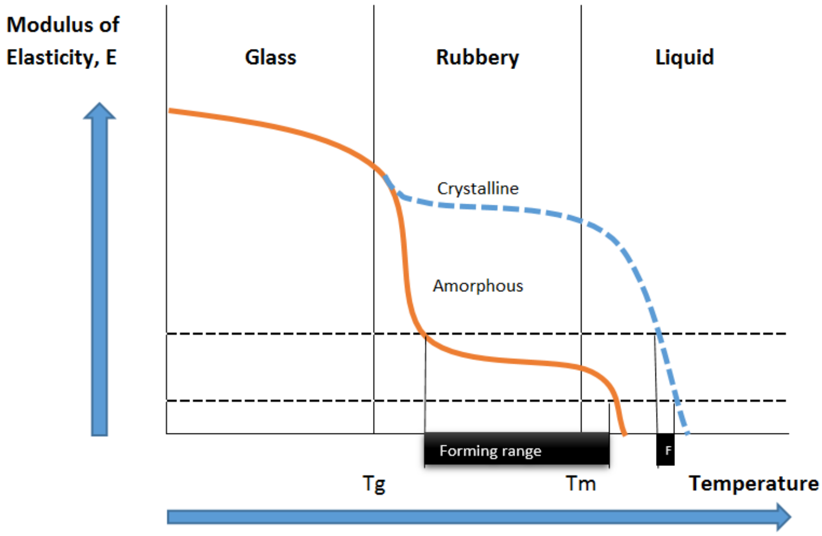


Figure 20 The thermoforming range of amorphous and semi-crystalline plastic. Typical curves of amorphous and crystalline polymers. Amorphous materials, such as PS, have a wider forming area than PP. The temperature scale is not equal between the two curves. (Throne J. 2013)

PS requires less cutting force than PP, especially in thin gauge sheets. In thicker sheets, PP is relatively easier to cut but still needs more force and accuracy than PS. PET is even more difficult and needs almost a doubled amount of force in order to be cut. Thorne´s experiments show that PET and PP are easier to cut with a heated blade. PS is more brittle so the cutting is more rapid and the cutting effect continues automatically after the first crack. The cutting quality can be lower if the cutting process is not under control. PP and PET are tougher so the blade needs to press until the wall thickness is almost cut through. Cutting blades may have a shorter life when cutting harder materials. This may result in increased maintenance or in the use of more expensive blades during the initial stages of cutting. (Throne J. 2013)

A comparison of characteristics data for thermoforming materials is given in table 7. Numbers are indicative, not precise because different grades vary quite a lot. These numbers gives information from material forming properties but also something about price factors and protectiveness.

Table 7 Material comparison for thermoforming. (Illig A., Hope B., Yam K.L., Scanfill)

		GPPS	HIPS	PPC	PPH	APET	Scan PP	Foam PP	PLA
Density	g/cm2	1,05	1,05	0,9	0,9	1,34	1,38	0,5-0,7	1,25
Flexural modulus	Mpa	3200	1800	1400	1600	2300	+2000?	-	2200-3000
Shrinkage	%	0,5	0,5	1,5-2	1,5-2	0,5	0,5-1,5?	-	0,3-0,5
Usage temp range	C	0 - 85	-105	-170	5 - 130	-90	-20 – 130?	-	0-110
Tg /(Tm)	C	100	100	(158)	(163)	72			55
Forming range	C	120-160	115-150	145-155	152-160	145-170	140-150?	-	55-80
O2 permeability	cm3/m2/d (23C,65%RH)	6000	6000	3200	2000	100	1000-1500?	-	
CO2 permeability	cm3/m2/d (23C,65%RH)	18000	18000	9000	6000	500	3000?	-	
Drying	Yes or No (h/C)	No	No	No	No	4/50-70	3/80	No	4/50-80

1.3 Requirements for the package

Package selection is very important in the long term. If the package does not achieve its objectives, it is meaningless. Below in figures 21 and 22 is illustrated the working scene in which package experts operate. Design is sometimes divided to two categories; user centered and product centered. These dictate which requirements are first designed and which compromised after the leading requirements. Figure 21 presents all the levels of requirements, environmental and functional, in general. The Lockhart packaging matrix is one way of illustrating the requirements of a package. It includes the physical, ecosphere, and human aspects in environmental requirements. In addition to the matrix, protection, utility and communication are included in the functional properties. (Yam 2009)

In this thesis, the package is a primary package and the requirements of primary packages are mostly functional. Figure 22 roughly presents the package selection criteria for a dairy product. The product being packaged has a major impact on the package selection, thus it can be found in the inner circle. The outer circles present the environment where the package is. Many of these circle topics, such as legislation, microbial changes, gas environments, costs and physical stress are discussed in more detail in this thesis.

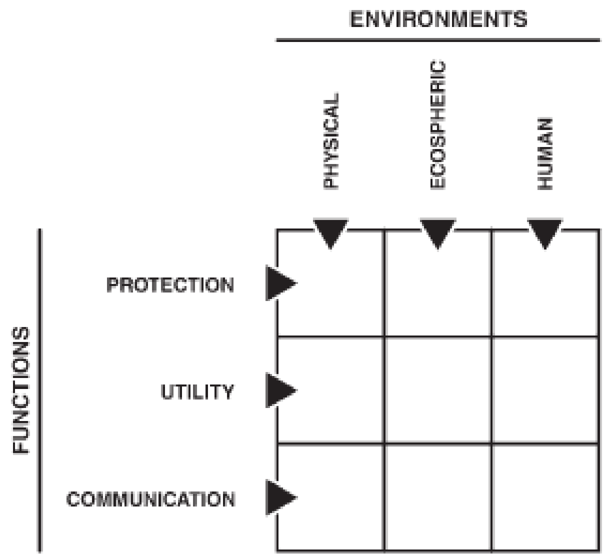


Figure 21 The Lockhart packaging matrix. (Yam 2009)

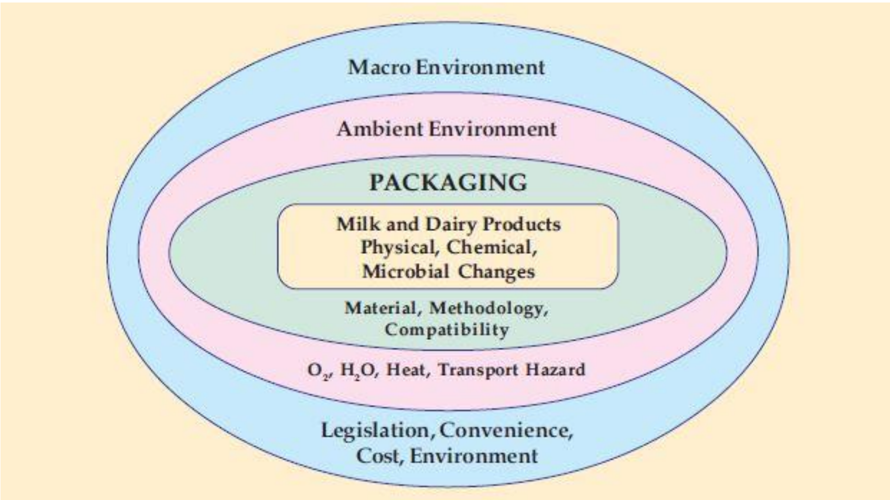


Figure 22 Package selection criteria for a dairy product. (ICPE 2013)

1.3.1 The role and functions of food packaging

A package and its content needs to strive towards the same goals when it comes to providing the end user with a satisfying consumer experience. The package is made for the product and when the requirements for a package are set, it is important to understand which variables have relevant effects, what these effects are and what risks they pose during the package lifetime. Package design is optimization within the different parameters of packages. The designer needs to exceed many expectations simultaneously. The most important function of the package is containment. Protection includes a wide range of functions against risks. Mechanical, chemical and microbial stresses occur throughout the life cycle of the package. There are numerous studies which reveal that the largest environmental damage results from food production, not from package production. If we cannot decrease the effects of food production, at least the package can decrease the risk that the product will be spoiled before use. Thus the product is safely available for a longer time and we have lower spoilage rate, which lowers the total emissions of production and allows for less product to be produced in the long run. (Siracusa 2012)

The European Organization for Packaging and the Environment has categorized the major functions of the package under seven topics on their website. The topics are: protection, promotion, information, convenience, unitisation, handling, and waste reduction. These functions are more or less the same as in the Packaging Encyclopedia and Brody´s article. In addition, Brody has listed dispersing, dispensing, tampering and pilferage deterrence. (Yam 2009) (Brody 2000) (PSPC 2013)

Protectiveness

One of the most important features of the package is to protect the food product in the package. Packages face many risks en route to the end user. It is not easy to understand all the mechanical, chemical, and thermal properties which are needed. Requirements are strongly dependent on the protected product. As dairy products are normally liquid with little fat, they are sensitive to oxygen, light, temperatures over 2-4ºC. The products have to be transported thousands of kilometers before use. Transportation from beginning to the end user is the main factor inducing mechanical stresses. A cold chain is also needed when dairy products are transported. (Yam 2009)

In Europe, where food packages are widely used, only a few percent of the food produced spoils during transportation. In the developing world, nearly half of foodstuffs are not used as supposed and all the spoiled food is bound for disposal. Spoiled food causes as much emissions as protected food, excluding its packaging. (PSPC 2013; Styron 2013)

Safety, shelf-life and environmental issues

Food safety is the primary requirement. The end user and customers do not want to find a contaminated product in the package. The package needs to be as secure as possible. Every manufacturing company wants to produce high quality products which satisfy customers' needs. Shelf life development is achieved mostly due to material knowledge and wider possibilities of multilayer structured materials. (Brody 2000)

Intelligent and active packages have recently been studied in many research centers, but practical applications are still too expensive in "bulk" packages. Intelligent packaging is one way to communicate with the retailer and the end user. The package could inform if it has been transported in too high a temperature or if the gas profile is unwanted for some reason. (Brody 2000)

Communication and information sharing

The package is one of the product's major communication mediums. It is a link between the consumer and the manufacturer at the point of purchase and point of use. (Brody 2000) Communication between the producer and the end user is often a neglected function of the package. In recent years, its importance has increased. Product information is dictated by regulations and the marketing feature is more and more important for brand owners and marketers. Brand owners want to boost brand awareness and marketers have a strong need to differentiate on shop shelves. This makes it clear that package attraction plays a major role. Consumers more readily choose clearly adjusted, new, shiny and therefore attractive packaging. New decoration methods and new manufacturing innovations are today highly valued by customers. This sets harder challenges for a package manufacturer. Requirements for the printing quality are higher and the amount of information which should be printed on the package is increasing. (Brody 2000)

1.3.2 Requirements in Dairy

Special features of cultured dairy products

Dairy products are living products and the general composition of raw milk is ideal for the fermentation process. Milk consists of fat, proteins, and carbohydrates, such as lactose, which are needed for fermentative activities of microorganisms. The fermentation process in the package increases the requirements for the package. For example Finnish curd milk, viili, produces compounds such as lactic acid, acetaldehyde, diacetyl, acetic acid and carbon dioxide while in the package. The chemical process is called lactic acid fermentation. (Kukkoniemi 2012)

Fermentation is a method which has been known for a long time to reduce the risk of food spoilage and to extend shelf life. This is because most spoilage bacteria cannot live in a low pH environment. Lower pH and increasing carbon dioxide also modify the aroma and flavor characteristics of the product, directly or indirectly. (Jay & Co 2009) The starter culture is a multi-bacterial compound which reacts with milk sugar and produces lactic acid. Figure 23 below presents the chemical substances of a few exemplary fermentation processes.

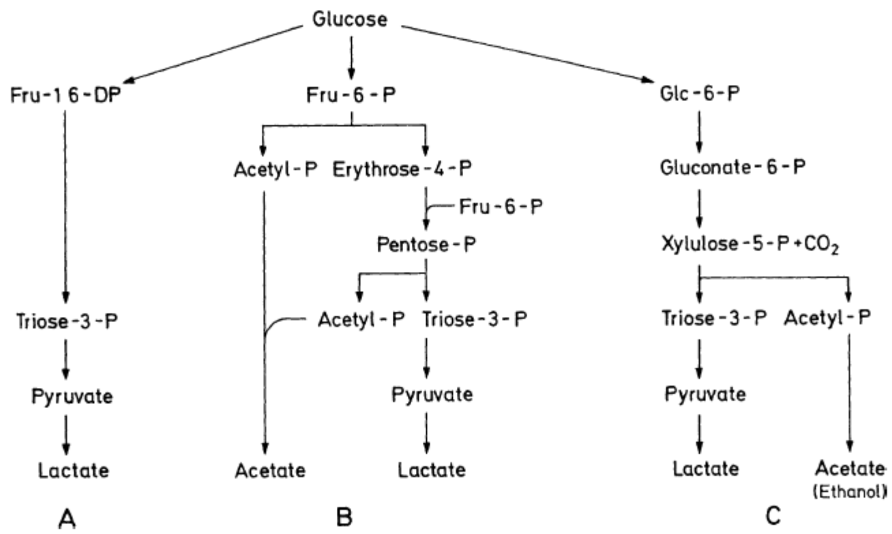


Figure 23 The fermentation process, where lactic acid bacteria and other microorganisms react. a) homofermentation, b) Bifidus and c) heterofermentation pathaway. (Belitz & Co 2009)

Cultured milk products are divided into groups: drinkable (soured milk, jogurt), package fermented spoonable (viili, sour cream, set type jogurt), mixed tank fermented spoonable (basic jogurt) and consentrated products, such as curd. (Saarela 2004)

In this thesis, the major focus is on cup fermented product packages. Finnish curd milk and all sour creams with different fat contents and with different names are made by using fermentation. Smetana (34-42%), crème fraiche (28-34%), low fat crème fraiche (6-18%) and low fat sour cream (2-6%) are the most typical products in Finland, to name a few. Yoghurts are normally categorized in dairies by structural properties but also by their fat content or special features. Product structures can be divided into types, such as mixed, drinkable, compressed, frozen or dried. Fat content usually varies between 0-3.5 %. Special features can include a flavor or a healthy additive, such as probiotics, vitamins or fibers. Cultured milk products are made in many countries in the world but Scandinavian countries represent a major production area. (Maitotietoa 2007) (Kukkoniemi 2012)

Processes in dairies

The basic process steps of yoghurt and viili are presented in Figure 24. The process flows are different for different products. The set type yoghurt, for example, is fermented in a cup while mixed yoghurt is fermented in a tank. Viili is one of the cup fermented products. The biggest changes happen while the lactic acid fermentation is ongoing in the package. This is important to know when the criteria of the package are determined.

