Investigation of high-barrier materials development for long shelf-life dairy based products with enhanced properties

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Abstract

This thesis has been pursuing an objective to investigate the recent developments in the field of high oxygen barrier materials for the dairy based medical nutrition portfolio of Danone Nutricia Research. The main goal of this research was to identify the materials and/or approaches that would allow the decrease of oxygen ingress with resulting shelf-life extension. Both flexible (pouch) and rigid (bottles) packaging has been evaluated. Based on the findings of the research, the list of selected materials has been created, followed by the preliminary evaluation of materials' suitability as an alternative for current packaging solutions. All evaluations have been conducted based on oxygen barrier performance, expressed in oxygen transmission rate (OTR, cm^3/ package/day).
The selected alternatives for flexible packaging in most cases exhibited stronger oxygen barrier performance comparing to the current packaging solution. That can potentially extend the current shelf-life of 12 months.

For the rigid packaging, the theoretical and experimental study on the barrier performance impact via modification of current barrier material (EVOH) has been performed. The theoretical assumption has been partly backed up by the experimental data showing an inversely proportional relationship between the EVOH thickness' increase and OTR. Nonetheless, the experimental data also shown dissimilitude to some of the theoretical predictions, therefore further OTR tests must be performed before the conclusion is drawn. Other approaches investigated were the modification of bottle headspace volume or oxygen content (%) in a headspace after filling. Lastly, active rigid PET-based monolayer packaging has been evaluated for Nutricia bottle versus the currently used passive multilayer packaging.

Keywords: barrier materials, OTR, shelf-life, flexible packaging, rigid packaging

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Lund, May 2016

Anna Kim

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1. Introduction

1.1 Background of the study

In modern world, an increasingly high demand is being placed on food packaging. The latter plays a defining role in preserving the quality of the product throughout its lifecycle, from manufacturing to the consumption.

The requirements of packaging material are dependent on the type of food product it will contain; materials need to fulfill different products' needs in terms of protection against moisture and gas barriers.

Barrier requirements for packaging of selected foods, in terms of oxygen and water vapor transmission, are summarized on the Figure 1 adapted from Schmid (2012).

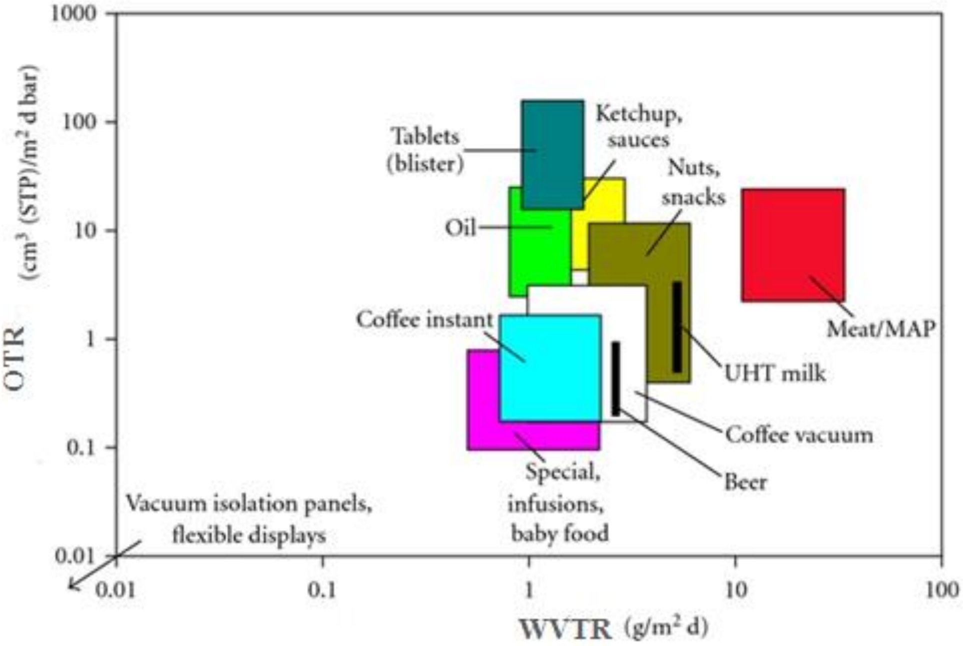


Figure 1. Barrier requirements for packaging of selected foods

Oxygen and moisture barrier are the defining criteria used when evaluating barrier packaging materials. These barrier properties can be expressed either as permeability or transmission rate. To put it simply, the material that is a good barrier has a low permeability or transmission rate for oxygen and/or moisture (Appendix A).

1.1.1 Case description

The wide portfolio of Danone products can be grouped into three categories, as Figure 2 demonstrates.

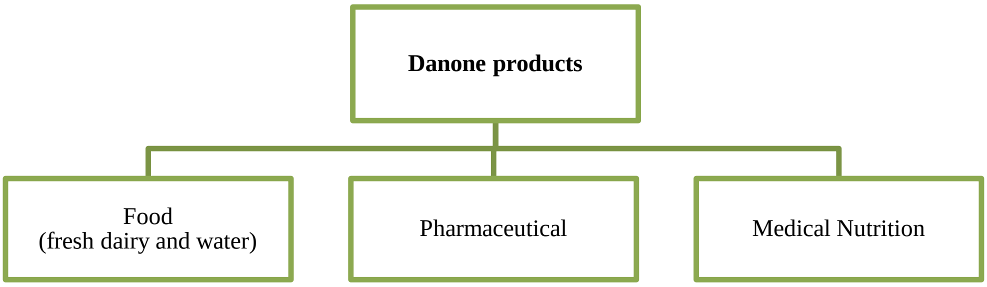


Figure 2. Portfolio of Danone products

Medical nutrition products are being developed by Danone Nutricia Research division of Danone and pursue several objectives:

- Firstly, these products are designed to complement the nutritive needs of patients' diet during the recovery phase, as well as the diet requirements arisen with age

- Secondly, some of them are being recommended to consumption as preventive measures against the continuation of diseases, such as Alzheimer's disease.

Shelf life range of Nutricia products is within 9-15 months, with average being 12 months. Medical nutrition products are, in majority, presented by dairy-based liquids and characterized by a fat content reaching up to 52% in some of them. The majority of Medical Nutrition products also contain vitamins that are added as premixes. The latter include water-soluble forms of vitamin A and E, fat-soluble β-carotene and α-tocopherol.

In regard to dairy-based products, the maximum protection against oxygen permeation is imperative, as it causes the oxidation process with the consequent loss of product nutritive and organoleptic qualities. As a result, due to oxidative reactions the shelf life of the product shortens considerably.
High fatty oils' content makes Nutricia products highly subjected to oxidation, with the group of risk including LCPUFA (Long Chain Poly-Unsaturated Fatty Acids). The latter enter into the reaction with oxygen with a consequent formation of hydroperoxides, alkanes, alkenes and other components that are responsible for rancid odors and flavors. Further in the process of oxidation, oxygen enters into reaction with other functional groups deteriorating the physical properties of foods. As one of the examples, cross-linking of aldehydes with amino groups in proteins may cause structural damage and textural change.

Therefore, from a packaging perspective, oxygen permeability is of a particular importance and defines the major characteristics of packaging materials suitable for a particular product.

Speaking broadly, the presence of oxygen in food product can happen in one of the following scenarios (L Rooney, 2005):

- It can be already present in the package's headspace at the time of sealing
- It can be present in the product itself at the time of sealing
- It can enter the package by permeation or leakage over the storage (oxygen ingress over time)

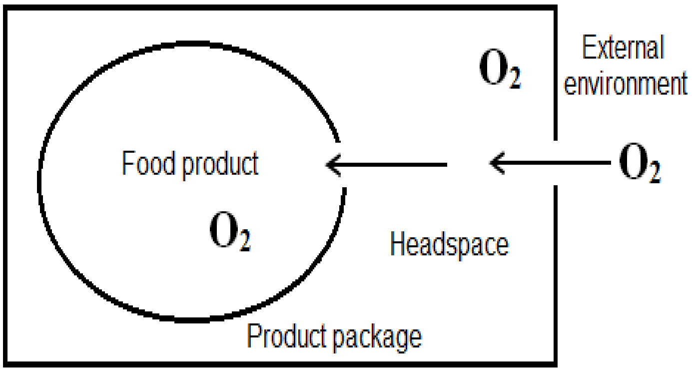


Figure 3. Oxygen presence in foods

The final oxygen content in the headspace and product will depend on the filling characteristics such as filling volume, inert gas (N_2) flushing, etc.
From the other side, the oxygen ingress over time is in the direct dependence on barrier properties of packaging material. Over the decades, packaging materials have evolved tremendously, with glass and metal packaging being gradually

replaced by polymer/plastics. However, comparing to glass or metal, all plastics are characterized by certain permeability to gases and water vapor. In application to oxygen sensitive foods, low permeability to oxygen remains the prerequisite for plastic packaging. The final package shall also meet a number of other requirements, such as water permeability, sealing strength, puncture resistance, transparency, compliance with food safety regulations, etc. In order to fulfill these functions, commonly multilayer structures of several polymers are used, with each one contributing to the resulting performance. (Kim L.Y., 2009).