Some dairy products are filled when the product is still hot. Hot filling and cup fermentation set new requirements compared to other products as they cause higher temperature stress. Thermal stability should be stable enough, at least between 5 and 45 ºC, when the product is cup fermented. Hot filling sets the requirements as high as 80 ºC. In the first instance, a higher temperature softens the polymer and weakens strength properties. At the same time, the internal stress relaxations of the package may be released. An amorphous material shows a more linear softening during heating and smaller dimensional changes, but a crystalline material has a rigid phase until its crystallites broken. It has been proved (eg. Diez A.) that thermoplastics have a shape memory and that the material is always trying to reach its natural shape. For example, a thermoformed dairy cup will return to its original flat shape when heated enough. In thermoforming, the orientation of molecules is normal. Orientation is actually one of the benefits in thermoforming, due to its reinforcing effects. In literature, the long term service temperature for PP is about 110 ºC and for PS about 70 ºC. After the glass transition area of PS, the material begins to reform back to the original shape. PP loses its strength during heating but the biggest impact is close to melting point. The heat deflection temperature (HDT) of PP with 0.45MPa is 100 ºC and with 1.8MPa only 55 ºC (Muoviplast 2014). The deflection temperature is a measure of a polymer's ability to bear a given load at elevated temperatures. Close to the melting point, PP is soft and the hot strength is low. Actual melting begins generally after 145 ºC so short-term temperature resistivity is higher. This can be observed from a differential scanning calorimeter (DSC) curve. (Illig 2001)

The storage and transportation of packages requires a high enough top load resistance, sometimes also at higher temperatures when the fermentation is in progress. In the transportation unit, packages are packed to secondary packages, which are stacked and wrapped. The pressure on the package in the bottom of the transportation unit can be more than ten times its own weight. In some cases, secondary packages relieve the pressure and thus requirements for primary packages are not so high. (Kimpimäki S. 2013)

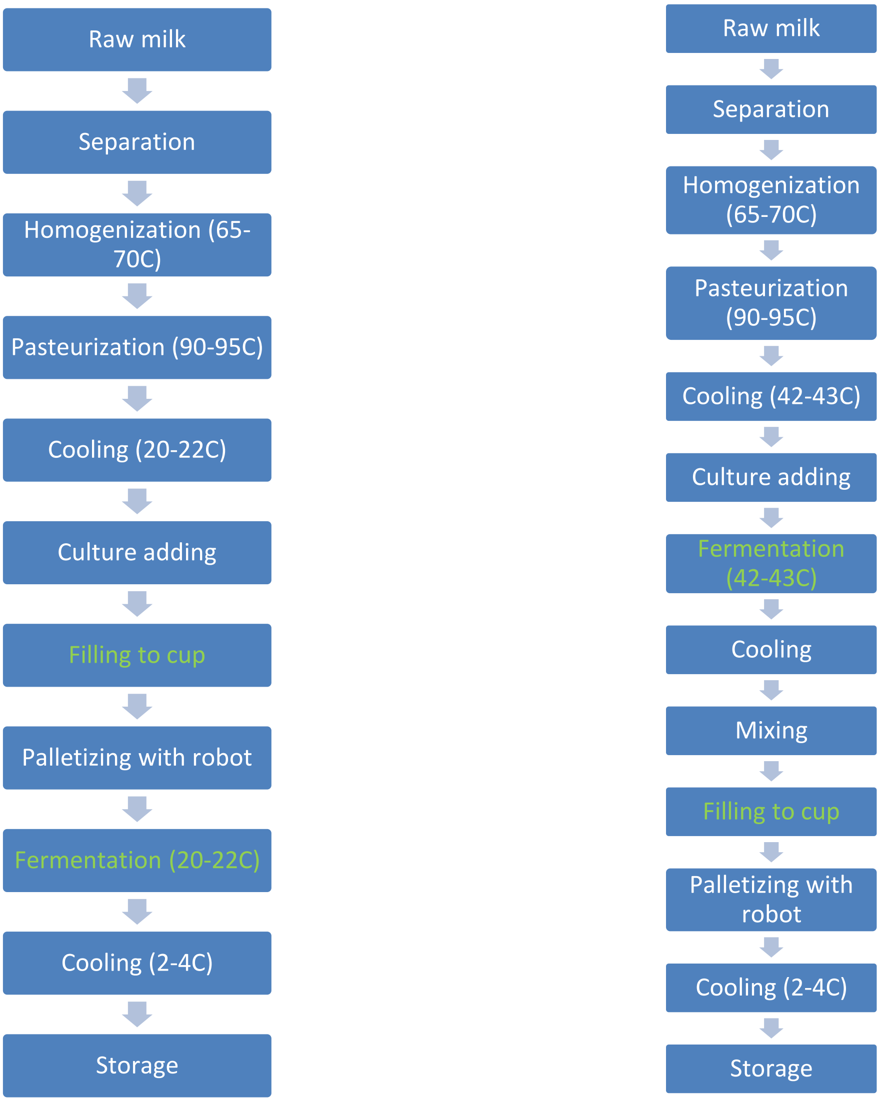


Figure 24. The processes of viili (left) and yogurt (right) (Kukkoniemi 2012; Väistö 2010)

1.3.3 Interactions between package, environment, and content

Gases in the package and in the surrounding environment are different. The product inside the package needs the right gas mixture, which guarantees correct organoleptic and mechanical properties. One of the aims of the package is to keep the right gases inside the package and to set barriers for harmful gases, which would otherwise permeate into the package. The harmful gas from the outer environment is typically oxygen, whereas the desired gas inside the package is either nitrogen or carbon dioxide. The following paragraphs will explain the most critical factors with regards to this issue. The terms permeation, diffusion, migration, solubility, absorption, desorption and transmission rate will be specified. In Figures 25 and 26, the package wall is the middle layer and the outer layers are the environments inside and outside the package. These environment circles have been presented earlier in this thesis. Transmission rate is used to figure out how much gas goes through the packaging material. Permeation is the transmission value which goes through a defined wall thickness. Permeation complies with Fick´s law and consists of three processes; absorption of the permeating species into the polymer, diffusion through the polymer and desorption of the permeating species from the polymer surface and removal. Solubility and diffusivity are the factors which indicate how much the polymer permeates. More specific properties of the polymer are chain packing, side group complexity, polarity, crystallinity, orientation, fillers, humidity, and plasticization.

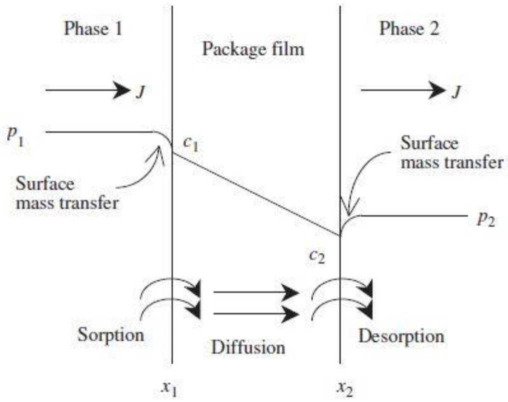


Figure 25 Gas permeation through packaging material, where p=pressure, c= permeant consentration. (Siracusa 2012)

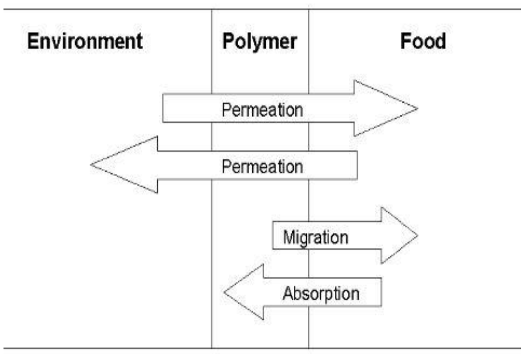


Figure 26 Typical transmission types between atmospheres, food and packaging materials. (Stoffers 2005)

Permeability

Permeability is the qualification of permeate transmission, gas or vapor, through a resisting material. It is strongly dependent on the material is used and the surrounding conditions. When calculating the permeability of the package or changes during the dairy product storage in the package, the package properties need to be understood, that is, the differences between the gases and some of the most critical properties of the gases. CO_2 is the largest gas molecule of the most typical gases in a package. It is more active and more prone to permeate than oxygen or nitrogen. (See Table 7)

Other factors which affect permeation can be divided into two groups: material properties and environment properties. Affecting factors include thickness, molar mass, density, crystallization rate, orientation, and the ageing of polymer. In addition molecular size, velocity, the chemical structure of the molecule and humidity, pressure and the temperature of the surroundings have an impact.

Table 7. Important properties of gases used in the permeability experiments. (Siracusa 2012)

Properties	N_2	CO_2	O_2
Molecular diameter/cm $\cdot 10^{-8}$	3.15	3.34	2.98
Mean free path/cm $\cdot 10^{-6}$	9.29	6.15	9.93
Average velocity/cm $s^{-1} \cdot 10^{-2}$	471	376	440
Van der Waals constant a/bar L^2 mol^{-2}	1.39	3.59	1.36
Van der Waals constant b/L mol $\cdot 10^{-2}$	3.91	4.27	3.18
Molar mass/kg $kmol^{-1}$	28.013	44.01	31.999
Critical volume/cm^3 mol^{-1}	90.1	94	78
Viscosity/μP	176	147	204
Gas density/kg m^{-3}	1.25	1.98	1.43
Molecular volume/cm^3 mol^{-1}	31.2	30.7	25.6
Solubilities of gases in water at different temperatures/cm^3 dm^{-3}	16.0 (20°C) 12.5 (40°C) 10.2 (60°C)	878 (20°C) 530 (40°C) 360 (60°C)	31 (20°C) 23 (40°C) 19 (60°C)
Diffusion coefficients of gases in water at 20°C/cm^2 $s^{-1} \cdot 10^5$	1.64	1.77	1.8
Kinetic diameter/cm 10^{-8}	3.64	3.30	3.46
Critical temperature/K	126.2	304.2	154.8
Critical pressure/MPa	3.39	7.39	5.08
Gas constant/kJ kg^{-1} K^{-1}	0.2968	0.1889	0.2598
Effective diameter/cm 10^{-8}	3.66	3.63	3.44
Collision diameter/cm 10^{-8}	3.68	4.00	3.43
Lennard-Jones force constant	91.5	190	113

Table 8 and Figure 27 present results from the Norner GTR calculator. In the calculator cup dimensions and polymer material are entered in the table, and the software calculates gas transmission values for the selected material. Values are calculated with different wall thicknesses: 0.2, 0.3, 0.4 and 0.5 mm. Permeation through the lid is not accounted for in these calculations. The Norner calculator provides the possibility of information in advance regarding package transmissions.

Table 8. Oxygen transmission rates if the thickness of the cup varies. (Norner 2013)

Oxygen Transmission Rate				
Thickness	**0.2**	**0.3**	**0.4**	**0.5**
PS	0.266	0.177	0.136	0.106
PP	0.237	0.158	0.118	0.095

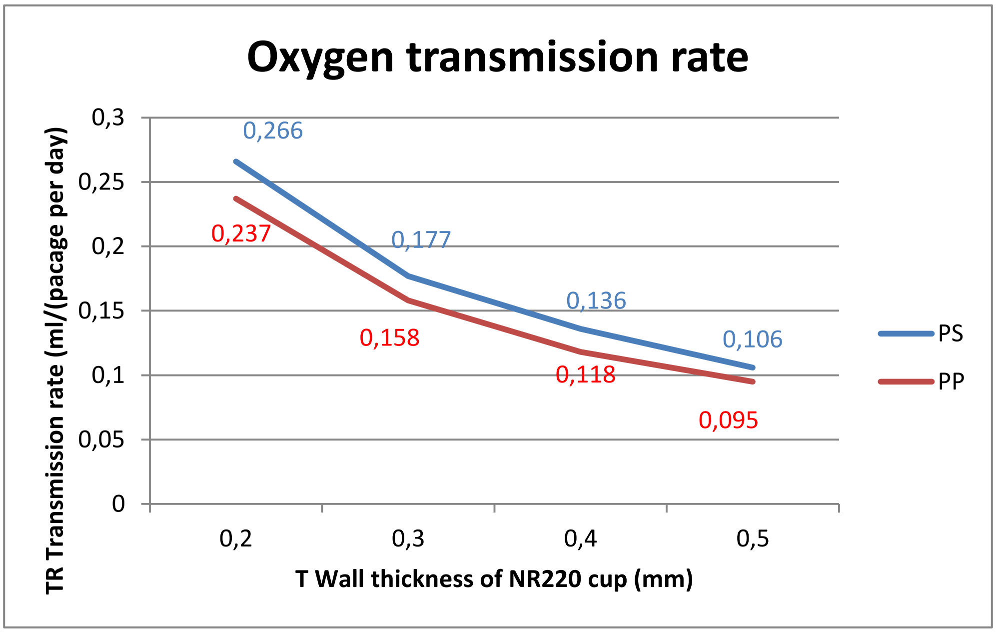


Figure 27 Oxygen transmission rates if the thickness of the cup varies. Lid transmission is not taken into account; the lid is usually made from high barrier material. (Norner 2013)

Migration

Food contact materials (FCM) in packages are made from polymers worldwide. Approximately 50 % of these packages are plastics. There are many plastic applications on the market, as plastics have a competitive advantage because of their customizable properties. Plastics have excellent functional properties and a light weight, so plastics fulfil most of the requirements of a package. In addition, the package needs to be inert and not contaminate the foodstuffs. All plastic materials are not suitable for food contact. Most commonly used food package materials are PE, PP, PS and PET. The base of regulations and control is to ensure human health. Growing interest in green issues seems to press manufactures to use more recycled raw material. (Barnes K. A, & Co 2007; Kanishka B. 2013)

Plastic food contact materials should meet the requirements of the Directive 2002/72/EC. There are amendments that include various limits: overall migration limits (OML), specific migration limits (SML) for monomers and additives, and compositional limits. Converters, fillers, and packers have the primary responsibility to obey these limits. Coveris is a plastics converter, so with regards to Figure 28, it needs to agree on specifications with the customer and the supplier and has responsibility for any modification to formulation. The converter is also responsible for migration levels and quality checking for any kind of external impurities. The customer should provide all necessary details about the product and its special features. The customer has the right to select the material, but is also responsible for said selection. Normally material manufacturers and converters provide good information about materials and applications. Materials should meet the requirements and comply with current legislation. The raw material manufacturer is responsible for producing the defined high quality material, and no changes to composition are allowed. (Barnes K. A, & Co 2007)

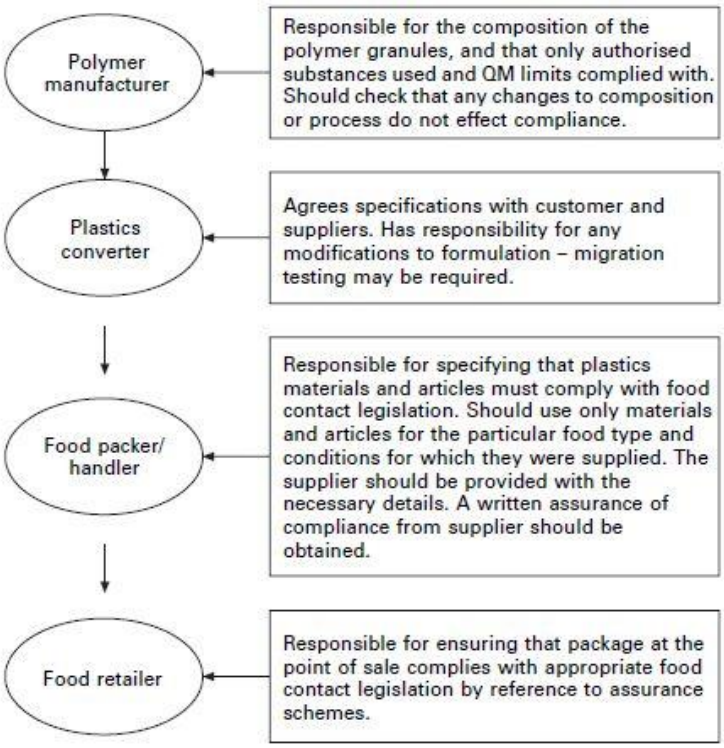


Figure 28 Migration responsibilities in the food package supply chain. (Barnes K. A, & Co 2007)

OML and SML are based on human health. Limits are set to acceptable levels for humans. Specific migration limits are tested by using standard simulants and test methods. Temperature, pressure, and other surrounding parameters are constant in a specific method. Oil, alcohol, fat and water are typical simulants in tests. (Barnes K. A, & Co 2007)

1.4 Conclusion of theory part

As earlier sections described, changing the package material has a significant impact on production and on the whole supply chain. The following sections will examine in practice how different materials differ from others in chosen trials, and which materials would be the best for the chosen fermented dairy products.

2 METHODS

As stated earlier, the target of practical tests is to compare different packaging materials and estimate how these fit to the specific products. The plan is to produce sheets from different interesting materials and then to produce dairy cups using those sheets. As many of the critical mechanical parameters as possible will be measured. Finally, these preparations allow for the measurement of gas transmission rates as a function of the package wall thickness and for finding a suitable OTR range for cup cultured dairy products. The outline of the experimental part of the thesis is illustrated in figure 29.

Figure 29 Outline of the experimental part of the thesis

2.1 Sheet production and forming machinery

Due to the nature of this study, the sheets are collected from different sites, which makes collecting parameters challenging. All the sheets are made by professional operators at their production units in Europe, but the forming of all sheets was done at Coveris Rigid Finland in Hämeenlinna. The test cups were formed by using ILLIG's one cavity semi-automatic forming machine. Parameters in this machine were adjusted manually and this may have resulted in inaccuracies, but the trials provide good information before more extensive tests. Heating in the forming machine is adjusted by heating time and percentage of power, the mold is not cooled. Machine and mold parts are shown in figure 30 below.

Figure 30 ILLIG forming machine (left), plug (center) and lower mold (right). (Coveris)

2.2 Wall thickness distribution and shrinkage rate

2.2.1 Objectives

The objective of the wall thickness measurement was to define wall thicknesses of cups before compression and barrier tests as wall thickness measurement helps to understand reasons behind the test results. Maximum top load is largely dependent on wall thickness, wall thickness distribution, the shape of the package and material characteristics. The aim was to get base information for further tests where material characteristics were to be analyzed.

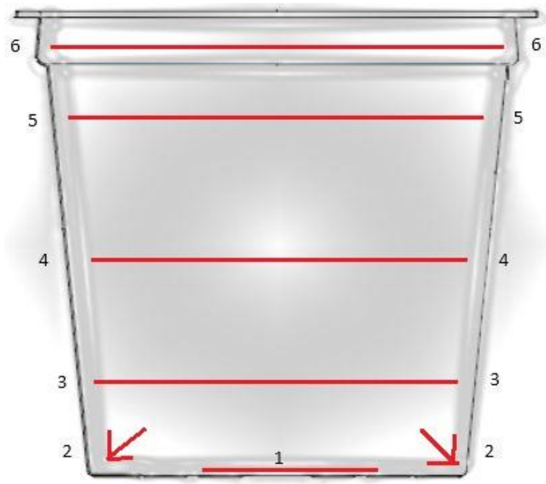


Figure 31 Measuring areas of thickness.

The objective of the shrinkage test was to define the shrinkage rate of the tested polymers. Shrinkage rate affects, for example, the mold design and dimensional stability. A lower shrinkage rate provides the possibility to manufacture packages with more accurate dimensions. Higher shrinkage may more easily cause elliptic cups and further problems if process control is not perfect.

2.2.2 Experimental procedures

Magna Mike is an excellent machine for thickness measurement at both one point and a wider area. A small metal ball is rolled on the opposite side of cup wall and the machine can measure the difference between the ball and the other surface (see figure 32). In this case, the aim was to measure the most critical areas around the cups based on experimental knowledge (see figure 31). Minimum points were measured because they are most likely the weakest points of the wall.

Shrinkage rate is measured with a caliper solution which is attached to an adjustable rack. The rack helps the measurement and keeps the measuring device more stable. Values are measured from transverse and machine directions, which are also often the maximum and minimum values of a cup.

Figure 32 Magna-Mike 8500 ball measuring machine (Coveris)

2.3 Top load performance of cups

2.3.1 Objective

During transportation, dairy cups are usually loaded onto secondary packages and pallets. The cup needs to carry the load of ten to fifteen filled packages over it. Due to this, the minimum strength limit of the package should be more than fifteen times to that of a filled package´s mass. During transportation vibration also exposes the packaging to failure. The top load test measures the compression strength of a cup. The aim of this test is to find the extreme compression strength of the cup. If the strength amounts to more than the required limit, the package is strong enough. The test does not include a vibration test.

2.3.2 Experimental procedures

The compression test for cups was performed with a Zwick/Roell machine (see figure 33). The machine can be used to test tensile strength, bending strength and compression strength. In this case, the maximum top load was the most critical feature of the cup. In practice, the tested cup was set to the lower plate and then the upper plate began to press slowly. Test parameters were the same as used in daily quality tests, where the compression speed is 100mm/min.

Figure 33. Zwick/Roell load test machine (Zwick/Roell)

2.4 Gas transmission tests for sheet materials

Gas transmission rate (GTR) indicates the volume of gas passing through a plastic material, per unit area and unit time. Under the unit there is a partial pressure difference between the two sides of the material. OTR is the oxygen transmission rate, expressed in moles per square meter second pascal [mol / (m^2·s·Pa)], however, it is generally expressed in cubic centimeters per square meter 24h [cm^3 / (m^2·24h)].

2.4.1 Objective

The objective of this part of testing was to determine the gas transmission rates of specific materials. Determination of OTR and CO_2TR was done at a controlled relative humidity through materials by using a coulometric detector. The tests were conducted employing widely used ASTM-standards.

2.4.2 Standard

ASTM D3985 - 05(2010) e1

Standard test method for **Oxygen Gas Transmission Rate through plastic film and sheeting** using a coulometric sensor

This test method covers a procedure for the determination of the steady-state rate of transmission of oxygen gas through a plastics sheet. It is used for the determination of oxygen gas transmission rate (OTR), the permeance of the film to oxygen gas and the oxygen permeability coefficient in the case of homogeneous materials. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. (ASTM 2014)

The gas transmission rate tester and the OTR method are presented in figure 34. In short, two different gas mixtures are located on different sides of a sheet. The other side has a higher pressure, when the indicator can detect odd molecules in the other side. The amount of passed molecules indicates how good the barrier sheets are.

Measuring conditions

- Temperature 23 °C
- Humidity 0% and 50%
- Permeant consentration 10%
- Barometric pressure 760 mmHg
- Sample type 50cm^3

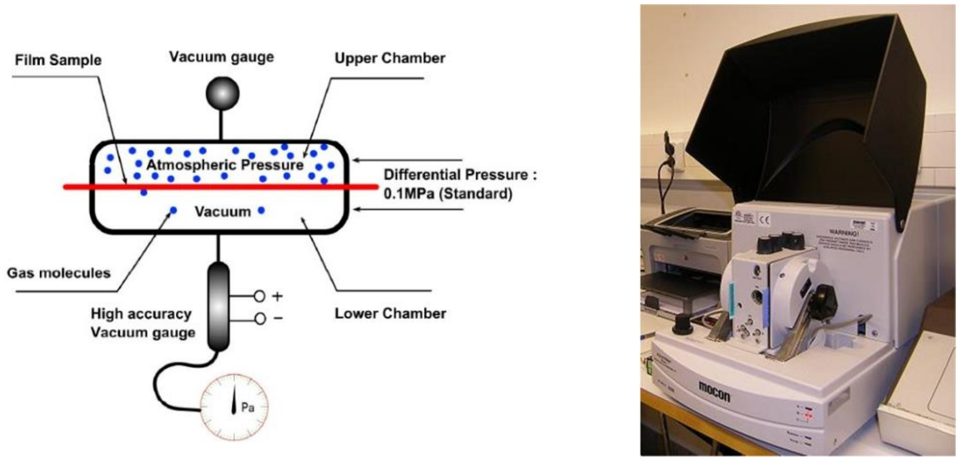


Figure 34 GTR testing method in theory and in the Mocon Ox-tran device in practice. (Labthink 2013, Tampere University of Technology 2014)

ASTM F2476 – 05

Test Method for the Determination of **Carbon Dioxide Gas Transmission Rate (CO_2TR) Through Barrier Materials** Using Infrared Detector

This method covers a procedure for the determination of the steady-state rate of transmission of carbon dioxide gas through plastics in the form of a film. It is used for the determination of carbon dioxide gas transmission rate, the permeance of the film to carbon dioxide gas, and the carbon dioxide permeability coefficient in the case of homogeneous materials. (ASTM 2014)

Measuring conditions

- Temperature 23 °C
- Humidity 0%
- Permeant consentration 100%
- Barometric pressure 730±10 mmHg
- Sample type 50cm^3

Gas transmission configurations which are used in GTR tests are Mocon Ox-tran 2/21MH when OTR with 50% humidity and Mocon Ox-tran 2/21SH when OTR with 0% humidity. CO_2 tests is done by using Mocon Permatran-C 4/41 MH and humidity is set to 0%. Higher humidity in CO_2 test may affect acid problems.

2.4.3 Experimental procedures

All materials which were selected to this trial are interesting according to some criteria. Interests in the materials were based on material character, environmental benefit, economical benefit or public image. The tested materials are listed below.

- M1 - Impact modified PLA
- M2 - $CaCO_3$ -filled PP
- M3 - PP copolymer
- M4 - GPPS/HIPS
- M5 - Nitrogen-foamed PP

The device configuration is listed below:

- Mainframe
- Professional Software
- Communication Cable
- Vacuum Grease
- Diamond Sample Template and sample cutter
- Valve Sets
- Temperature Control Device

2.5 Headspace gas analysis of ready product

2.5.1 Objective

The purpose of this test was to find out the storage environment that the product needs. This will help us understand the real situation in the supply chain and moreover make better products for our customers. This method can be used to evaluate the gas components, content, and the mixing proportion in the package rapidly and accurately in a laboratory or in a production plant.

2.5.2 Experimental procedures

Filled cups were measured and checked visually. Measurements provided results with regards to gas content and mixing proportion. A higher CO_2 rate indicated higher CO_2 release from the product or conversely a tighter package. By comparing material tightness and CO_2 release, it is possible to find a good combination. The practical measurement was made by puncturing the lid with a needle which sucked and measured the proportional gas content in the package. The gas content analyzer is presented in figure 35.

Figure 35. Wittgas Oxybaby gas analyzator

3 RESULTS AND ANALYSIS

3.1 Results from the laboratory tests

3.1.1 The gas profile of specific products

The gas profile in the package is interesting because it sets limitations on the packaging material. The gas profiles of some fermented products from different producers were measured in this test. The level of CO_2 in a cup head space was assumed to be higher with cup fermented products than with tank fermented products. Samples for this test were bought from local groceries. Selected samples contained a variety of flavors and fat contents with different filling days, but also different mold cavity numbers and lid materials. These are factors which may affect the gas composition. Deeper analysis of reasons behind this would require a wider test scheme. These tests provide a range for the typical gas content in dairy cups.

The results of this test prove that gas content is totally different in cup fermented products. In air, the carbon dioxide level is typically about 0.028-0.038% of the composition. In viili packages from producer one, the average CO_2 content had increased to 6.3%. This was an average of the tests conducted during the writing of this thesis. The average level of the second viili producer was as high as 20.9%. At the same time, the average oxygen level, which is normally about 21% in air, had decreased to 3.2% (Prod.1) and 0.15% (Prod.2). There are huge differences between producers, even if the product category is the same and the production method should be the same. The differences must arise from different overall package solutions or the contents of the packages. In the first figure below (Fig. 36) there are three different dairy products packed in polystyrene cups. Viili is the only cup fermented product of the three. The two other products have a clearly lower CO_2 level. The second and third figure (Fig. 37 and 38) present the difference in gas profiles between selected dairies in the same product category. The reason why the profiles are so different may be the lid material, cup material, a differing dairy process flow or the product inside. The starter culture, fat content, fermentation conditions and cooling speed may chance the profile. There are lots of affecting variables which need to be taken in consideration, if deemed critical knowledge. The gas profile of viili with jam was one of the most interesting product profiles because its CO_2 impact is significant. In addition, the impact of jam was not studied but its sugar must affect the results in some way.

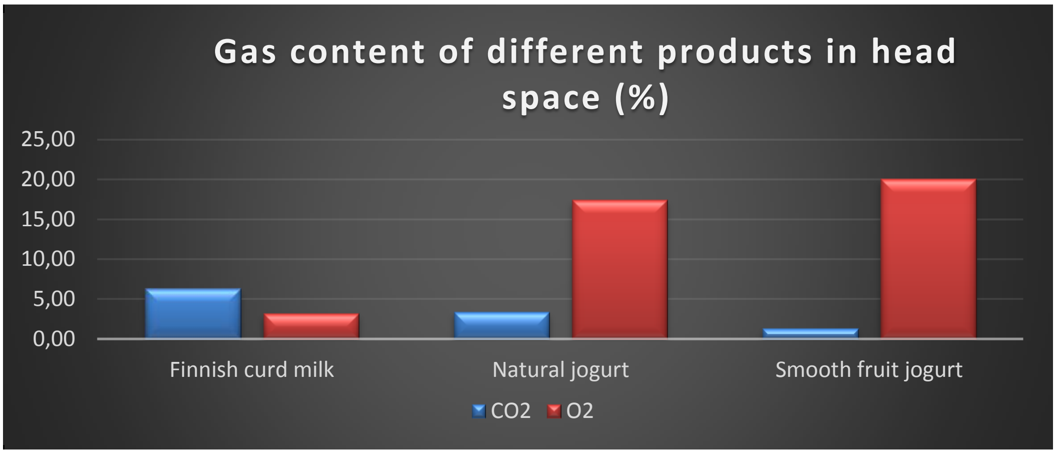


Figure 36 Viili is a cup fermented product and it increases the level of CO_2 in package head space

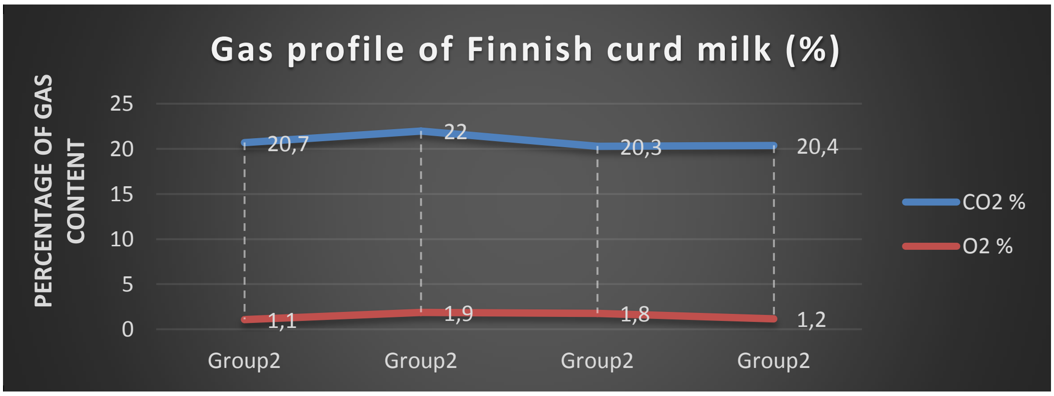


Figure 37 Gas profile of Viili, four parallel samples from producer 1.

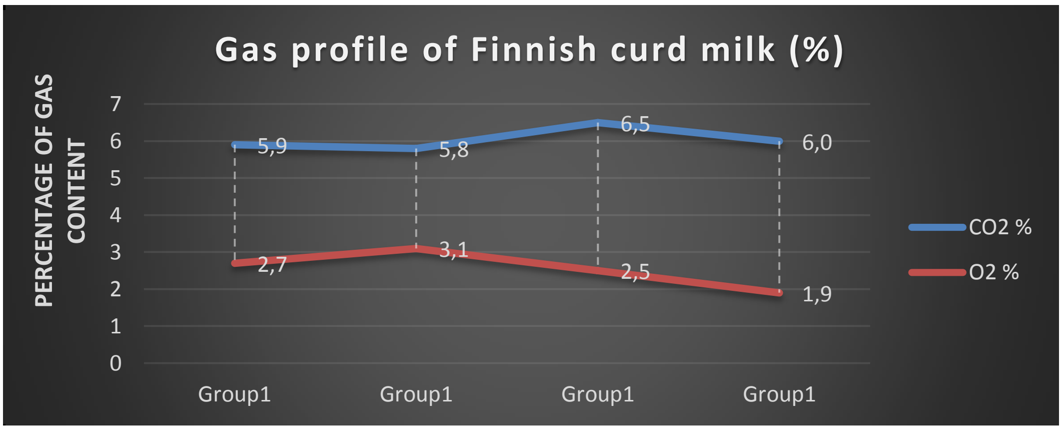


Figure 38 Gas profile of Viili, four parallel samples from producer 2.