1.2 Problem formulation and study goals

Considering the case of Danone Nutricia Research, two main forms of packaging are presented by:

- **Rigid packaging** (plastic bottle)
- **Flexible packaging** (pouch laminate)

At the current moment, Danone Nutricia uses conventional multilayer structures for both types of packaging, with barrier materials such as aluminum foil in flexible and ethylene vinyl alcohol (EVOH) in rigid packaging. These materials give the required protection against oxygen and moisture ingress for Nutricia products.

While both of these materials are considered as a nearly-perfect barrier, their performance is highly dependent on specific conditions. For example, at a thickness less than 25 µm, aluminum foil is subjected to the formation of pin holes and flex crack which dramatically lowers it barrier properties. More than that, the use of foil in multilayer packaging creates non-recyclable material resulting in an excess waste.

Danone Nutricia realizes the importance of moving in the direction of eco-sustainability, optimization of packaging physical parameter, such as weight and thickness that are resulting into down gauging and cost reduction.

Speaking objectively, the main obstacle for the implementation of new packaging technologies may be thwarted due to several reasons, most prominent being:

- Processing machinery is adapted to certain materials and installing new packaging processing line will lead to big financial investments
- Bigger number of converting companies working with traditional materials

However, these reasons exhibit a bigger impact when the packaging development is considered in a long run. Before that, there is a very first hurdle to overcome at the starting phases of research. As identified by Danone Nutricia, this impediment is a lack of thorough comparative research of a general scope of packaging materials currently being present on the market. Only with this knowledge, the company is equipped to undertake a study to consider the alternatives to current packaging solutions. The constant tracking of emerging trends has to be followed and evaluated on its potential applicability.

The situation is further complicated by scarce research on how the modification of the physical parameters of currently used materials will impact the package performance and shelf-life of the product it contains. This case refers to the currently accepted standard for the thickness of EVOH as an oxygen barrier material.

In order to address the challenges stated above, the main goal and several sub-goals were identified to serve as a guidelines for the exploratory part of the research. The **principal goal** was described as the thorough investigation on the recent and ongoing developments, as well as prevailing trends on the market of high barrier materials for oxygen-sensitive foods, particularly applicable for dairy-based foods.

The completion of main goal allows to achieve several sub-goals stated by Nutricia such as:

- Selection of alternatives for the current flexible and rigid packaging of Nutricia products, based on the preliminary analysis of barrier performance

- Theoretical and experimental study on the barrier performance impact via modification of current barrier material for rigid packaging.

- Exploration of the alternative ways rather than the modification of barrier material in existing rigid packaging, with the purpose of the extension of shelf-life

2. Methodology

2.1 Study approach

The study flow needed to be organized in a way that would allow the accomplishment of the main goal and sub-goals stated in Section 1.1.2. The foremost intention of this research was to understand what are the changes, trends and promising developments on the market of barrier materials for food packaging, with a particular focus on oxygen-sensitive foods. For that, the study method had to facilitate the extensive and thorough surveying through the vast amount of information to identify the points of exclusive interest.

The technology scouting approach chosen as the most appropriate to undertake was adapted from Rohrbeck (2006). As he rightly points out, in the environment of increasing technological complexity and of globalization of R&D the successful identification and usage of external sources of knowledge becomes increasingly important. According to Rohrbeck, the role of the technology scouting is twofold:

- Firstly, it identifies advances in science and technology that can be of use for the company. This activity might be directed (technology monitoring), i.e. searching in specific technological fields or undirected (technology scanning), i.e. searching for new technological opportunities in white spaces not yet covered in the technological scope of the company.

- Secondly, it facilitates or executes the sourcing of technology

The dual role of technology scouting also best describes the beginning of the research process in this study. From one side, the focus has been set on high oxygen barrier materials. From the other side, there was no set outcome for a particular finding, but rather an objective to create the encompassing portfolio of the emerging technologies on the market, not necessarily feasible to be applied to the company products at the current moment.

The standpoint of Rohrbeck was widely supported by range of authors, among them Shohet (2008):

> *"In a world where technology and product knowledge has become globally distributed, companies must also look outside their R&D departments for sources of new technology and innovation".*

Shohet has placed the technology scouting process as an essential and powerful tool that incorporated the elements of "open innovation". The latter is widely applied nowadays in wide range of companies, most notably IT enterprises.

One of the best explanations for open innovation process as applied on the bug company scale has been found in work of Järrehult (2011). He describes it as the favorable approach to the studies where the initial phase features the absence of strict limitations for research scope – so-called "fuzzy front end". The latter best characterizes the research position of the beginning of this study for Nutricia. Therefore, technology scouting process as integrating the parts of open innovation has been modelled by author of this paper, as demonstrated on Figure 7.

Apart from its importance in broadening of company knowledge portfolio, technology sourcing determines the successful transition to package specification and development phase, where the knowledge obtained during scouting is implemented into specific project. (Figure 4)

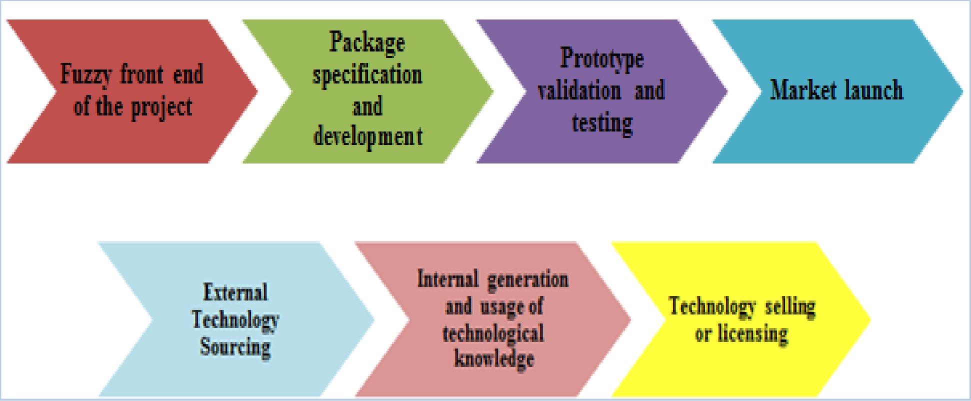


Figure 4. Technology scouting as part of R&D development project

Another core advantage of technology scouting is that it closely overlaps with technology intelligence and management of R&D packaging department, all of them being a part of innovation management process. As a result, it expands the network of companies with technologies of interest, as well as creates information database for other packaging development projects. The relationship between three components is `best illustrated by Harrison Hayes, as shown on Figure 5 (Harrison Hayes, n.d.).

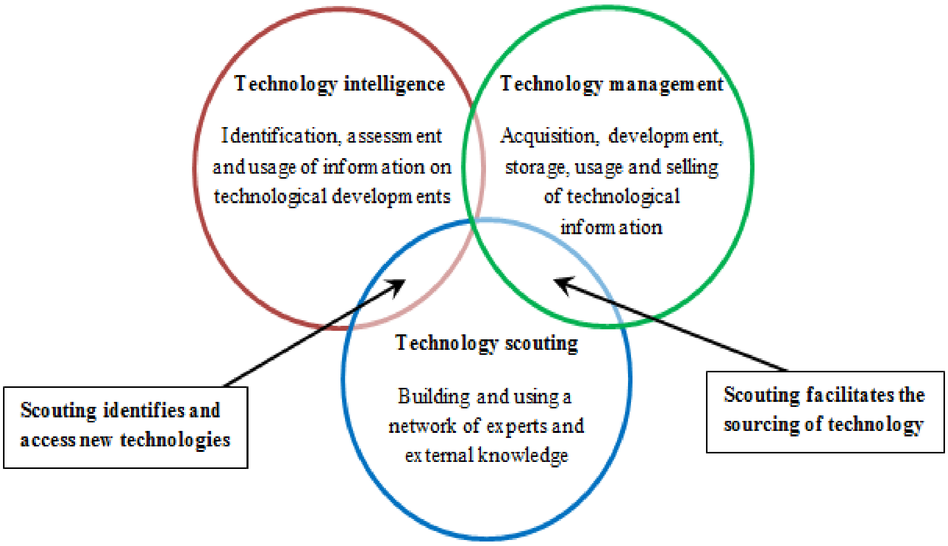


Figure 5. Place of technology scouting in innovation management process

The steps of the technology scouting process integrate the components of qualitative and quantitative research. It consisted of six steps as adapted from Reger (2001) and shown on Figure 6.

Figure 6. Steps in technology scouting process

These steps have formed the analytical framework for this research study, demonstrated in detail in the next section. Figure 7 will demonstrate the data collection and analysis flow as the determinants of the technology scouting evolution. Important to note is that data collection and analysis were not consecutive in nature but complimenting and overlapping one another.

Lastly, some of the study goals have led to a combination of technology scouting and scientific methods. While the technology scouting has covered both flexible and rigid packaging, the scientific method was applied only to rigid packaging (bottles) with the aim to evaluate the effect of material change on barrier performance (Section 4.2). The facilities of Nutricia Research and suppliers have allowed to design experimental studies in this regard.

Nonetheless, the further discussion on methodology will be dedicated to technology scouting process, as the experimental studies were also formed based on its findings.

2.2 Analytical framework

2.2.1 Establishment of the search criteria and selection of sources

The direction of technology scouting has to be built in accordance with the project objectives; therefore it was essential to establish the clear search criteria at the very beginning. It also allowed narrowing down the scope of scouting. As a consequence, the scouting was designed to meet the following attributes:

- **a.** Focus exclusively on polymeric materials, such as plastics. The only exclusion can be made for bio-based and/or biodegradable developments.
- **b.** Focus on the technologies and/or materials developed to meet high oxygen barrier requirements of food products
- **c.** Water barrier requirement of the studied technologies shall not fall below the limit established for selected Danone Nutricia products
- **d.** All of the findings must be already commercialized and available. However, the exclusion can be made for technologies of a particular relevance (ex. Biodegradable). Then, the latest stage of development is acceptable as well.

2.2.2 Data collection and analysis

The process of data collection and analysis is best expressed on the Figure 7.

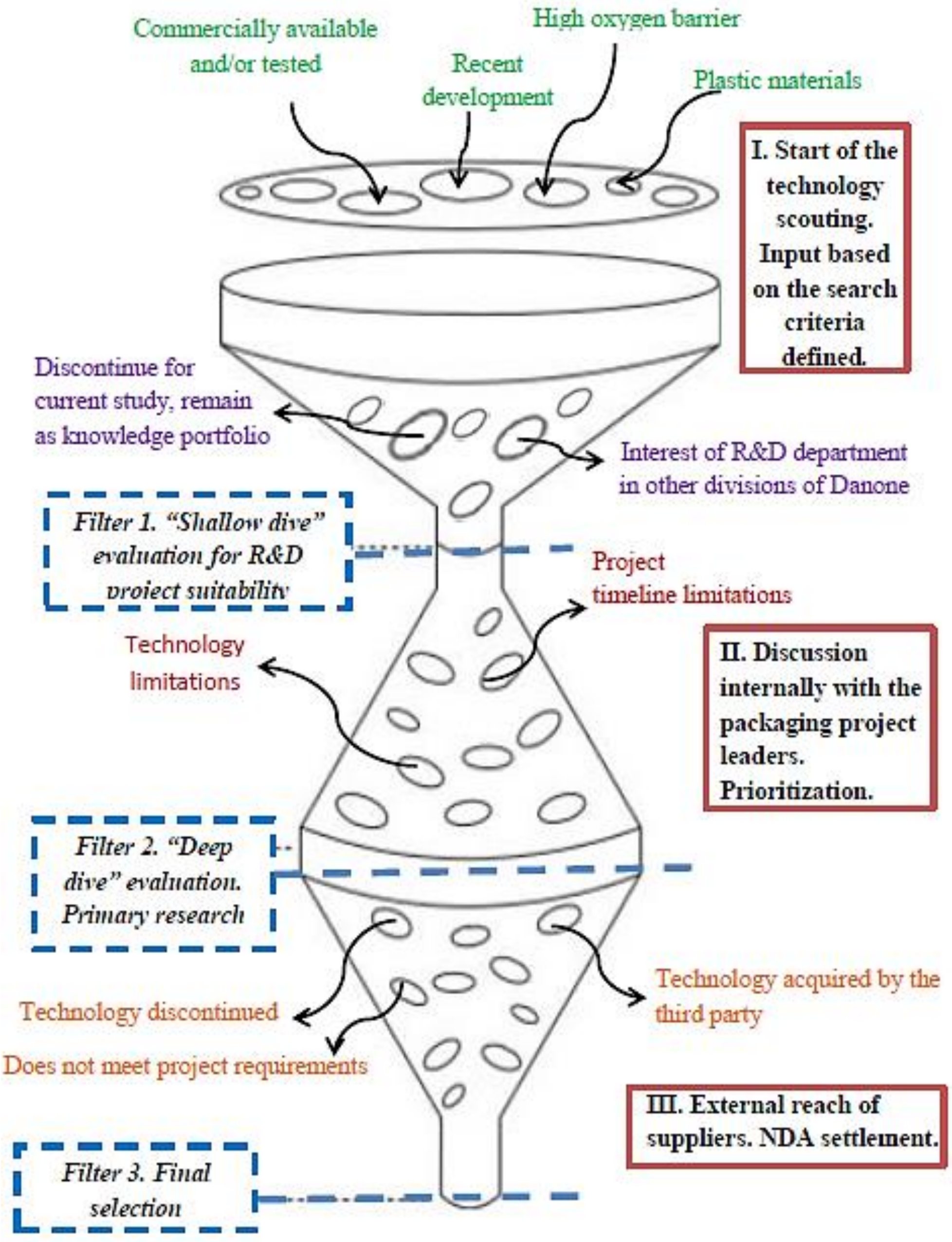


Figure 7. Evolution of technology scouting (Author's own figure)

After the focus of search has been identified, the next step was to select the sources of information. Those can be classified as secondary and primary. The secondary research was essential to understand the scope of developments in the area of interest. It included scientific reviews and publications, online information available from suppliers' websites (datasheets, product/technology description), publicly available patent database, packaging forums and magazines. The secondary research was followed by primary, the latter based on the information obtained from the suppliers via direct contact.

Every short listed technology had to be explored in deep details. The information available publicly was not sufficient to justify the technology fit to the packaging project of the company. Therefore, the suppliers of the technology have been approached directly via email, with the subsequent phone discussion. Based on the additional information obtained, the further meeting had been scheduled. Information not in the public domain can be obtained from technology owners and if external agencies can't disclose client details, non-disclosure agreements can help. This phase is so called "deep-dive". The general recommendation during this stage is to employ the scorecard approach to evaluate each technology competitively.

Nonetheless, due to the very early stage of this packaging development project, the evaluative criteria were limited. The reason is that the physical tests, such as sealing, drop test and etc., have to be performed in order to compare the performance competitively.

It leads to the only criteria considered such as:

- Comparative oxygen barrier performance
- Comparative water barrier performance
- Transparency of the material
- Suitability for retort applications

2.2.3 Secondary research

The very first and the crucial stage of the scouting were represented by secondary data gathering.