3.1.2 Mechanical and chemical dimensions and performances of sheets and cups

Thicknesses of sheets and cups

The thickness of a package gives better top load strength and higher barrier properties, which are critical to dairy cups. The thickness of the cup is mainly dependent on the thickness of the extruded plastic sheet which is used in thermoforming. In thermoforming, the thickness profile is not perfectly even due to the characteristics of the manufacturing method. The PLA sheet test was not directly proportional to others, as it was it was thicker than others. The foamed sheet was not as thick as wanted. All the sheets were planned to be 1.08mm but the PLA and foamed PP sheet manufacturer could not produce the wanted sheet for this study in the required schedule. The average thickness of tested sheets was: PLA 1.32, PP filled 1.07, PP 1.08, PS 1.08 and PP foamed 1.02. The thickness was measured from six areas throughout package as explained in the method section.

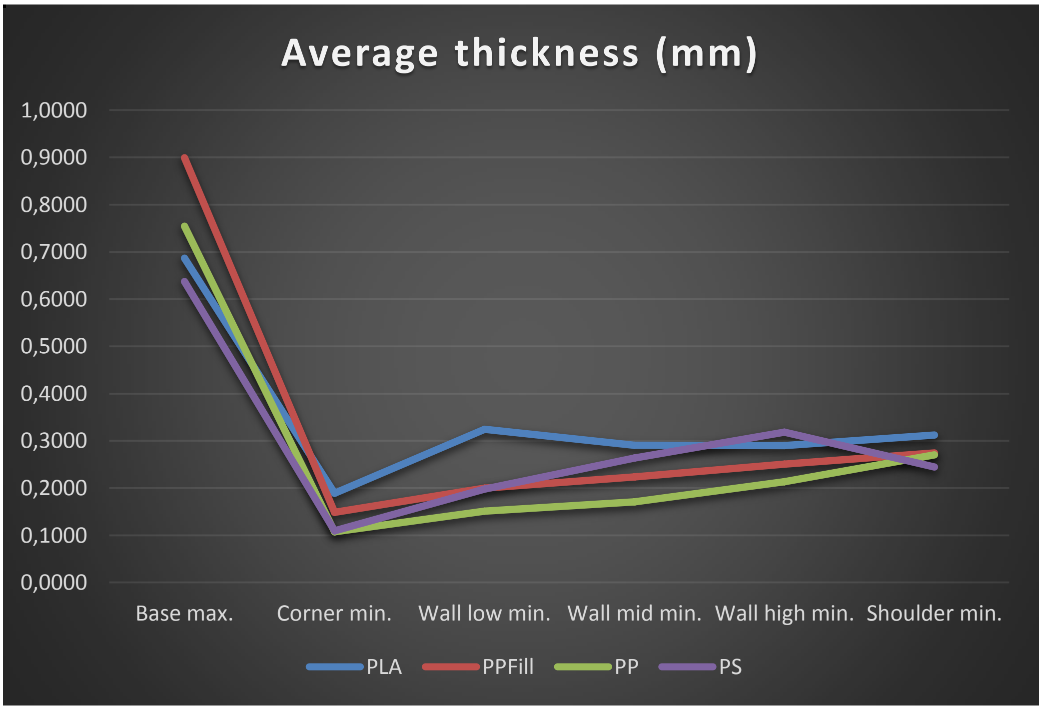


Figure 39. Average thickness profile of formed cups.

In figure 39 above, it can be observed that the thinnest area is the corner between the bottom and the side wall, while the thickest areas are the bottom and the shoulder near the seaming surface. The bottom is the area where the sheet elongation is changed the least. PLA was the thickest sheet but still both of the PP sheets have a thicker bottom than PLA or PS. The most logical reason for that is the amorphous/crystalline phase difference. Both partially crystalline materials have a thicker bottom than needed. The material provides more strength to the cup if it is placed to the sides of the cup, not to the bottom. In the crystalline material, the physical strength changes a lot at melting point. In thermoforming, the material temperature is near to the melting point, and when the cool plug or mold surface touches the material, the material will begin to crystallize and get stronger. Then the plug stretches the material, which still has a higher temperature. The change in melt strength is not as quick in amorphous material, which makes the thickness more equal around the cup. The bottom thickness needs to be thick enough to take the pressure of the bottom plate when the cup is ejected from the mold. As the top load results show in the next chapter, the PP cups have their weakest point very near the bottom corner. PLA and PS, on the other hand, plunge somewhere in the middle of the wall.

Mechanical strength tests

The top load test is one of the most useful and reliable mechanical strength tests available. The test method measures only direct compression force between two plates. In this study, it was assumed that if the seaming surface is not flat, the result can be wrong. Trial cups were not cut sharply because the test forming machine has no cutting dies. Before top load tests, the extra sheet around the cup needed to be cut away. The result of PLA is higher than it would be with equal thickness. The PLA sheet was about 23 % thicker than PS and PP, but its top load strength was 247 % higher. It is clear that a 23 % thickness increase provides a lot more strength, but, still, the result is higher than expected. It is more relevant to compare formed cup thicknesses and strength than original sheet thicknesses. If the material distribution of a thicker material is wrong, the wall thickness can still be the same in critical areas. As we see in figure 40, the materials have a significant impact on the strength. These results give a good understanding of the effect the same cup is made from different materials (see figure 41). Cup pictures in figure 41 illustrate how the packages were pressed and what the impacts of pressing are.

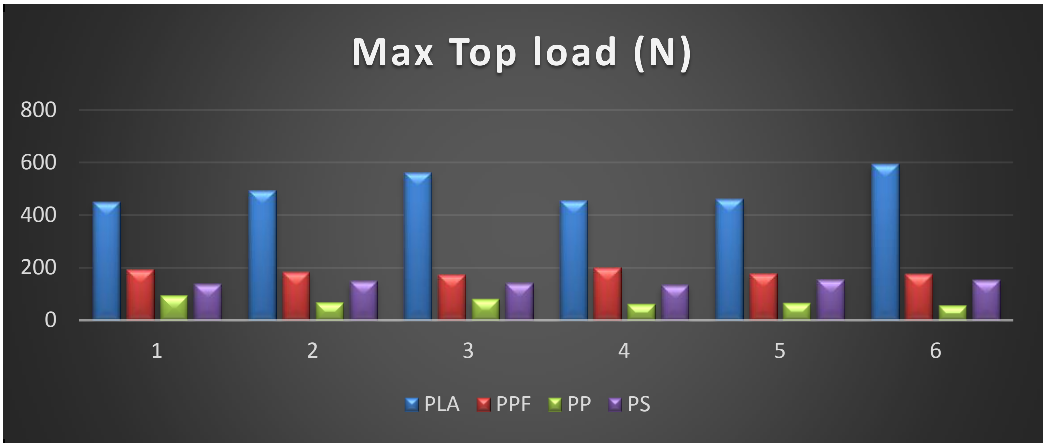


Figure 40 The compression tests results for four materials.

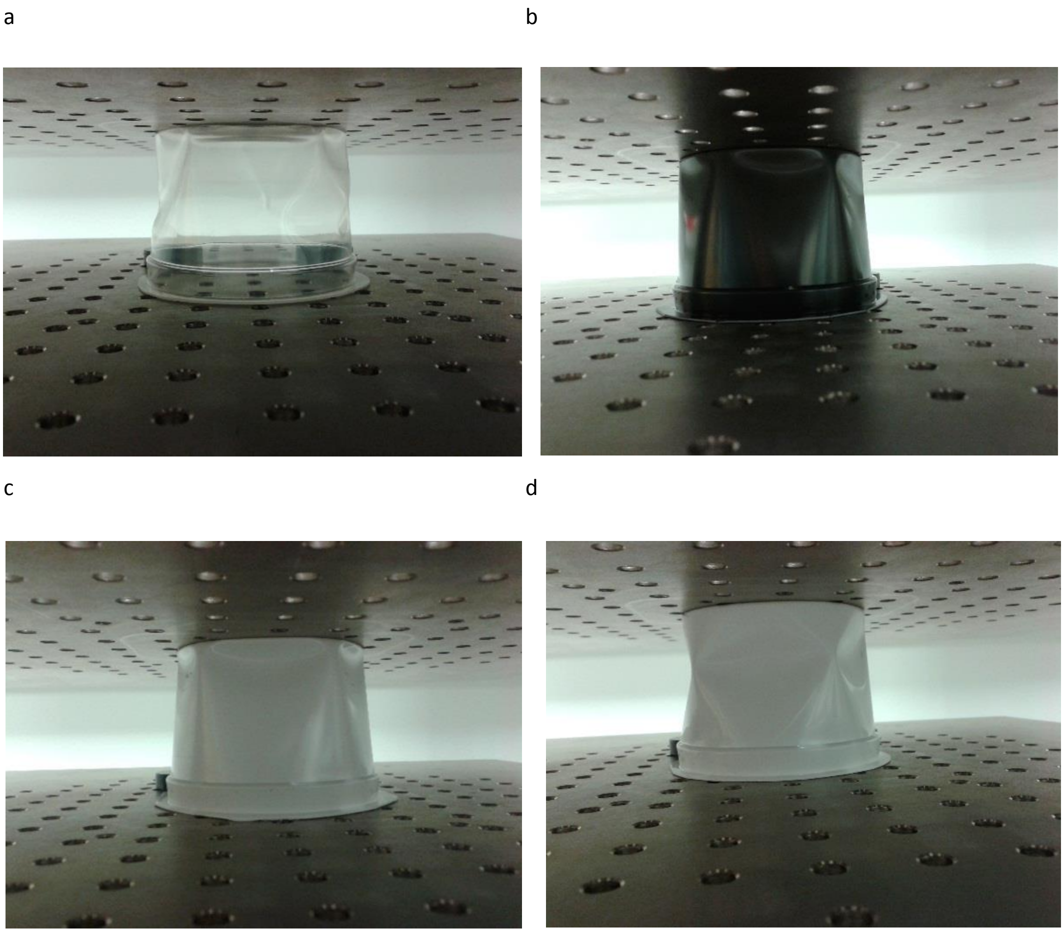


Figure 41 Pressed cups under compression (a-d). Normally the weakest point is the thinnest point. PLA (Up-left), PPF (Up-right), PS (Down-left), PP (Down-right).

Cup shrinkage and dimensional stability

The shrinkage of a plastic cup is a natural reaction when polymer crystallization occurs. The higher the characteristic crystallization rate of the polymer, the higher the proportional shrinkage rate. Sheet orientation, end product orientation, and the cooling process have either an increasing or decreasing effect to the final shrinkage. As can be expected, the amorphous materials had a lower shrinkage than partially crystallized materials, as they do not have a crystallization reaction. Figure 42 shows that, the PS and PLA shrinkage rate was about 0.5% and PP materials was about 1.5-2%. The biggest difference between machine and transverse directions were observed with filled polypropylene where the MD rate was almost 2% but TD rate was only 0.5%. Differences such as this can arise, if the sheet is oriented too much in the longitude direction or if the cup cooling is not equal around the cup. These reasons at least may cause more shrinkage on the other side of the cup. Unequal shrinkage means an oval shape of cup, which is not allowed.

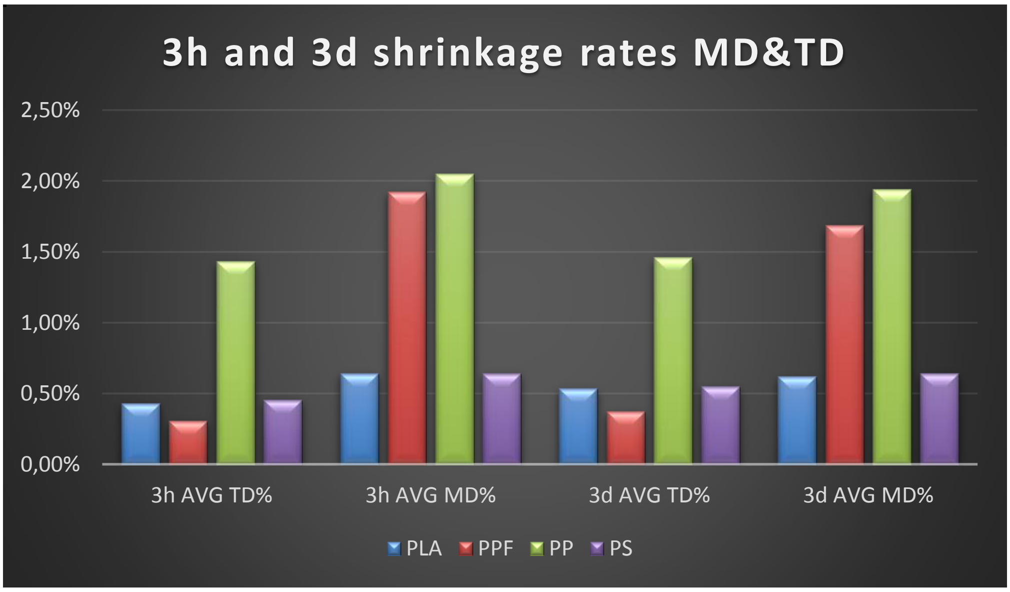


Figure 42. Transverse and machine directional shrinkages are measured three hours and three days after forming.

3.1.3 Sheet Transmission Rates

Transmission rates were measured with calibrated Mocon test devices. Tests were made with different gas contents so that the barrier characteristics of the polymers could be seen. Results are presented below in four different figures. One of the figures (46) collects all the information and the results there is weighted by the thickness of the sheet. The three others figure (43-45) are more detailed, where the sheet thickness is not taken into account. As the figures present, the first and the second test were almost identical so the reliability of test seems to be of a high level. The profile of all these figures seems to be almost the same; the better the barrier, the further left the material is in the figure. There are a few exceptions: PLA seems to react with moisture and due to this the OTR level is higher, even higher than that of filled PP. The second expected figure was the CO_2TR-level of PS, as its value was higher than that of foamed PP. It seems that PS has the worst CO_2 gas barrier and due to this is the best material for cup fermented products. PS is the reference material for this study. Typically the slow transmission stage is reached after ten hours but the final stabilization point needs more time, depending on the material. The saturation point varies between 14 hours to 70 hours.