It is important to say, that the success of this stage has been determinative for the outcome of the technology scouting. The results of this technology scouting phase have been a fundament for any of the further steps to be undertaken in this study. The steps including but not limited to internal/external interviewees, evaluation and proposition of the options to be considered as an alternative to current packaging of Danone Nutricia products.

The exploratory objective of the study did not limit the search to a singular technology and/or material, allowing the collection across a vast scope of resources. As a result, it made the following stage of data analysis more efficient, as several options could be considered for one application and comparative evaluation would be more representative comparing to the case when only few search results were available. Also, as this technology scouting was commercial, the more companies offering the same technology/product are found the better it is for the project development. Firstly, it would allow creating suppliers' portfolio for company's knowledge; secondly it would allow to filter the suppliers based on convenience of geographic location and/or previous business contacts made.

2.2.4 Primary research

2.2.4.1 Internal interviews

Internal interviews were a necessary part of the **Phases I and II** of technology scouting. These interviews were preceded by the introductory team meeting, where the exploratory results of the technology scouting were presented briefly. It was followed by face-to-face meeting with R&D packaging team members, particularly those involved in Advanced Medical Nutrition projects. This approach has allowed to reach several objectives. Firstly, the author was able to understand the scope and phase of the projects she is going to be involved in. Especially, it clarified the understanding of how the initial scouting results can be matched to separate projects. For the interviewees, represented in its majority by packaging engineers and project leaders, these first meetings gave an opportunity to go in details on technology/materials presented during team meeting previously and to see the project fit. This kind of interviews is characterized by both sides acting as an interviewer and interviewee. The semi-structured way of interview was the only one relevant to apply, as it allowed much flexibility in course of discussion. First round of interviews has led to the filter Gate 1, due to the fact that the results were filtered according to the first suggestions.

On the subsequent phases of technology scouting, internal interviews remained a core element in analysis and selection of technologies for a further work.

Also, the internal discussions had to be extended beyond R&D Packaging Division of Danone Nutricia to R&D Product Development team. These round of interviews have happened later in the course of the project, after the winning technologies have been identified. For the purpose of theoretical evaluation of shelf-life of the products contained in package, it was necessary to understand its nature of interaction with initial oxygen in the package, as well as vitamins. This kind of information has helped to make a preliminary prediction of packaging effect on shelf-life.

2.2.4.2 External interviews

External interviews were conducted with the owners and /or suppliers and/or distributors of the technologies/products selected during the process of internal R&D discussion. Therefore, these interviews were conducted on the **Phase III** of the technology scouting where the "deep-dive" was needed to evaluate the relevancy and feasibility of technology if applied to the packaging development project.

Filter 2 (Figure 7) marks the initiation of external interviews. Important to notice that due to the proprietary nature of the technologies, no further information could be obtained without Danone Nutricia commencing the process of non-disclosure agreement (NDA) with external party. The process can be characterized by both benefits and disadvantages affecting the time efficiency of the project.

From one side, NDA is crucial to ensure the protection of proprietary data from both Danone Nutricia and external company, therefore no further progress can be made without its settlement. On the other hand, NDA process can take much longer than initially planned due to the negotiation with legal departments of both sides as the latter are most likely to change some parts of the agreement and it has to be mutually approved.

To understand the complexity of the process, the diagram below shows the steps in NDA settlement process. Time factors influencing the duration of the process are also illustrated. In this project, the time to secure NDA in order to start initial discussions ranged from 4 days to 3 weeks.

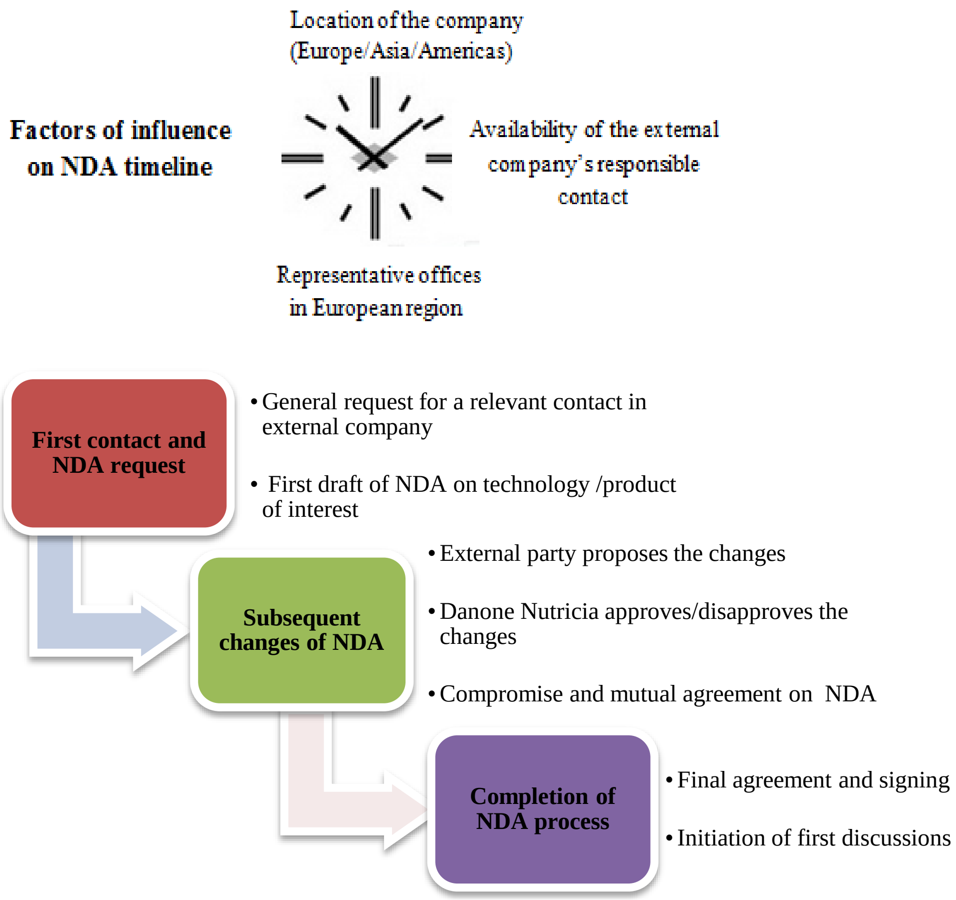


Figure 8. Factors of influence and steps in NDA process

Completion of NDA process marks the beginning of the external interviews that, in its turn, were structured in a way allowing to filter some of the technologies at the very beginning, without dedication much of time resource. For that purpose, interviews were designed in 2 rounds:

Interview via Telephone Conference. The objective is to understand the technology from the primary source and get the data on the latest tests from the supplier. It was often preceded by interviewee sending the general presentation of the company and the topic of discussion. These interviews were conducted in "talk-through" presentation approach. It was proven to be very efficient due to several reasons. Firstly, R&D team of Danone Nutricia and author were able to look through the material in advance and prepare the questions. Secondly, the interviewee could also design his/her "talk-through" presentation based on our degree of understanding.

Personal meeting with supplier at the facility of Danone Nutricia. This step allowed the supplier to introduce the technology/product in the most effective way - personal communication. Of course, this step was not deemed obligatory, as the geographic location in many ways justified the ability of supplier to visit Danone Nutricia R&D site in Netherlands. These types of interviews were complemented by the demonstration of samples from supplier's side and by sharing of the current packaging design from the side of Danone Nutricia. During the phone call, suppliers have introduced the "most-winning" concepts of the product. However, personal discussion has opened a gate to discuss some of the drawbacks of the product/technology. One of the advantages and disadvantages of the phone call is that it may give a distorted understanding of some nuances due to the absence of personal contact. Personal contact does not give the "virtual protection", all answers can be evaluated together with the degree of confidence and knowledge coming from supplier. Especially, when met with the specific questions from R&D packaging team. In this case, it was easy to see how truly the technology/product fits with the prioritized requirements identified by Nutricia. The last but not least, personal meeting helped to create the professional bond between Danone Nutricia R&D and the supplier, create the sense of shared commitment to the project. As truly emphasized by Farber (2004):

> *"Personal communication allows to pick up details you might otherwise miss via phone or videoconference, particularly via means of body language"*.