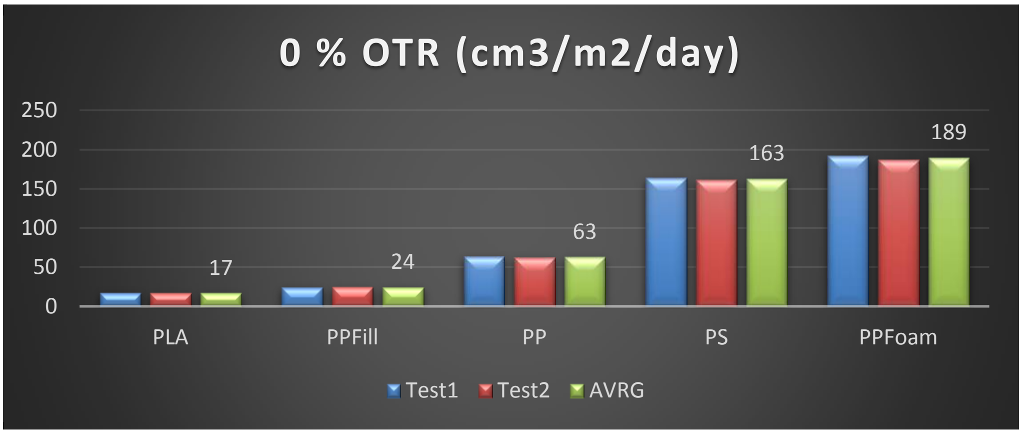


Figure 43. 0% humidity Oxygen Transmission Rate

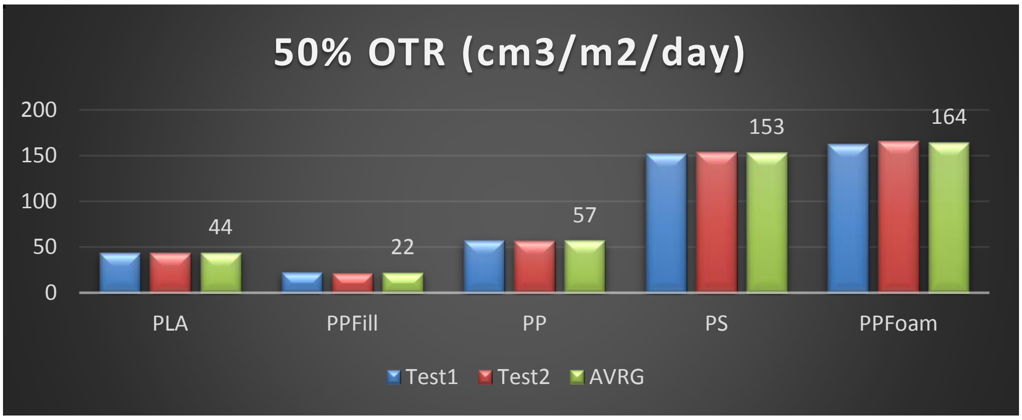


Figure 44 50% humidity Oxygen Transmission Rate

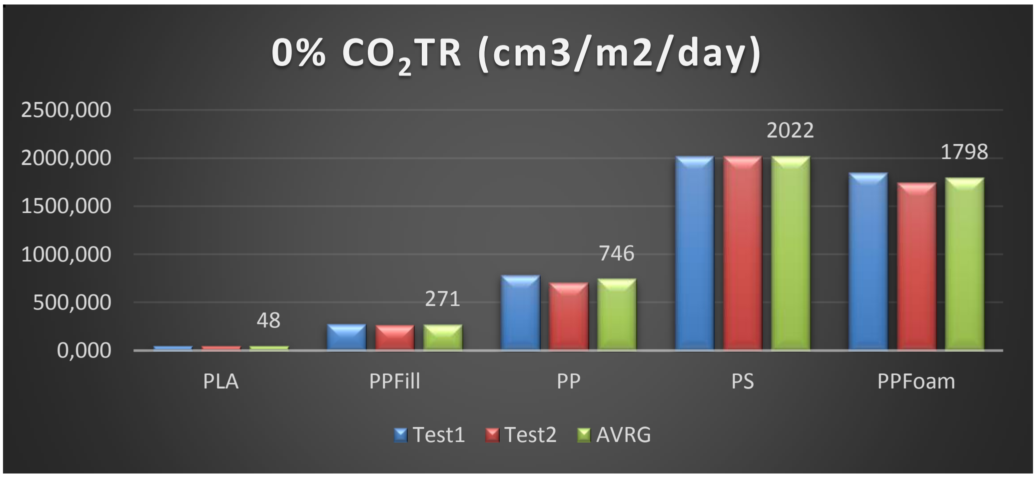


Figure 45. 0% humidity Carbon dioxide Transmission Rate

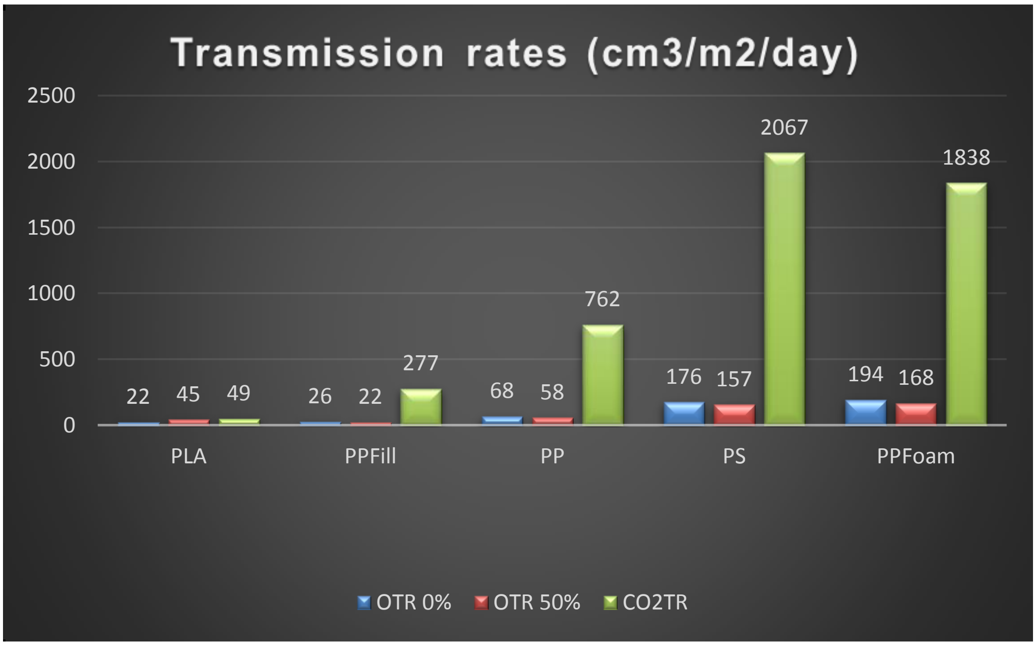


Figure 46. Thickness corrected results. OTR values are corrected to respond to 1mm thick sheet.

3.1.4 Cup transmission rates

The formed cups were tested at the same time as the sheets. The cups could not be measured with the test machine at the Tampere University of Technology with their sensor solution. The gas transmission values were higher than the maximum measuring capacity of the test sensor. The maximum sensor capacity was 200 $cm^3/m^2/d$ with oxygen and 1000 $cm^3/m^2/d$ with carbon dioxide. The cups had too thin areas in the corners and the total transmission area was about three times bigger than $50cm^2$, which was the measured area in sheet tests. Due to about a three times lower wall thickness on average and three times bigger transmission area, the total transmission effect was multiplied. The OTR value of the PLA sheet was about 20 $cm^3/m^2/d$ but, nonetheless, the cup which was made from that sheet provided the high result. The connection surface and the thinnest area of cups were also tested to exclude the possibility of leakages. Cups were analyzed with a nitrogen analyzer, which indicated if there was a gas leakage somewhere. No leakage was found, which proves that the limits were simply exceeded.

3.2 Requirement window modeling

The requirements of a package are dependent on many factors, which are defined further with exact examples. A good example is that if the package is shaped for strength, the material does not need to be as strong. In this case it is possible to use a cheaper, lighter, or a more environmentally friendly material, which has weaker strength characteristics. One possibility is to use a thinner sheet and use less raw material.

The stiffness of a polystyrene cup is, according to these results, assumed to be optimized with a press strength 100 in 2-5 °C environment. We know that copolymerized polypropylene’s flexural strength is about 1400 MPa while impact modified polystyrene has a 1800 MPa, which would mean that the strength of polypropylene cups is about 78 % of PS, if the thickness of cups is exactly the same. Top load results of this thesis show that maximum top loads are 155 N on PS and 91 N on PP cup. It seems that PP material is 40 % weaker than PS. This difference is larger than in the calculation from flexural strengths, most likely because the thickness profiles are not equal, and also because the flexural strength values are common values, not precise figures for specific materials. Polypropylene density is about 0.9 g/cm3 and polystyrene has 1.05 g/cm3. A 22 % thicker polypropylene cup, which is indicated by the flexural rate values, will be 1.32mm thick. Similarly, a 40 % thicker, which comes from top load tests, provides a thickness of 1.51 mm. The mass of the cup would be equal if the PP cup is made from a 1.26 mm sheet and PS from a 1.08 mm sheet. 1.26 mm is quite close to the mentioned assumptions. Although the thickness has not increased as much as the flexural strength requires 1.32 mm, the cup may still have enough strength, because thickness is not directly proportional to the strength. Increase in strength is more dependent on wall thickness than material choice. If the assumption is that the polypropylene cup from 1.26 mm sheet and polystyrene cup from 1.08 mm have equal mass, it can be assumed that the strengths are almost equal as well. A 1.08 mm thickness is only 85 % compared to 1.26 mm, which increases the difference of total gas transmission rate. The general understanding is that the PP transmission rate is one third of the polystyrene transmission. If the PP cup is made from a thicker sheet 1.26 mm, its transmission rate will be 28.5 %, and with a similar thickness of 33 %. Further filling tests will show that the wall is too tight.

If we widen the discussion to the lid, more variances can be found. Because lids today are very tight materials, such as aluminum and metallized polyethylene terephtalate, it might be wise to modify the lid material for providing optimal barrier properties, and choose the cup material based on price, mechanical properties, protective properties and environmental friendliness. Lid material is almost always made with a multi-layered structure, in order for it to be easier to customize the package that way, and secondly, keep or even improve the characteristics of the cup. Finding the best cup solution will have the largest environmental impact, because a major part of the total mass of package comes from the cup, not the lid. Sufficient light and grease barrier of the lid should also be possible to achieve with other materials.

4 DISCUSSION AND CONCLUSION

The aim of this thesis was mainly to collect critical information of suitable cup materials, test the more specific properties of the materials and help research, as well as the development department in choosing which direction they should take in future with materials. The direction is based on the requirements of customer, the suitability of the package, production efficiency and more environmentally friendly products. A good understanding of packaging materials may give long term competitive advantage compared to competitors, if the company could find a more sustainable solution for customers and improve its own production towards the future trends and challenges. Active development with the customer is the key to improving cooperation with customers and due to this the better profitability for all parties. During the writing of this thesis, were established contacts with customers to have a good understanding of what their future directions and priorities are. A major issue is polystyrene replacement due to its relatively high price and unwanted image in media and critical articles. Another issue was the new legislation for recycling and waste management, and the new Extended Producer Responsibility, EPR. A further interesting topic was the environmental effects and future targets of customers. A lot of research data was collected on polymer properties. This thesis tried to describe the new circumstances in which the packaging industry is and what the material palette for the dairy package is at the moment. Some of the other topics discussed in the thesis were dairy processes learning, challenges in dairy processes and variables in package production. A better understanding of customer products and production will help further development.

The major practical activities and results of this thesis were material collection, cup thermoforming, laboratory test planning and execution for critical performances of dairy cups. Materials for thermoforming were collected from sheet suppliers and from the company’s own production in Nordic countries and also from group partners in Poland. In the future, most of the sheets can be done in the company’s own production plant, if the used amount is bigger and some new devices are invested in. Thermoforming was done at the Hämeenlinna production unit. The results and learning derived from the forming trials are important if and when a new material is introduced. All of the materials which were formed have a special behavior. After these trials, the company has a lower threshold to proceed. Before the final selection of the new material, longer test runs are required, where the optimal parameters for specific products can be achieved. Laboratory test planning is based on comprehensive tests, which provide information on critical properties of materials. Mechanical strength, barrier properties and shrinkage rate were selected among the most important features.

A precise analysis of which material will be the best for a specific product, is impossible to decide without dairy product limits for optimal barrier properties. In the future, it would be wise to clarify the needed properties of each product group, viili, crème fraiche, yogurt and others. This will be more or less a dairy project and outside of the converter´s core competence, but Coveris would offer good material knowledge during such a study. At the moment, we were able to compare materials with each other and find out which material was the most comparable with polystyrene.

The conclusion was that in the next stage polypropylene cup will replace part of polystyrene cups step by step. PS is still the first choice for cultured dairy products. Even though polypropylene has higher barrier and lower strength, further tests will be done after thesis. If the results from these tests are encouraging, PP cups continue to cultured products also. Price and carbon footprint of polypropylene were the most attractive benefits. Further study with PLA is interesting, but now material is at least too expensive. Material using in special ecological products might be the first possibility if the atmosphere and the prices are more favorable. Foamed PP really decreases barrier properties and weight of the package. Material development with foamed materials will continue in the development unit in order to obtain material suitability for the production. Filled PP is opaque, which makes material using in dairy packages more difficult. Filled material gives more benefits to meat packages which are more often colored. The results from the strength test with filled PP were truly inspiring in generally, not only in dairy cups.

At the moment it is known that the cup fermentation really increases the need of higher permeation, in order to decrease CO_2 inside the package. One option in this case is to measure the overall gas throughput of the package, and compare different products with different packages. During this step, lids should be included. All the comments should be documented with regards to fermentation reactions and organoleptic triangle tests by comparing the original product. The next step is to calculate more detailed price impacts of each interesting scenario and effects to the total production capacity with new lead times. Further on, a discussion with the customers and a future plan regarding materials is required. In the future, the environmental prospects, such as recycling and material impacts will be more important and would be of key importance for success on the market. New modifications to laws and increasingly strict regulations will contribute to this development

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APPENDICES

Appendices 1-15

Appendices 1-5 are OTR with 0% humidity, 6-10 are OTR with 50% humidity and 11-15 are CO_2TR with 0% humidity. There is some wrong information in data tables which have no impact to the GTR-results. Correct values in all tests were sample area 50cm^2 and sheet thicknesses, approximately 1.06-1.33mm, not 1 mil. Transmission rate is not dependent on sheet thickness, but the permeation rate is. A part of permeation values which in the reports is wrong due to wrong base data. In this thesis materials are compared, with permeation not being the focus of the study. Transmission rates provide better information about polymer differences and permeation's total transmission amount package in actual thicknesses and environment.

In the appendices section, only one example of each test is presented because all of the tests conducted were almost equal. Two or more duplicates of the tests were tested in every different test and results which are in the result section were calculated from all of them.

MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M1
Using Method: Default Method

MODULE INFORMATION:

Module 4, Serial	SS_01303
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.0 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

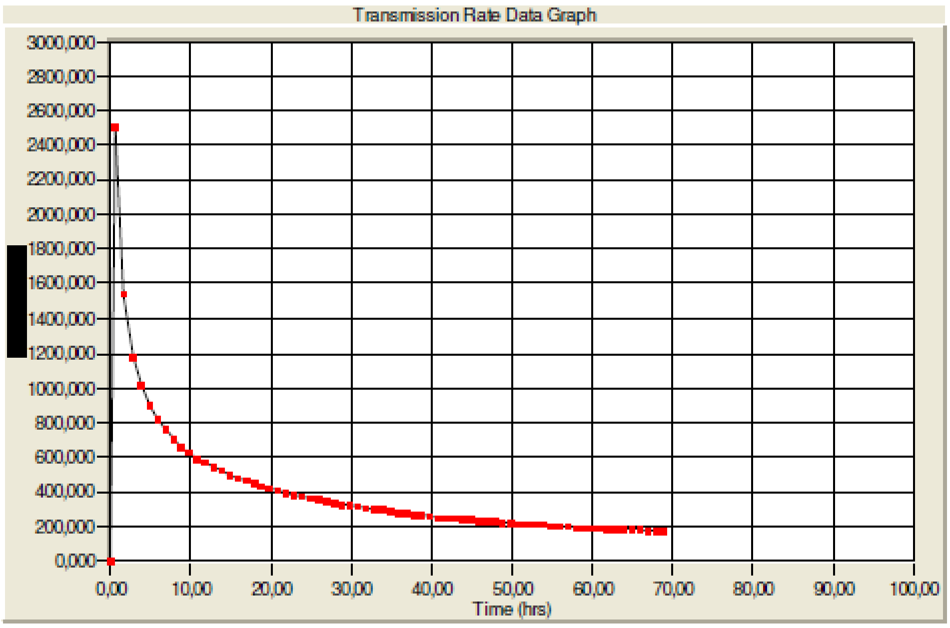
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	69
Current Status:	Finished
Started Testing:	2/11/2014 10:48:22 AM
Elapsed Time:	68:52

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	17.16964	cc / [m² - day]
Transmission @ 100%	171.6964	cc / [m² - day]
Permeation:	171.6964	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	2508.719	1:40	1538.862	2:52	1174.628
3:52	1012.766	4:52	900.4227	5:52	819.3007	6:52	755.2878
7:52	704.1560	8:52	659.6251	9:52	623.3371	10:52	592.8777
11:52	565.4846	12:52	539.8302	13:52	518.6482	14:52	498.1629
15:52	476.4866	16:52	462.8258	17:52	443.4951	18:52	431.1752
19:52	419.0977	20:52	406.5098	21:52	393.9320	22:52	381.6460
23:52	370.9242	24:52	362.2082	25:52	352.9744	26:52	344.2743
27:52	336.4174	28:52	327.2796	29:52	320.3125	30:52	312.5678
31:52	305.1979	32:52	297.9487	33:52	291.1784	34:52	284.3579
35:52	278.3136	36:52	273.1477	37:52	267.4981	38:52	262.5398
39:52	256.9429	40:52	249.9812	41:52	245.2508	42:52	242.3995
43:52	236.8420	44:52	234.8138	45:52	229.1573	46:52	226.7821
47:52	223.2821	48:52	219.4521	49:52	217.5962	50:52	212.8904
51:52	210.9835	52:52	207.0654	53:52	204.3480	54:52	200.3409
55:52	197.4560	56:52	195.8572	57:52	193.7374	58:52	189.9329
59:52	188.3588	60:52	186.9149	61:52	184.0985	62:52	183.3885
63:52	180.8354	64:52	178.1651	65:52	175.8498	66:52	174.2200
67:52	172.6875	68:52	171.6964	68:53	Complete	68:53	Finished



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M2
Using Method: Default Method

MODULE INFORMATION:

Module 4, Serial	SS_01303
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.0 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

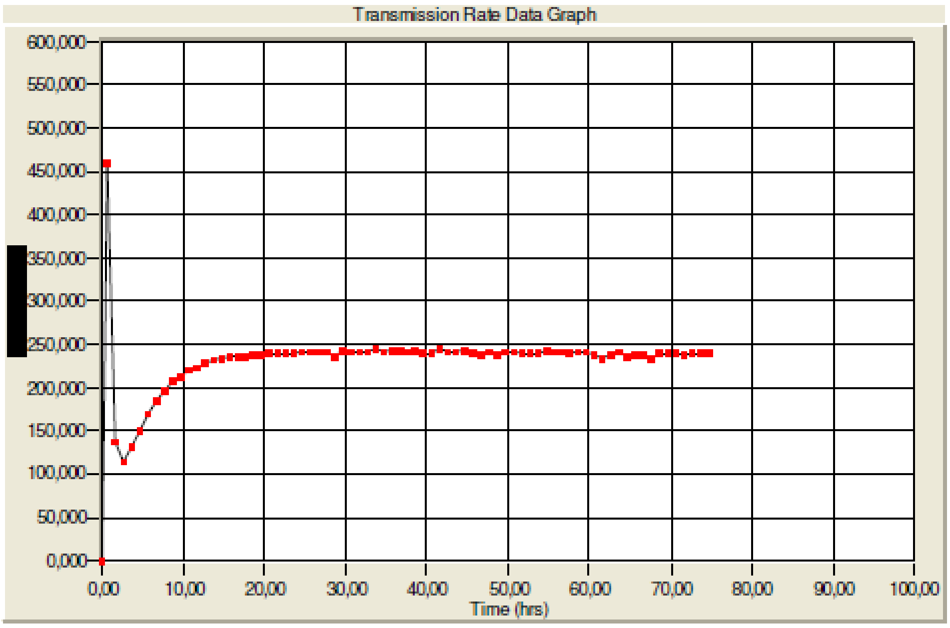
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	75
Current Status:	Test Done
Started Testing:	2/14/2014 7:50:10 AM
Elapsed Time:	74:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	23.91295	cc / [m² - day]
Transmission @ 100%	239.1295	cc / [m² - day]
Permeation:	239.1295	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	459.6963	1:40	137.4927	2:40	114.3577
3:40	130.2216	4:40	150.3503	5:40	168.2602	6:40	183.7411
7:40	196.3947	8:40	206.5428	9:40	212.3838	10:40	219.5875
11:40	223.0408	12:40	227.2246	13:40	231.0651	14:40	233.4756
15:40	235.1817	16:40	235.3855	17:40	236.3219	18:40	237.1208
19:40	238.1764	20:40	238.6392	21:40	238.9492	22:40	239.4290
23:40	239.7682	24:40	240.2218	25:40	241.2564	26:40	241.0583
27:40	240.6696	28:40	236.3154	29:40	243.4910	30:40	240.2010
31:40	241.5730	32:40	241.9774	33:40	245.7997	34:40	240.9826
35:40	243.2881	36:40	243.0254	37:40	241.0351	38:40	242.1296
39:40	239.9388	40:40	238.3008	41:40	245.1991	42:40	240.6767
43:40	240.6081	44:40	243.2830	45:40	238.7795	46:40	237.9928
47:40	241.0014	48:40	238.2573	49:40	240.7131	50:40	241.6077
51:40	240.1259	52:40	239.3547	53:40	239.4071	54:40	242.8659
55:40	241.0089	56:40	240.4175	57:40	238.3293	58:40	240.6504
59:40	240.5366	60:40	237.5034	61:40	233.1123	62:40	238.0142
63:40	240.8593	64:40	236.2308	65:40	237.8761	66:40	238.0074
67:40	234.2932	68:40	238.7522	69:40	238.6197	70:40	239.7213
71:40	237.7499	72:40	239.0438	73:40	238.7423	74:40	239.1295
75:26	Complete						



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M3
Using Method: Default Method

MODULE INFORMATION:

Module 4, Serial	SS 01303
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.0 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	18
Current Status:	Test Done
Started Testing:	2/18/2014 2:01:46 PM
Elapsed Time:	17:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	6.361483	cc / [m² - day]
Transmission @ 100%	63.61483	cc / [m² - day]
Permeation:	63.61483	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	456.2862	1:40	280.7557	2:40	208.1343
3:40	156.3325	4:40	126.2012	5:40	105.9733	6:40	92.29052
7:40	83.01555	8:40	76.66821	9:40	72.48168	10:40	69.60108
11:40	67.48303	12:40	66.10842	13:40	65.17502	14:40	64.52631
15:40	64.01282	16:40	63.78444	17:40	63.61483		

MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M4
Using Method: Default Method

MODULE INFORMATION:

Module 4, Serial	SS_01303
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.0 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

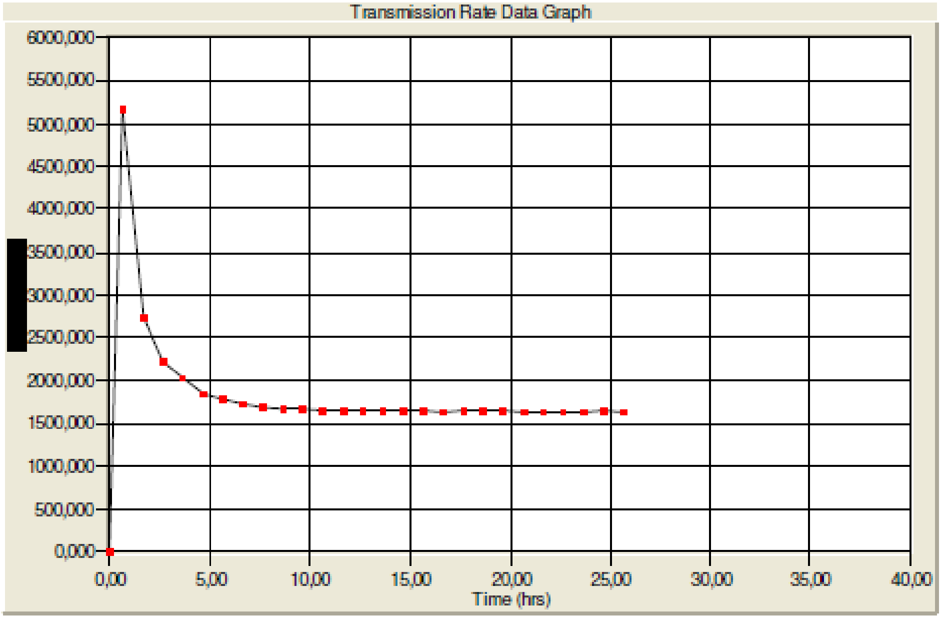
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	26
Current Status:	Test Done
Started Testing:	2/17/2014 11:24:11 AM
Elapsed Time:	25:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	164.1498	cc / [m² - day]
Transmission @ 100%	1641.498	cc / [m² - day]
Permeation:	1641.498	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	5165.185	1:40	2734.398	2:40	2224.510
3:40	2031.360	4:40	1849.567	5:40	1777.019	6:40	1727.421
7:40	1695.733	8:40	1674.508	9:40	1663.243	10:40	1656.967
11:40	1649.664	12:40	1646.649	13:40	1646.624	14:40	1646.076
15:40	1643.039	16:40	1642.242	17:40	1644.229	18:40	1643.059
19:40	1644.873	20:40	1641.987	21:40	1639.519	22:40	1642.312
23:40	1641.623	24:40	1644.281	25:40	1641.498	26:32	Complete



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy Test Number: M5
Using Method: Default Method

MODULE INFORMATION:

Module 4, Serial	SS_01303
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.0 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

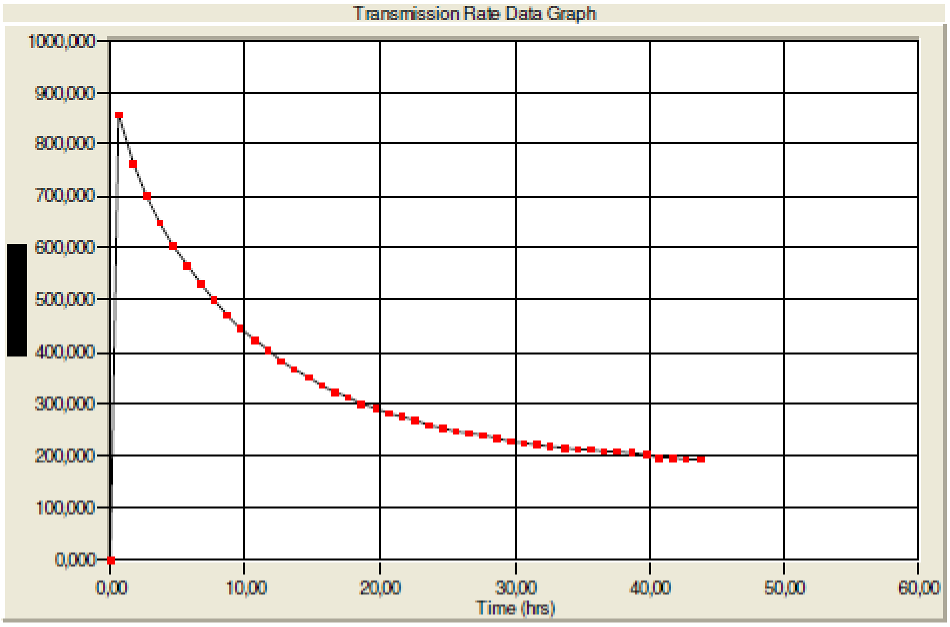
CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	44
Current Status:	Test Done
Started Testing:	2/19/2014 2:07:58 PM
Elapsed Time:	43:45

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	19.19925	cc / [m² - day]
Transmission @ 100%	191.9925	cc / [m² - day]
Permeation:	191.9925	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	858.7217	1:40	762.3875	2:40	700.1778
3:40	648.8999	4:40	605.9781	5:40	566.7053	6:40	531.7912
7:40	500.8162	8:40	472.6407	9:40	447.4020	10:40	424.0387
11:40	403.6091	12:40	384.2079	13:40	367.0698	14:40	351.1697
15:40	336.6281	16:40	324.0586	17:40	311.8834	18:40	301.7459
19:40	291.6475	20:40	282.3832	21:40	273.8254	22:40	267.5835
23:40	259.7440	24:40	253.1469	25:40	247.9732	26:40	242.6047
27:40	239.2469	28:40	233.3591	29:40	229.1460	30:40	224.5864
31:40	221.6345	32:40	218.8080	33:40	215.3700	34:40	213.4407
35:40	211.2388	36:40	209.2961	37:40	207.6317	38:40	204.6432
39:45	203.7141	40:45	196.2526	41:45	194.8656	42:45	193.4210
43:45	191.9925	44:44	Complete				



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy Test Number: M1
Using Method: Default Method

MODULE INFORMATION:

Module 1, Serial	MH_01797
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Auto: 33.7%, Carrier - Auto: 49.7%
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

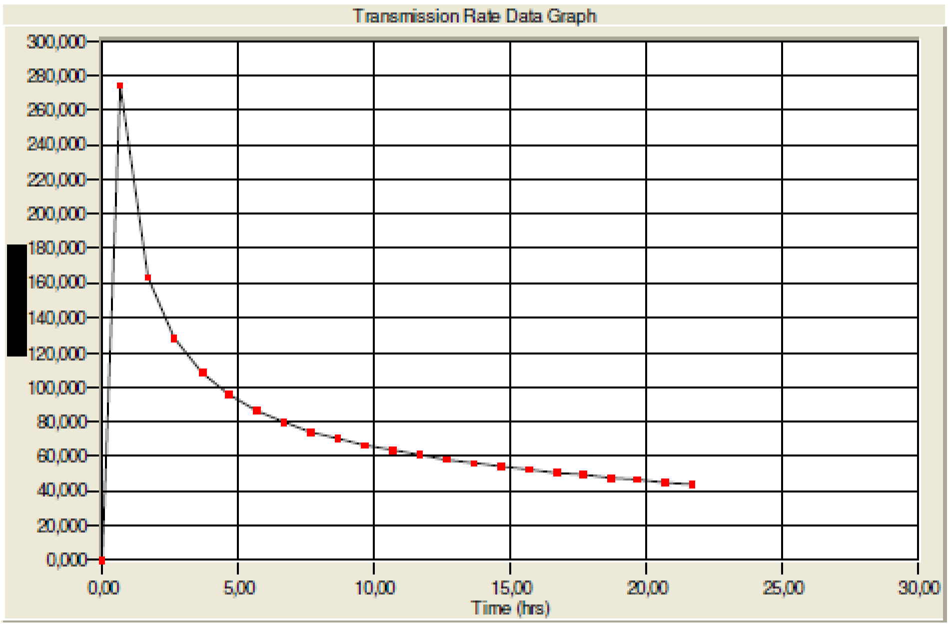
CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	22
Current Status:	Finished
Started Testing:	2/26/2014 10:15:39 AM
Elapsed Time:	21:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	4.369897	cc / [m² - day]
Transmission @ 100%	43.69897	cc / [m² - day]
Permeation:	43.69897	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	274.6083	1:40	163.3303	2:40	127.7933
3:40	108.4346	4:40	95.74384	5:40	86.73458	6:40	79.86418
7:40	74.37831	8:40	69.94991	9:40	66.32901	10:40	63.25096
11:40	60.54994	12:40	58.17410	13:40	56.03719	14:40	54.11446
15:40	52.30865	16:40	50.69004	17:40	49.09080	18:40	47.62730
19:40	46.24269	20:40	44.92175	21:40	43.69897	22:39	Complete
22:39	Finished						



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: <unspecified>   Test Number: M2
Using Method: Default Method

MODULE INFORMATION:

Module 1, Serial	MH_01797
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Auto: 44.0%, Carrier - Auto: 48.7%
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

CELL A INFORMATION:

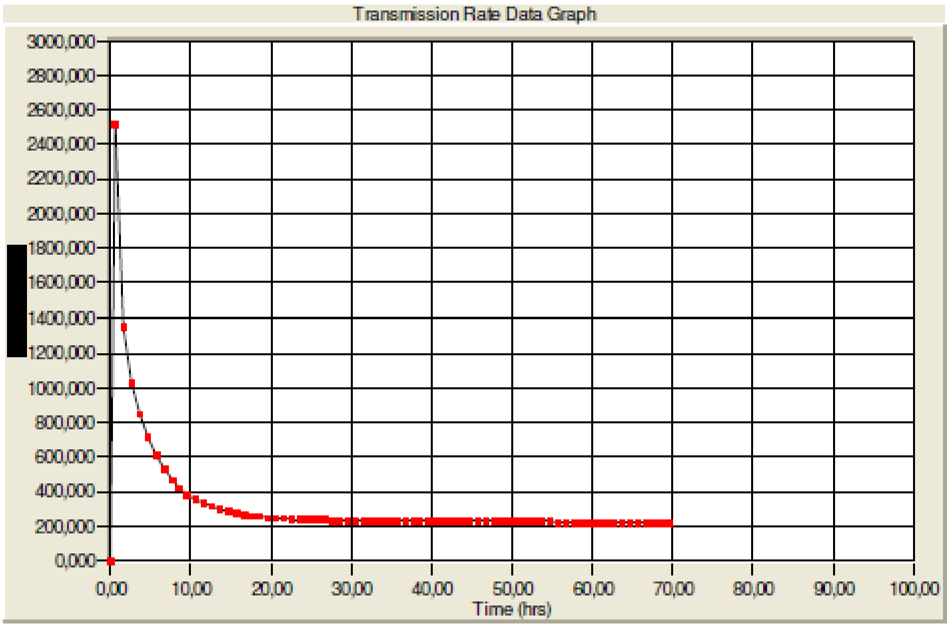
Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	70
Current Status:	Finished
Started Testing:	2/7/2014 11:00:11 AM
Elapsed Time:	69:40

TEST RESULTS — IN SELECTED UNITS

Transmission @ 10 %	22.18678	cc / [m² - day]
Transmission @ 100%	221.8678	cc / [m² - day]
Permeation:	221.8678	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	2513.007	1:40	1350.846	2:40	1029.816
3:40	841.9330	4:40	707.6943	5:40	606.7935	6:40	529.4231
7:40	468.3201	8:40	420.7014	9:40	383.0630	10:40	353.5031
11:40	329.7784	12:40	310.8248	13:40	295.3027	14:40	283.6055
15:40	273.3462	16:40	265.4800	17:40	259.0264	18:40	253.5512
19:40	249.9457	20:40	246.6637	21:40	243.2445	22:40	240.2083
23:40	237.9735	24:40	235.8676	25:40	234.0697	26:40	233.0271
27:40	231.5444	28:40	230.6503	29:40	229.6789	30:40	229.0297
31:40	228.4479	32:40	227.6840	33:40	227.2060	34:40	226.3531
35:40	226.1542	36:40	225.7896	37:40	225.4556	38:40	225.4322
39:40	225.3663	40:40	225.2658	41:40	224.9832	42:40	224.8009
43:40	224.5473	44:40	224.5673	45:40	224.2763	46:40	224.2562
47:40	224.1303	48:40	224.1474	49:40	223.7546	50:40	223.7848
51:40	223.7878	52:40	223.6868	53:40	223.3320	54:40	223.1991
55:40	222.9938	56:40	222.9131	57:40	222.8951	58:40	222.6295
59:40	222.5857	60:40	222.4002	61:40	222.2449	62:40	222.2588
63:40	222.1860	64:40	222.2053	65:40	222.1693	66:40	221.9035
67:40	222.0421	68:40	222.0119	69:40	221.8678	70:07	Complete
70:07	Finished						



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M3
Using Method: Default Method

MODULE INFORMATION:

Module 1, Serial	MH_01797
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Auto: 45.3%, Carrier - Auto: 48.7%
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

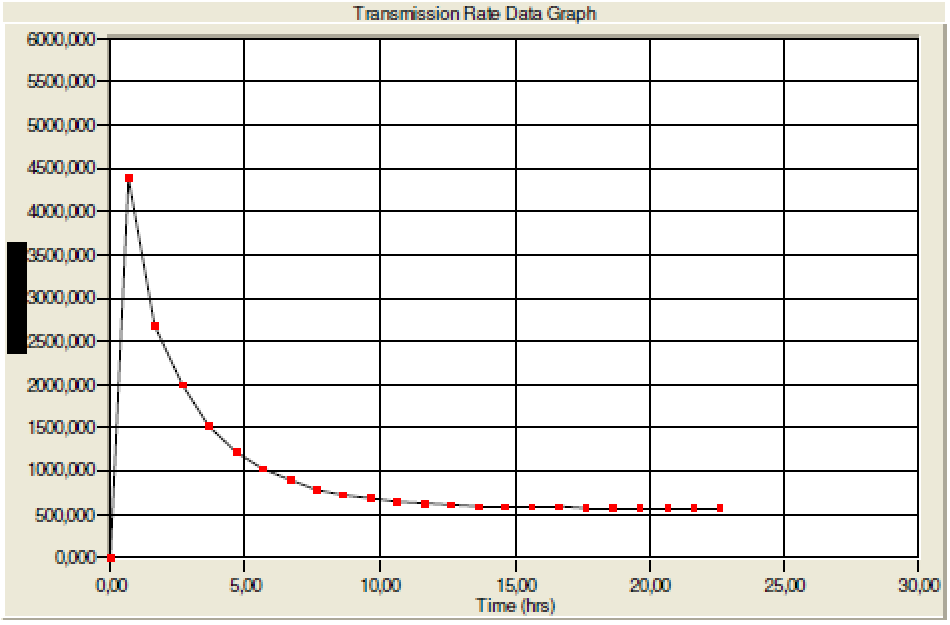
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	23
Current Status:	Test Done
Started Testing:	2/10/2014 9:34:24 AM
Elapsed Time:	22:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	57.10683	cc / [m² - day]
Transmission @ 100%	571.0683	cc / [m² - day]
Permeation:	571.0683	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	4394.712	1:40	2685.163	2:40	1998.135
3:40	1515.001	4:40	1222.665	5:40	1021.797	6:40	883.4703
7:40	787.2940	8:40	721.2192	9:40	676.2182	10:40	644.7678
11:40	622.6466	12:40	607.0278	13:40	596.3902	14:40	589.0325
15:40	583.5107	16:40	579.7139	17:40	577.1848	18:40	574.8438
19:40	573.4859	20:40	572.0063	21:40	571.4631	22:40	571.0683
22:42	Complete						



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy   Test Number: M4
Using Method: Default Method

MODULE INFORMATION:

Module 1, Serial	MH_01797
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Auto: 47.8%, Carrier - Auto: 48.5%
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

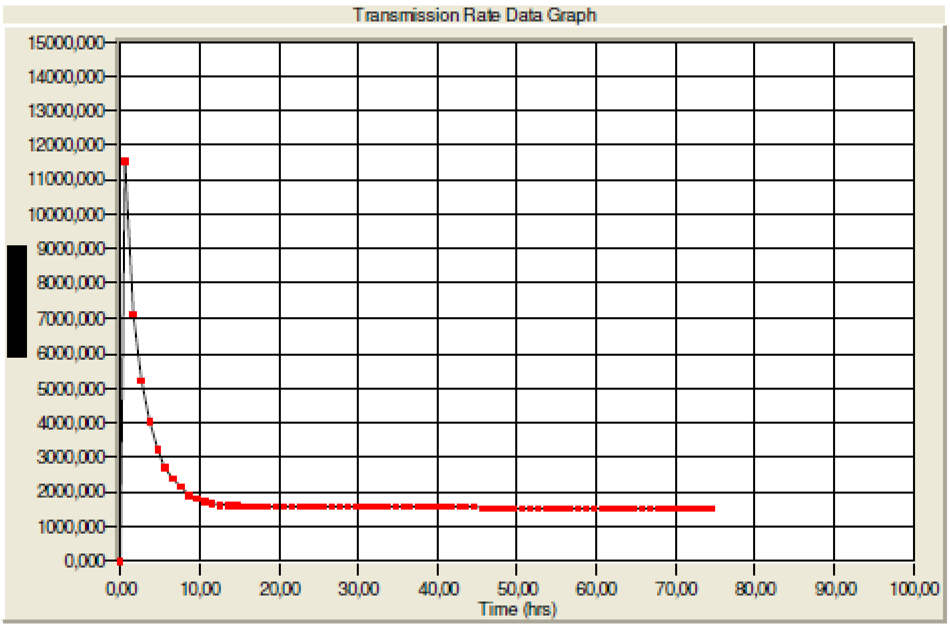
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	75
Current Status:	Test Done
Started Testing:	2/14/2014 7:33:00 AM
Elapsed Time:	74:40

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	152.6743	cc / [m² - day]
Transmission @ 100%	1526.743	cc / [m² - day]
Permeation:	1526.743	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	11525.16	1:40	7118.533	2:40	5219.847
3:40	4030.651	4:40	3244.087	5:40	2717.489	6:40	2361.325
7:40	2121.801	8:40	1905.159	9:40	1794.797	10:40	1720.060
11:40	1669.440	12:40	1635.205	13:40	1611.470	14:40	1595.286
15:40	1584.201	16:40	1576.616	17:40	1571.251	18:40	1567.085
19:40	1564.335	20:40	1562.724	21:40	1561.340	22:40	1560.162
23:40	1559.520	24:40	1558.860	25:40	1558.365	26:40	1557.701
27:40	1557.533	28:40	1557.330	29:40	1557.051	30:40	1556.917
31:40	1556.095	32:40	1555.605	33:40	1555.230	34:40	1554.747
35:40	1553.758	36:40	1552.627	37:40	1551.752	38:40	1550.925
39:40	1550.016	40:40	1548.877	41:40	1547.762	42:40	1546.247
43:40	1544.937	44:40	1543.487	45:40	1541.898	46:40	1540.235
47:40	1539.089	48:40	1537.774	49:40	1536.730	50:40	1535.737
51:40	1535.051	52:40	1534.375	53:40	1533.504	54:40	1532.709
55:40	1531.917	56:40	1531.294	57:40	1530.498	58:40	1529.728
59:40	1529.094	60:40	1528.007	61:40	1527.422	62:40	1526.693
63:40	1525.992	64:40	1525.498	65:40	1525.065	66:40	1524.831
67:40	1524.486	68:40	1524.472	69:40	1524.256	70:40	1523.883
71:40	1523.885	72:40	1523.944	73:40	1526.129	74:40	1526.743
75:24	Complete						



MOCON OX-TRAN® 2/21 - Single Test Report

Material Id: PACCOR Oy Test Number: M5
Using Method: Default Method

MODULE INFORMATION:

Module 1, Serial	MH_01797
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Auto: 46.9%, Carrier - Auto: 48.4%
Permeant Concentration:	10 %
Ambient Temp:	Manual: 23.0 °C.

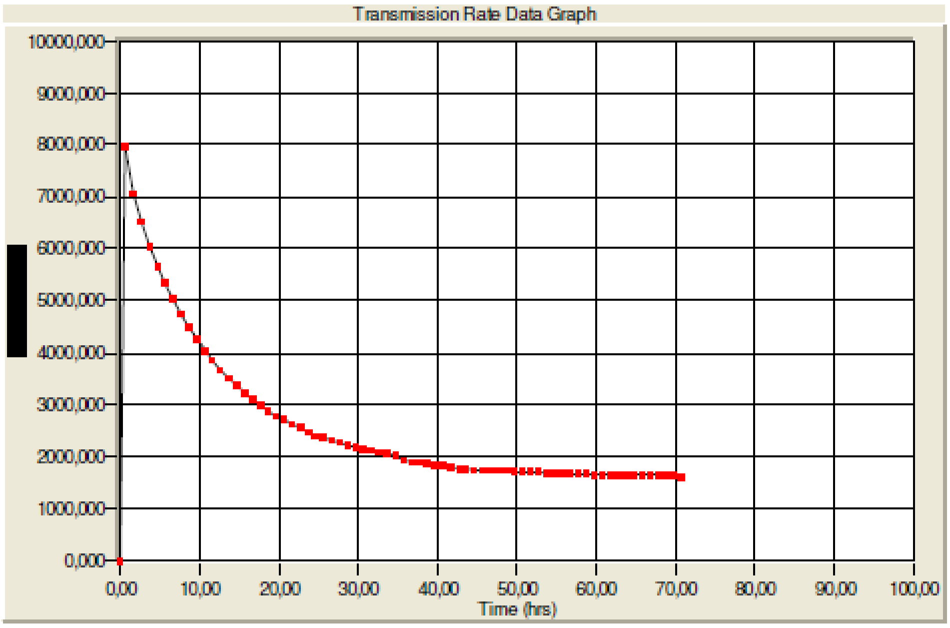
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	20
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	71
Current Status:	Test Done
Started Testing:	2/11/2014 8:28:55 AM
Elapsed Time:	70:41

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 10 %	162.9100	cc / [m² - day]
Transmission @ 100%	1629.100	cc / [m² - day]
Permeation:	1629.100	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:40	7962.990	1:40	7046.149	2:40	6507.543
3:40	6057.219	4:40	5675.182	5:40	5333.175	6:40	5024.614
7:40	4747.794	8:40	4491.513	9:40	4261.838	10:40	4052.446
11:40	3859.915	12:40	3683.688	13:40	3522.281	14:40	3375.382
15:40	3238.229	16:40	3113.108	17:40	2999.121	18:40	2892.853
19:40	2796.138	20:40	2706.515	21:40	2624.332	22:40	2548.679
23:40	2480.420	24:40	2419.560	25:40	2361.895	26:40	2307.899
27:40	2268.918	28:40	2221.651	29:40	2183.411	30:40	2142.499
31:40	2110.707	32:40	2076.489	33:40	2048.280	34:41	2017.329
35:41	1937.388	36:41	1912.752	37:41	1890.751	38:41	1869.391
39:41	1850.968	40:41	1833.447	41:41	1809.482	42:41	1787.774
43:41	1771.041	44:41	1756.198	45:41	1744.249	46:41	1744.380
47:41	1735.197	48:41	1729.758	49:41	1721.979	50:41	1716.263
51:41	1707.828	52:41	1695.160	53:41	1687.720	54:41	1682.523
55:41	1678.392	56:41	1672.095	57:41	1667.214	58:41	1662.503
59:41	1658.165	60:41	1654.985	61:41	1651.296	62:41	1647.577
63:41	1644.435	64:41	1641.943	65:41	1639.471	66:41	1636.920
67:41	1634.517	68:41	1632.761	69:41	1630.999	70:41	1629.100
70:55	Complete						



MOCON PERMATRAN-C™ 4/41 - Single Test Report

Material Id: PACCOR OY   Test Number: M1
Using Method: Default Method

MODULE INFORMATION:

Module 3, Serial	MC_01091
Setup Name:	SsSsefault Setup
Temp Setpoint/Actual:	Manual: 23.0 / 23.0 °C.
Barometric Pressure:	Auto: 740.93 mmHg
Flow Rate:	Auto: 18.07 SCCM
Permeant Concentration:	100 %
Ambient Temp:	Manual: 23.0 °C.