3. Theoretical framework

3.1 Definition of plastic barrier materials

Plastic polymers-based packaging is not showing any signs of slower growth. In effect, it continues to replace both metal and glass packaging. No surprise, as polymeric packaging offers the advantages of weight reduction, formability into useful and attractive shapes, reduced breakage, transparency, and cost savings. As have been mentioned earlier in the paper, different foodstuffs require various degrees of protection; therefore the importance of barrier polymers is rising.

What is the plastic barrier material for food packaging application?

In a nutshell, the barrier property of a plastic structure is the physical resistance that it opposes to the passage of any molecule or compound able to diffuse through the polymer: oxygen, carbon dioxide, water, and odors from air or headspace; flavors, aromas, and components from food; and external compounds contained either in secondary packages (e.g., corrugated boxes), board components (like vanillin and o-vanillin), or remains of solvents. In packaging design, it is very important to know the barrier characteristics of a package as it will directly affect the shelf-life of the product it contains. The barrier characteristics of the polymeric material relates mainly to its chemical structure. While polar hydrophilic polymers are good gas and organic vapor barriers when dry, their gas barrier drops in wet conditions (e.g., nylons and EVOH). Nonpolar polymers, e.g., polyolefins, are not affected by the presence of water, but they are not as good a barrier as the polar polymer, except against a polar water molecule itself. (Rotstein, Singh, Valentas, 1997)

Traditionally, the definition of a barrier polymer has been strongly attached to the oxygen permeability. Barrier polymers can be characterized by oxygen permeability less than about 1 cc*mil/100 in^2*day*atm that is equal to 19,7 cc*mm/m^2 *day*atm. Important to remember, that the definition of barrier material has to depend on the field of application, as polymers with higher oxygen permeability may still be an exceptional barrier to other molecules (such as water or CO_2) (Kim L.Y., 2009).

Out of the vast variety of plastic materials available for use in food packaging industry, two main categories can be identified:

- Passive barrier materials
- Active barrier materials

3.2 Passive barrier materials

3.2.1 Common passive barrier polymers

The protective function of packaging in case of passive barrier is obtained by the modifications of polymers morphology, structural arrangements and combinations of different materials, including blending of various polymers and coatings.

In passive barrier technologies, there is no occurrence of the interaction between the packaging and foodstuff.

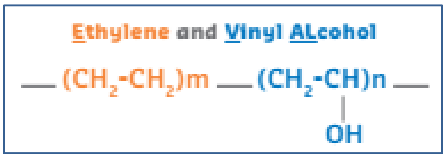
Generally, any of the new developments in the field of passive barriers are based on the commonly used plastics in food packaging. The Table 1, adopted from Lange and Wyser (2003) gives an understanding of barrier performance of widely used polymers.

Table 1. Permeability of polymers commonly used in packaging

Polymer	***Oxygen permeability 23^0C 50 or 0% RH [cm^3.mm/m^2.day.atm]***	***Water vapor permeability 23^0C 85% RH [g.mm/m^2.day]***
Polyethylene terephthalate (PET)	1-5	0.5-2
Polypropylene (PP)	50-100	0.2-0.4
Polyethylene (PE)	50-200	0.5-2
Polystyrene (PS)	100-150	1-4
Poly(vinyl chloride) (PVC)	2-8	1-2
Poly(ethylene naphthalate) (PEN)	0.5	0.7
Polyamide (PA)	0.1-1 (dry)	0.5-10
Poly(vinyl alcohol) (PVAL)	0.02 (dry)	30
Ethylene vinyl alcohol (EVOH)	0.001-0.01(dry)	1-3
Poly(vinylidene chloride) (PVDC)	0.01-0.3	0.1

3.2.2 EVOH as an oxygen barrier

EVOH has one of the lowest oxygen permeability reported among polymers commonly used in packaging. By chemical structure, EVOH is a semi-crystalline copolymer of ethylene and vinyl alcohol monomer units.



$$—(CH_2\text{-}CH_2)_m—(CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}})_n—$$

Figure 9. Chemical structure of EVOH

These two components are determining the sensitivity of EVOH to water and oxygen. Polyvinyl alcohol, or PVOH, one of the monomer units in EVOH, has exceptional gas barrier properties, but it is water soluble and difficult to process. On the other hand, polyethylene (PE), has good water resistance, but also has one of the poorest gas barrier properties. Copolymerization of monomer units based on PVOH and PE results in EVOH copolymers which have improved properties in terms of gas barrier, processability, and sensitivity to moisture (Mokwena and Tang, 2012).
The hydroxyl groups of PVOH that provide the high cohesivity between the polymer chains also make the copolymers very hydrophilic, so that in the presence of water or in high humidity environments, the structure of the material becomes plasticized and the barrier properties are greatly deteriorated. (Loapez-Rubio, 2011) It is best illustrated on Figure 10 below, adapted from EVAL Americas (n.d.)

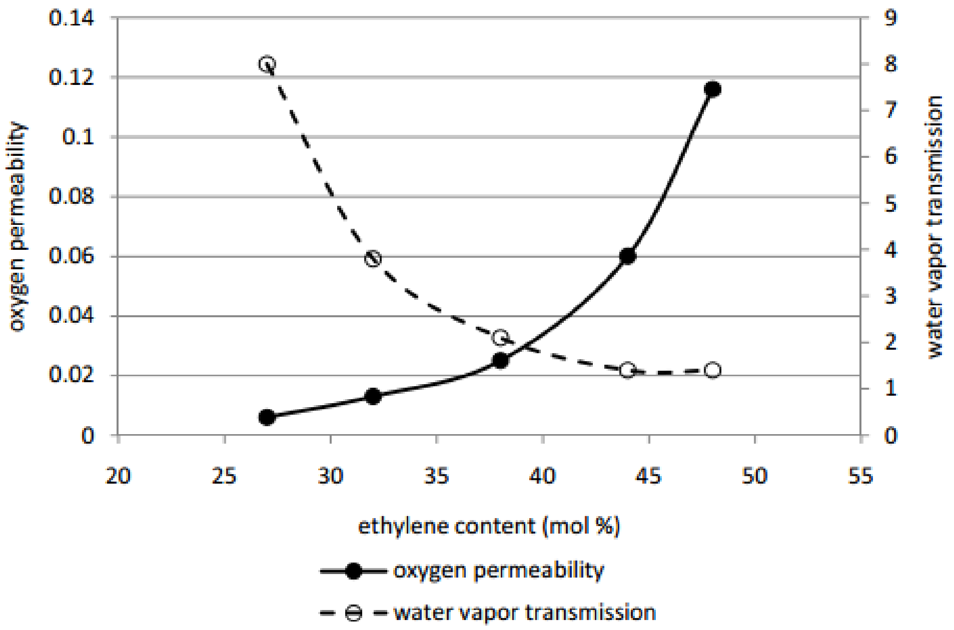


Figure 10. Oxygen permeability (cc mil/100 in2 day atm) and water vapor transmission (g mil/100 in2 day) as a function of ethylene content

The presence of hydrophilic group in EVOH also contributes to the fact that relative humidity of the environment strongly affects the oxygen permeability of the copolymer.

Due to its very low permeability to oxygen, EVOH is used in multilayer structures, where EVOH is “sandwiched” between the layers of water barrier polymer, such as polypropylene (PP).

Also, as its barrier strength varies depending on PVOH and PE content, suppliers offer numerous grades of EVOH, differing in its PE content in a range of 27 to 42 mol%. (73 to 52 mol% PVOH correspondingly).

Apart from that, the most recently introduced is the **EVAL™ AP (EVOH + oxygen scavenger)** grade that combines the oxygen barrier properties of EVOH with oxygen absorbing properties that prevent oxygen ingress. (EVAL, n.d.)

3.2.3 New developments in field of passive barrier materials

Secondary research phase of the technology scouting has resulted in big amount of information on barrier technologies/materials. For the purpose of comprehensive understanding, these finding were grouped by author of this study based on the principle of passive barrier applied.

As a result, 6 major groups have been identified and presented on Figure 11.

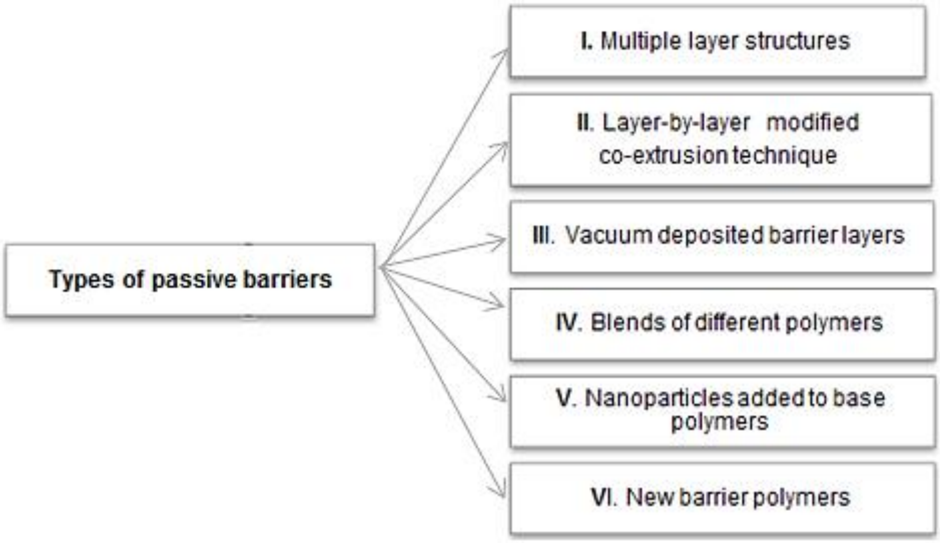


Figure 11. Types of passive barriers (author's own classification)

As can be seen from the Figure 11, the barrier materials are always a combination of few or more different polymers. It is justified by the fact that there is virtually no polymer on its own that can deliver the barrier performance both in oxygen and moisture.

In principle, a barrier function can be incorporated into a plastic-based packaging material in two different ways (Lange & Wyser, 2003):

- By adding a layer of barrier material
- By mixing the barrier material into the base polymer

3.2.3.1 Multiple layer structures

Multiple layer structures are the most common among the barrier materials for food packaging. Widely-used methods of creating multilayered structures are lamination or co-extrusion. For example, such polymers as ethylene vinyl alcohol (EVOH) or polyamide (PA) are good oxygen barriers only in the dry state, which means that they have to be sandwiched between water vapor barrier films in order to maintain their oxygen barrier function. The other preferable option for barrier materials is aluminum. The latter can also be applied via lamination in a form of a sheet in a few micrometer thickness on the base material, or being vacuumdeposited (the process called metallization) with a thickness in the nanometer range. An aluminum sheet provides a perfect barrier, whereas metalized layers may give almost as high barriers at a lower cost. The commonly used multiple structures for flexible packaging films are presented in Table 2, adapted from Lange and Wyser (2003)

Table 2. Barrier properties of common flexible packaging films. The number after each polymer is the layer thickness (mm)

* The polymer abbreviations are defined in Table 1.

Polymer*	***Oxygen transmission rate at 23^0C 50 % RH [$cm^3/m^2dayatm$]***	***Water vapor transmission rate at 23^0C 85% RH [g/m^2day]***
PET 12/Alu 9/PE 50	0	0
PET 12/Alu met./PE 50	1–2	0.1–0.5
PET 12/EVOH 5/PE 50	1	2–4
PET 12/PVAL 3/PE 50	2	4–6
PET 12/PE 50	15–20	4–6

While the conventional combinations for barrier properties of multilayered packaging structures are still dominating, there is a constant effort in search of better performing, yet environmentally neutral materials. Another trend is the avoidance of excessive packaging so that the strongest protection will be achieved with the minimum materials used. Few of the developments in this field are discussed further.

Companies on the market

Most of the developments in multilayer films are directed towards environmentally beneficial solutions. For example, weight reduction or biodegradability of the package. Most recent examples are given in Table 3. (Ecolean, 2015; Reynolds, 2012; BASF, n.d.)

Table 3. New multilayer materials

Company and technology	**Features**	**Known commercial application**
Ecolean AB Ecolean® Air Aseptic package	- “Light as air” packages with strong oxygen and water barrier performance. - Designed for ambient distribution and suitable	Dairy company in North-East China. According to the company, a package

based on based on Ecolean Calymer™ technology	for low and high acid aseptic products. - Multilayer structure of is presented by 8-layered material based on **Calymer** - a film comprising plastic (PE and PP) and calcium carbonate (40% by weight).	provides 1 year-long shelf life with no need of refrigeration.
BASF Compostable film based on Ecovio® polymer	- Film is comprised of six layers, including printing, barrier polymers and adhesive layer. - Based on combination of **Ecoflex® polymer (**made of fossil fuels) and polylactic acid (corn-based).	Not yet commercialized Was used for a "limited edition" of completely compostable peanut bag in USA.

3.2.3.2 Layer-by-layer (modified co-extrusion techniques)

The modified co-extrusion techniques have attracted lots of attention from research and industry, as it seems to be a next step on the market of barrier materials. In simple words, modified co-extrusion allows splitting the thicker polymer layer into several thinner which results in the increased barrier and mechanical performance. The benefits of layer-splitting techniques are as listed:

- "Plywood effect" - two-layer film will be stronger than a single-layer of the same overall thickness.

- Enhanced gas barrier. Barrier properties of a split-barrier-layer film will always be better than a co-ex film with a single barrier layer of the same material and same total thickness of barrier resin.

Why does the gas barrier improve? The explanation is that the energy required for O_2 penetration into the barrier layer is higher than the energy required for transmission through the barrier layer. Therefore, each interface enhances the barrier, resulting in a lower permeation rate.
The packaging industry interest in obvious, as this technique would allow increasing material barrier without adding material quantity. In its turn, it promises huge cost savings.

Companies on the market

The development in modified co-extrusion technology is progressing fast, with advances made from traditional 5, 7 and 9 – layers films to films composed of nano-layers. (Plastics Technology, 2012; Alpha Marathon, 2016)

Table 4. Companies with commercialized technologies for modified co-extrusion layer-splitting technique

Company and technology	Features	Known commercial application
Dual Spiral Systems Inc. Technology: Dual Spiral Systems (DSS) Extrusion Dies	Best suited for blown film, blow molding Alternative to foil lamination The system divides polymer flow from the extruder into two separate layers thus doubling the number of layers in the die. In this way, a 7-extruder die would in fact produce 14-layer film. Less expensive to produce than foil/coex structures Offers up to 32 layers split	Undisclosed processor in Southeastern Russia. Supplied DSS line: 10-layer, 10-extruder blown film system
Alpha Marathon Film Extrusion Technologies Inc. Alpha Glacier™ downward water cooled blown line with 200 layers NANO-DIE	Integrated with water cooling film blown line Offers up to 200 discrete NANO – layers Alternative to aluminum foil	Commercialized in China (details are not disclosed)

3.2.3.3 Thin barrier coating

It was already mentioned earlier in the report, that aluminum foil is being considered as almost perfect barrier and still widely used in food packaging. However, the performance of aluminum foil can be compromised when physical factors are applied. Also, it lacks transparency which is a desired feature for most of the food packaging. Most unfortunately, this material generates excessive waste and considered as “environmental evil”. As a result of a constant search for equally performing materials, thin barrier coatings applied on base polymer films are claiming to be as strong as aluminum foil, yet less sensitive to physical factors, lightweight and environmentally friendly.

Research results have revealed the growing popularity of barrier coatings and its intensifying competition with aluminum foil for high barrier applications.

Here four groups of coatings will be considered:

- Silicon oxide coatings
- Aluminum oxide coatings
- Organic coatings
- Inorganic/organic coatings

Silicon oxide coatings

Silicone oxide (SiOx), applied through physical vapor decomposition of SiO, or, plasma-enhanced chemical vapor deposition (PECVD) of gaseous organosilane and oxygen, on different base polymers, most often poly(ethylene terephthalate) (PET), polypropylene (PP) or PA.

Advantages of SiOx films over aluminum foil or aluminum metallized films lie in transparency, retortability, as well as water-resistance. The barrier performance is compared to this of metallized films.