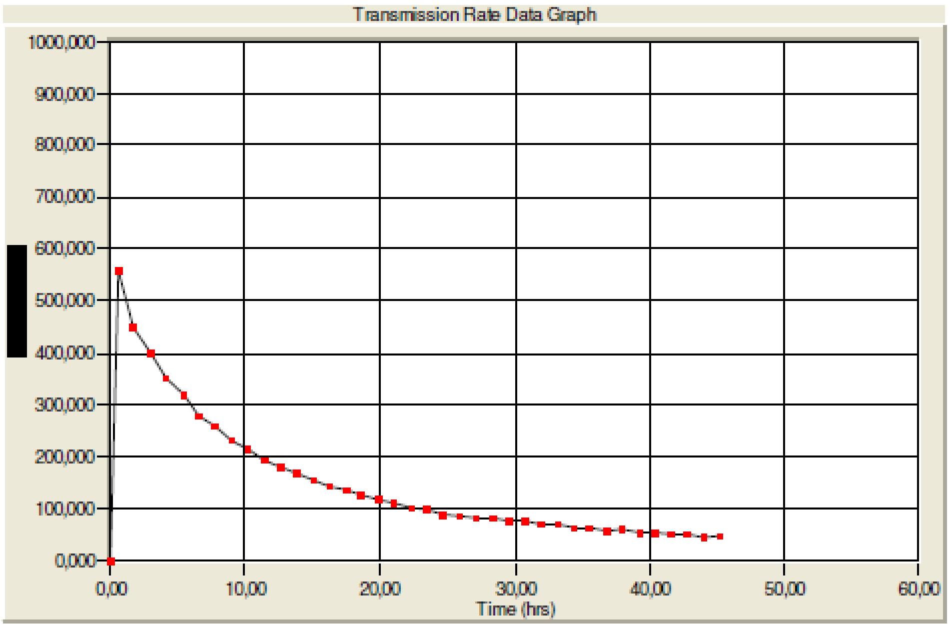
CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	38
Current Status:	Test Done
Started Testing:	2/18/2014 12:22:02 PM
Elapsed Time:	45:15

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 100 %	48.07575	cc / [m² - day]
Transmission @ 100%	48.07575	cc / [m² - day]
Permeation:	48.07575	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:35	557.0033	1:45	448.6085	3:00	398.6131
4:10	350.0182	5:25	318.5566	6:35	279.1532	7:50	259.1103
9:00	230.7577	10:15	214.3040	11:25	192.9364	12:40	180.7699
13:50	166.4219	15:05	154.2279	16:15	143.9836	17:30	135.3671
18:40	126.7897	19:55	118.4929	21:05	110.9504	22:20	100.7756
23:30	97.53062	24:45	89.02516	25:55	86.58267	27:10	81.93102
28:20	81.52781	29:35	75.70864	30:45	74.77834	32:00	70.02990
33:10	69.97076	34:25	63.72952	35:35	64.62469	36:50	58.15437
38:00	59.99198	39:15	53.93882	40:25	54.48386	41:40	49.26197
42:50	50.99258	44:05	44.86989	45:15	48.07575	46:22	Complete



MOCON PERMATRAN-C™ 4/41 - Single Test Report

Material Id: PACCOR OY   Test Number: M2
Using Method: Default Method

MODULE INFORMATION:

Module 3, Serial	MC_01091
Setup Name:	SsSsefault Setup
Temp Setpoint/Actual:	Manual: 23.0 / 23.0 °C.
Barometric Pressure:	Auto: 738.36 mmHg
Flow Rate:	Auto: 18.35 SCCM
Permeant Concentration:	100 %
Ambient Temp:	Manual: 23.0 °C.

CELL A INFORMATION:

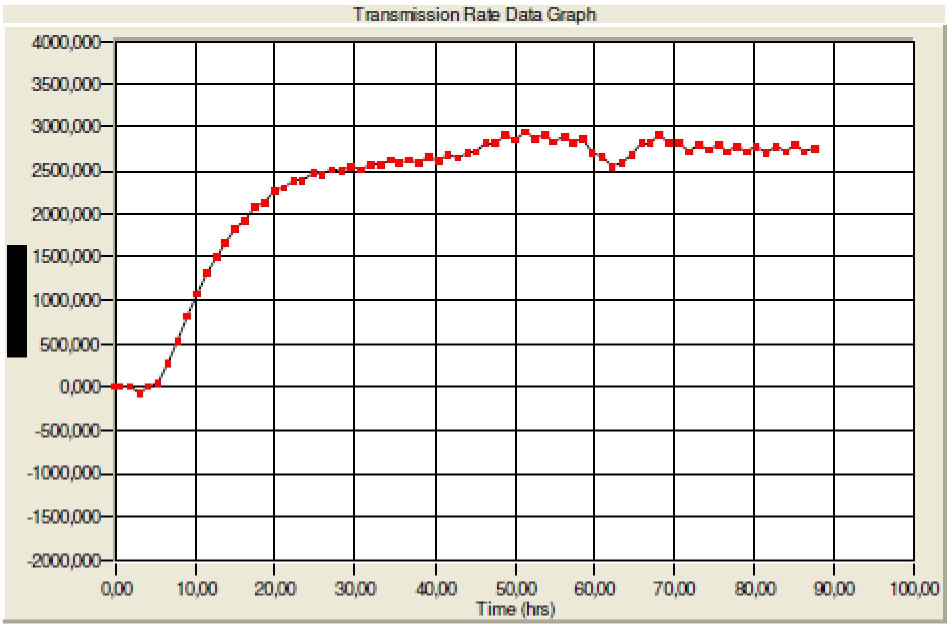
Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	73
Current Status:	Finished
Started Testing:	2/10/2014 2:48:49 PM
Elapsed Time:	87:35

TEST RESULTS — **IN SELECTED UNITS**

Transmission @ 100 %	2766.722	cc / [m² - day]
Transmission @ 100%	2766.722	cc / [m² - day]
Permeation:	2766.722	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:35	5.300660	1:45	4.151339	3:00	-75.15819
4:10	5.632152	5:25	38.41211	6:35	280.1588	7:50	529.9440
9:00	817.1944	10:15	1070.489	11:25	1309.033	12:40	1514.934
13:50	1650.507	15:05	1830.536	16:15	1930.370	17:30	2066.870
18:40	2135.410	19:55	2272.166	21:05	2294.771	22:20	2381.212
23:30	2387.545	24:45	2478.044	25:55	2455.316	27:10	2515.138
28:20	2502.910	29:35	2558.704	30:45	2511.509	32:00	2576.209
33:10	2568.100	34:25	2619.737	35:35	2589.899	36:50	2634.842
38:00	2594.533	39:15	2666.423	40:25	2602.563	41:40	2684.269
42:50	2641.513	44:05	2705.222	45:15	2727.990	46:30	2816.641
47:40	2812.960	48:55	2911.506	50:05	2855.587	51:20	2940.841
52:30	2867.138	53:45	2919.120	54:55	2831.372	56:10	2893.444
57:20	2816.121	58:35	2877.645	59:45	2703.737	61:00	2667.267
62:10	2555.274	63:25	2585.280	64:35	2680.002	65:50	2818.312
67:00	2807.286	68:15	2906.681	69:25	2819.499	70:40	2814.709
71:50	2722.710	73:05	2803.493	74:15	2749.931	75:30	2792.000
76:40	2728.776	77:55	2787.552	79:05	2724.631	80:20	2777.391
81:30	2706.086	82:45	2778.882	83:55	2725.742	85:10	2798.801
86:20	2713.755	87:35	2766.722	88:44	Complete	88:45	Finished



MOCON PERMATRAN-C™ 4/41 - Single Test Report

Material Id: PACCOR OY Test Number: M3
Using Method: Default Method

MODULE INFORMATION:

Module 3, Serial	MC_01091
Setup Name:	SsSsefault Setup
Temp Setpoint/Actual:	Manual: 23.0 / 23.0 °C.
Barometric Pressure:	Auto: 727.83 mmHg
Flow Rate:	Auto: 18.12 SCCM
Permeant Concentration:	100 %
Ambient Temp:	Manual: 23.0 °C.

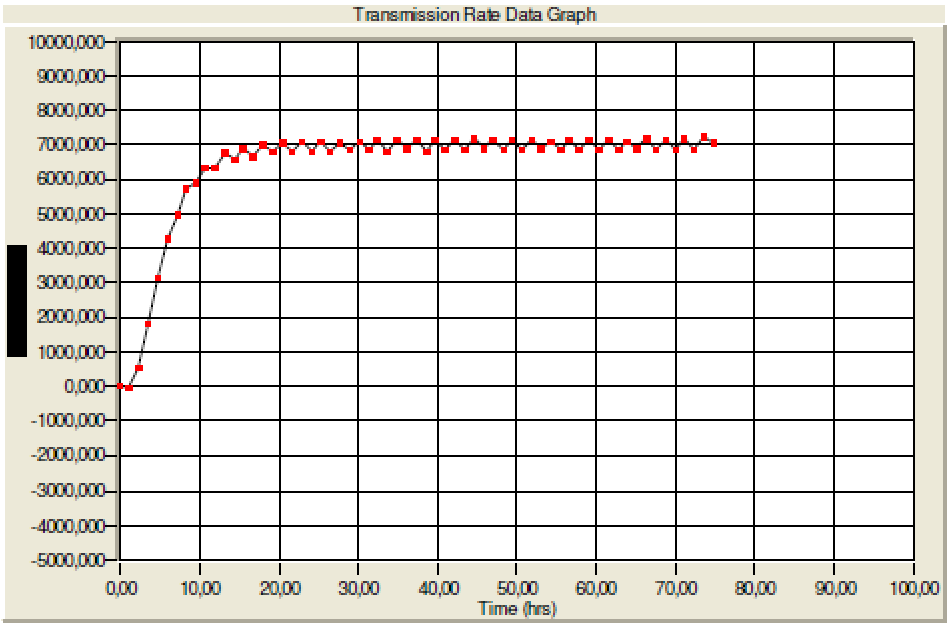
CELL A INFORMATION:

Sample Type:	Film: 5 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	63
Current Status:	Test Done
Started Testing:	2/14/2014 7:41:07 AM
Elapsed Time:	75:30

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 100 %	7859.883	cc / [m² - day]
Transmission @ 100%	7859.883	cc / [m² - day]
Permeation:	7859.883	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	0:35	0.036351	1:45	169.2258	3:00	1335.860
4:10	2817.813	5:25	4178.645	6:35	4957.736	7:50	5829.504
9:00	6137.650	10:15	6643.872	11:25	6713.912	12:40	7103.010
13:50	6980.403	15:05	7285.203	16:15	7101.065	17:30	7438.439
18:40	7206.718	19:55	7475.164	21:05	7248.007	22:20	7519.577
23:30	7225.729	24:45	7562.043	25:55	7239.207	27:10	7505.455
28:20	7271.748	29:35	7557.156	30:45	7281.029	32:00	7567.729
33:10	7328.644	34:25	7558.338	35:35	7342.222	36:50	7595.122
38:00	7368.543	39:15	7529.960	40:25	7319.365	41:40	7575.012
42:50	7367.552	44:05	7617.154	45:15	7351.471	46:30	7582.096
47:40	7335.313	48:55	7602.672	50:05	7294.486	51:20	7585.122
52:30	7337.442	53:45	7569.223	54:55	7325.052	56:10	7607.366
57:20	7363.705	58:35	7616.175	59:45	7326.946	61:00	7576.585
62:10	7293.472	63:25	7511.158	64:35	7295.701	65:50	7591.114
67:00	7308.094	68:15	7562.911	69:25	7340.197	70:40	7577.722
71:50	7338.596	73:05	7633.436	74:15	7494.012	75:30	7859.883
75:33	Complete						



MOCON PERMATRAN-C™ 4/41 - Single Test Report

Material Id: PACCOR OY   Test Number: M4
Using Method: Default Method

MODULE INFORMATION:

Module 3, Serial	MC_01091
Setup Name:	SsSsefault Setup
Temp Setpoint/Actual:	Manual: 23.0 / 23.0 °C.
Barometric Pressure:	Auto: 754.77 mmHg
Flow Rate:	Auto: 19.62 SCCM
Permeant Concentration:	100 %
Ambient Temp:	Manual: 23.0 °C.

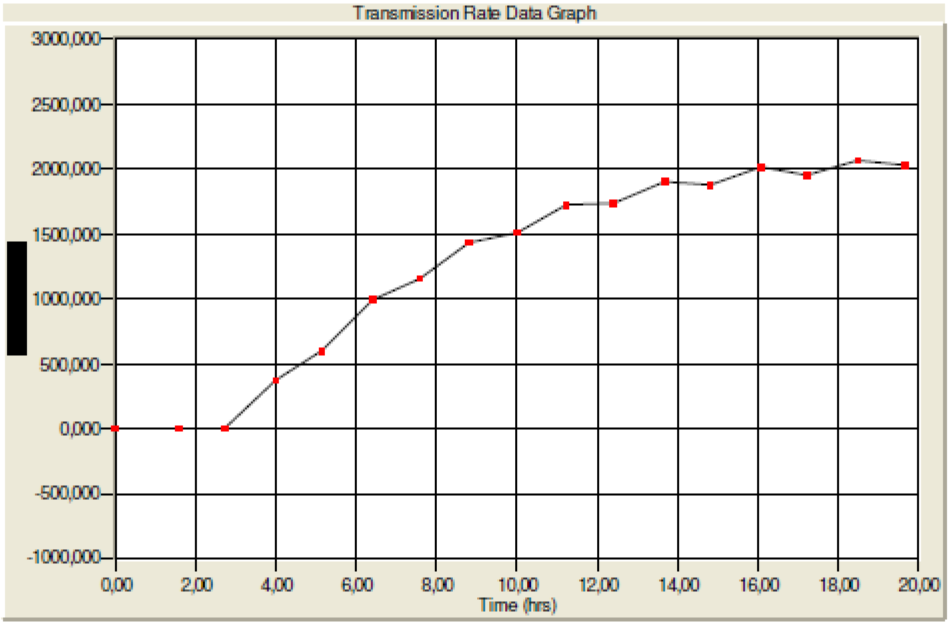
CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	16
Current Status:	Test Done
Started Testing:	2/25/2014 1:10:21 PM
Elapsed Time:	19:39

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 100 %	2022.468	cc / [m² - day]
Transmission @ 100%	2022.468	cc / [m² - day]
Permeation:	2022.468	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	1:34	5.236387	2:44	-1.308597	3:59	362.0192
5:09	593.1350	6:24	991.1284	7:34	1150.506	8:49	1435.035
9:59	1511.704	11:14	1724.269	12:24	1734.223	13:39	1897.136
14:49	1869.977	16:04	2008.187	17:14	1947.796	18:29	2061.610
19:39	2022.468	20:27	Complete				



MOCON PERMATRAN-C™ 4/41 - Single Test Report

Material Id: PACCOR OY   Test Number: M5
Using Method: Default Method

MODULE INFORMATION:

Module 3, Serial	MC_01091
Setup Name:	SsSsefault Setup
Temp Setpoint/Actual:	Manual: 23.0 / 23.0 °C.
Barometric Pressure:	Auto: 751.53 mmHg
Flow Rate:	Auto: 19.52 SCCM
Permeant Concentration:	100 %
Ambient Temp:	Manual: 23.0 °C.

CELL A INFORMATION:

Sample Type:	Film: 50 cm², 1 mil
Test Mode:	Continuous
Control Params:	Infinite
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	Disabled
Cycles Complete:	16
Current Status:	Finished
Started Testing:	2/26/2014 1:21:21 PM
Elapsed Time:	19:39

TEST RESULTS	IN SELECTED UNITS	
Transmission @ 100 %	1850.304	cc / [m² - day]
Transmission @ 100%	1850.304	cc / [m² - day]
Permeation:	1850.304	cc - mil / [m² - day]

DATA POINTS

Time	Rate/Event	Time	Rate/Event	Time	Rate/Event	Time	Rate/Event
0:00	Test	1:34	414.7022	2:44	841.3893	3:59	1211.515
5:09	1380.826	6:24	1585.247	7:34	1635.965	8:49	1756.915
9:59	1738.338	11:14	1838.870	12:24	1799.340	13:39	1868.990
14:49	1819.064	16:04	1906.521	17:14	1831.833	18:29	1907.491
19:39	1850.304	19:42	Complete	19:43	Finished