Silicone oxide coatings are extremely thin, as less as 0, 04 micron. Yet, the barrier provided is superior to that of PVDC, EVOH and vacuum metallized films. Some research claims that silica coated films are not affected by moisture or temperature. The thickness of the coating is a strictly regulated factor that influences the barrier performance. If is thickness increases 0,1 micron, the SiOx coated film exhibits limited crack and flex resistance. (Strupinsky., G., Brody., A., L., 1998)

There are numerous companies that offer silicone oxide coated materials applicable for both flexible and rigid packaging. Some of the most prominent and widely known are discussed here.

Companies on the market

The companies that offer this kind of technology are commonly specializing either in flexible packaging or in rigid packaging. In flexible packaging, SiOx can be applied on different substrates, such as PET, PA and PP. However, in rigid packaging the focus in on PET bottle predominantly. The reason is that food packaging is undergoing a transition from glass containers to more economically and environmentally sustainable plastics. Due to its glass-like appearance and mechanical strength, PET is often predicted to be the alternative to glass packaging. PET bottles coated with SiOx can offer a barrier even for long-shelf-life oxygen sensitive foods. The most notable developments of SiOx coating for films and PET bottles are presented in Table 5. (Mitsubishi, 2015; Mitsubishi, n.d.; Amcor, n.d.; KHS, 2011; KHS, 2015; Chadwick.,P, 2014; Greiner Packaging, 2015; Plastics, 2014; Sayers Publishing Group, 2015; Toyo Seikan, n.d)

Table 5. Companies with commercialized technologies for SiOx coating

SiOx coated materials for flexible packaging		
Company and technology	***Features***	***Packaging type***
Amcor Ceramis® High Barrier OPP For extremely sensitive oxygen foods	OTR: less than **0.1 cm^3 * 18 µm /m^2 24h bar** (23°C, 50% RH) WVTR: less than 0.1 (23°C, 85% RH) Non-SiOx coated side is sealable to PE and PP substrates	- \ - FFS (form-firm-seal) packs - Pre-made pouch applications
Mitsubishi Techbarrier™ SiOx coated films **Techbarrier™ T, TX**	OPET base, retortable Before retort: OTR **0.3-0.5 cm^3/m^2 24 h atm** WVTR **0.3 g/m^2 24 h** After retort: OTR 0.5-2 **cm^3/m^2 24 h atm** WVTR 0.5-1 **g/m^2 24 h**	Flat and stand-up pouches, lid films, primary bag for enteral nutrition
Techbarrier™ NR	OPA base, retortable Before retort: OTR **0.5 cm^3/m^2 24 h atm** WVTR **0.7 g/m^2 24 h** **After retort:** OTR **0.5 -1.5 cm^3/m^2 24 h atm** WVTR **0.7-2.2 g/m^2 24 h**	Packages for enteral nutrition Stand-up pouch for beverage
TECHBARRIER™ LS (specially	Substrate is confidential Before retort:	Retort food packaging

developed for retort applications, January 2015)	OTR **0.1 cm^3/m^2 24 h atm** at 25 ^{0}C, 80% RH WVTR **0.1 g/m^2 24h** at 40°C, 90% RH After retort: OTR 0.2 **cm^3/m^2 24 h atm** at 25 ^{0}C, 80% RH WVTR 0.3 g/(m^2 24h at 40°C, 90% RH	with a longer shelf-life
SiOx coated materials for flexible packaging		
KHS Plasmax GmbH InnoPET Plasmax barrier coating	Introduced for wine (Bronco Wine together with Amcor Packaging) Fully recyclable Transparent Ultra-thin SiOx coating of 0.0001 mm	PET bottles for beer, wine, juice
Waldorf Technik GmbH 3D barrier Cavonium®-coating	Designed to be installed in line with EVOH injection molding machine This technology helps to avoid the need for multilayered EVOH structures SiOx coating decreases the susceptibility of EVOH to moisture and temperature, as well as providing barrier to scalping and leaching	Injection molded EVOH containers (99 mm diameter cup) Introduced in Europe for almost a year for cream cheese, salads and jams
Greiner Packaging **Inert Barrier Technology**	- Increases oxygen barrier by 20 times for PP and by 30 times for PP - Barrier material is not sensitive to fluctuations in temperature and humidity - Coated packaging can simply be ground up and recycled	PP yogurt cups
Toyo Seikan SiBARD (SiOx Barrier-layer Development) for PET bottles	- Ultra-thin SiOx coating of 10-20 nm on PET bottle wall - Enhanced barrier to gases - Fully recyclable	PET bottles for beverages

Aluminum oxide coatings

Similar to silicone oxide coatings, aluminum oxide coating are presenting a viable alternative to aluminum foil. Aluminum oxide (AlOx) barrier coating is produced using industrial ‘boat-type’ roll-to-roll vacuum web coaters used for aluminum metallization process. The difference is that the latter can be modified by the injection of oxygen into the aluminum vapor in order to deposit a transparent aluminum oxide barrier layer. The use of such large scale and high speed coating equipment can potentially provide vast economic and environmental benefits, which is of great importance for the cost sensitive food packaging market. Also, AlOx coated films are cheaper when compared to SiOx coated films that makes it very attractive for the market, especially if performance is as strong as SiOx coated film. (suppliers’ data)

However, the evaluations of cost-savings while using AlOx shall be well grounded and take into account other numerous influencing factors. For example, SiOx coatings can be applied to a wide range of polymers, such as PVA, oPP, oPA and PET. As pointed out in a research by C.F. Struller et al. (2014), in case of AlOx coating, only polyethylene terephthalate can provide the reliable barrier properties against water vapor and oxygen. Other cheaper barrier polymers such as biaxially oriented polypropylene (BOPP) have proven to be rather a difficult substrate material.

Therefore, the careful examination is needed when jumping to the conclusion of cost benefit of AlOx versus SiOx.

Important to remember that in both cases, a further conversion step required after coating, in order to obtain the final packaging structure. This is either achieved by laminating the vacuum coated films (adhesive lamination, extrusion lamination) or via application of an additional polymer coating on top of the inorganic layer, both serving the purpose of protecting the thin barrier layer during its final packaging application. It also adds cost depending on the adhesive used etc.

Companies on the market

Concentrated primarily on flexible packaging, no mentions on the developments of rigid packaging with AlOx coating has been found. (Toppan Printing., n.d.)

Table 6. Companies with commercialized technologies for AlOx coating

Company and technology	**Features**	**Packaging type**
Toppan Printing **GL transparent barrier film** 1. High Barrier Grade (GX-P-F) 2. General Grade (GL-AE) 3. Retortable grade (GL-RD)	1. OTR: **0.1 cm^3 /m^2 24h atm** (30°C, 70% RH); WVTR: 0,05 (40°C, 90% RH) 2. OTR: **0.2 cm^3 /m^2 24h atm** (30°C, 70% RH); WVTR: 0,6 (40°C, 90% RH) 3. OTR: **0.1 cm^3 /m^2 24h atm** (30°C, 70% RH); WVTR: 0,2 (40°C, 90% RH)	- Retort food packaging – flat and stand-up pouches

Organic coatings

Hydrocarbon film coatings

Another development on the field of barrier coating is hydrocarbon film coatings. Comparing to inorganic aluminum or silica, hydrocarbon is an organic compound consisting entirely of hydrogen and carbon. The process of PECVD (plasma-enhanced chemical vapor deposition) allows to deposit hydrocarbon (HC) films on different substrates. However, while SiOx and AlOx coatings have been competing in the niche of flexible packaging, hydrocarbon coating is primarily focused on rigid packaging. (Packaging Network, n.d.; Sidel, n.d; Mitsubishi, 2012; Mitsubishi, 2015)

Table 7. Hydrocarbon Plasma Coatings

Company and technology	**Features**	**Packaging type**
Sidel (Part of Tetra-Laval Group) Actis™ gas-barrier technology.	- Application of hydrogenated amorphous carbon (layer thickness layer of 0.1 micron) on the inner wall of the single-layered PET bottles - 3mg of hydrocarbon is used to treat 500 ml bottle	Was implemented for PET bottles for beer
Mitsubishi DLC coating	Depending on bottle size, the oxygen permeability of PET can be reduced from 15 to 30 times	Introduced for PET bottles for tea, carbonated drinks, wine, sake and beer.

Poly-acrylic acid organic coating

Particular attention in this category must be given to the development of Kureha Chemical Industry – BESELA transparent barrier film with organic coating. What really make it to stand out of other developments, is that the coating is presented by the modified poly-acrylic acid (PLA) on PET base film. The organic mature of the coating gives the film superior flexibility and abuse resistance. More than that, the organic nature of the coating causes the cross-linking during retort conditions, therefore strengthening the oxygen barrier, while conventional barrier materials such as EVOH are negatively impacted by retort treatment with the subsequent drop in barrier strength.

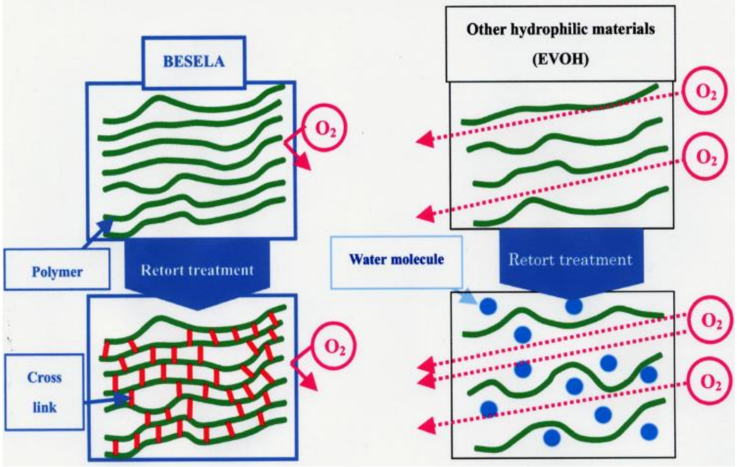


Figure 12. BESELA barrier before and after retort

The above-mentioned quality makes BESELA very attractive material for retort, boil and microwave applications. (http://www.abre.org.br/esp/wp-content/uploads/2012/07/secaoE.pdf, n.d.)

Organic/Inorganic coating

Though the development described in this section is yet to be tested on a large scale before its possible commercialization, it is definitely taking a lot of attention from both academia and industry. It is especially attractive if consider its environmental benefits. This development is called bioOrmocer and belongs to Fraunhofer ISC Institute, one of the members of a consortium of researchers who are collaborating within an EU project called DibbioPack. Fraunhofer has been developing hybrid polymers called ORMOCER for the past 20 years, resulting in a development of a biobased type of ORMORCER which is both biodegradable and compostable. bioOrmocers is a product of chemically modified biopolymers such as chitosan and cellulose, bonded to an inorganic scaffold of silicon dioxide, which provides the required barrier properties. While the rest of the ingredients used this scaffold does not biodegrade, only tiny remnants of silicon remain after bio-degradation. Additionally, bioOrmocer demonstrated the antimicrobial activity, achieved by the addition of antimicrobial agents within the matrix of a coating material. (BioPlastics, 2015; Dibbiopack (n.d.))

3.2.3.4 Polymer Blends

As an approach in passive barrier technology, blending of the polymers is still remaining in its initial phase. Though several commercial solutions are used, this technique implies the difficulty of the compatibilization between various polymers, which can lead to an unwanted result. However, this technology remains in a strong focus particularly due to the fact that it allows to produce barrier materials using only limited amounts of the often expensive barrier polymer in an inexpensive matrix material. The ultimate goal while blending is to create as tortuous path for gases as possible, so to prevent its permeation through packaging.

Lange and Wyser (2003) point the key advantages of blending to consider when applying for the development of packaging materials, such as:

- Blending is less complicated and therefore a less costly technology than e.g. co-extrusion and co-injection
- In some cases, synergies arise and the blend obtains improved properties over its separate components (stronger oxygen barrier, etc.)

At the same time, they warn of an equally pronounced drawbacks, including:

- Blends are as difficult to recycle as layered materials.
- The barrier properties will be strongly influenced by the morphology, which is directly dependent of the degree of the compatibility between different polymers

Polyamide Blends

Commercially, amorphous polyamide (PA) blends with polyamide-6 (PA-6) blends with various grades are used by various packaging film fabricators. Apart from blends of amorphous polyamides with PA-6, similar blends of poly(m-xylylene adipamide) (MXD6) with PA-6 have also been used as barrier films, such as by Mitsubishi Gas Chemical. (Dupont, 2005; Grivory EMS, 2005; Mitsubishi Gas Chemicals, n.d)

Table 8. Polyamides for blending applications with other polymers

Company and product	**Features**	**Processing techniques**	**Packaging applications**
DuPont Selar® PA 3426 Selar® PA 2072	Designed to be blended with Nylon-6 Particularly useful for application in refrigerated conditions Performs better than Nylon-6 at higher humidities Specially designed for blending with EVOH (up to 40 wt% addition) Provides better adhesion in blends with EVOH than other grades of amorphous nylon, thus allowing to employ less expensive adhesives in tie layers.	Can be processed on conventional extrusion, coextrusion, injection-molding or blow-molding equipment that is designed to process nylon or polyolefin resins.	Both flexible and rigid packaging structures
EMS Chemie Grivory Grivory G21	Improved gas and aroma barrier at elevated temperatures: OTR (23^0C, 0% RH, 50 µm film thickness): **30 cm^3 /m^2 24 h atm** OTR (23^0C, 85% RH,50 µm film thickness): **10 cm^3/m^2 24 h atm** WVTR (23^0C, 85% RH, 50 µm film thickness): **7 g/m^2 24 h**	Injection Molding, Extrusion - cast film, Extrusion - blow molding, Blown Film Extrusion	Co-extruded blown film, mono or coex cast film and coextruded tubes Additive for polyamide 6 and different opolyamides to improve film properties.
Mitsubishi PA - MXD6	Film is characterized by better oxygen barrier performance compared to EVOH film, starting from Very well suitable for lamination of PET bottles, as well as blending in with PET bottles	Can be used in combination with polyethylene terephthalate (PET), polypropylene (PP), or polyethylene (PE) to achieve co-injection molding and coextrusion molding	Laminated containers Bottles Packaging sheets.

3.2.3.5 Nanocomposite technology

The presence of nanoparticles in the polymer matrix materials improves the packaging properties of the polymer flexibility, gas-barrier properties, temperature/moisture stability. Nanoparticles, well dispersed in polymer matrix, create a tortuous path for gases to penetrate the package wall, thus inhibiting their permeability.

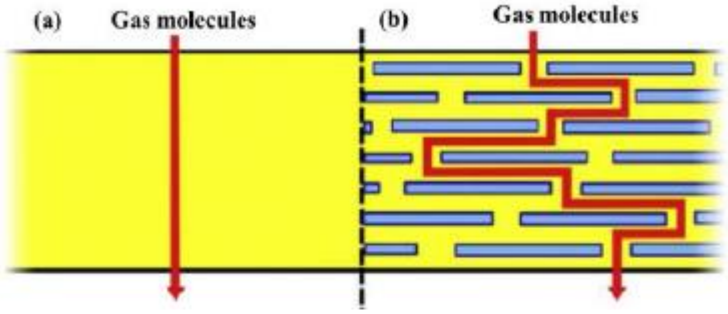


Figure 13. Effect of nanoparticles on gas permeation through polymeric packaging

Nanocomposites can be applied either by blending in with polymer or as a component of the coating. In either case, the barrier properties are improving considerably. (Nanocor, n.d.; SpecialChem., 2012; Nanolock, n.d)

Table 9. Developments in nano-composite technology

Nanocomposites blended in with polymer		
Company and technology	**Features**	**Known commercial application**
Nanocor	Nanoclays are dispersed into polyamide MXD6 Barrier improvement is universal for all permeating gases and the improvement is seen across a broad range of relative humidities.	Said to be applied widely in food companies, but list of customers is confidential
Imperm® 103	Designed specifically for multilayer PET bottles. Compared to EVOH, this grade demonstrates considerably better barrier at humidities exceeding 80%.	
Imperm® 105	Designed for multilayer films/sheet in combination with PE, PP, PET, Nylon and other typical matrix resins	

NanoBioMatters O_2Block® Barrier	- Surface-modified organoclay additives based on a selection of layered minerals (phyllosilicates) and food contact approved surface modification systems. - Barrier performance was claimed to be doubled at 90% RH by adding 4 % of O2Block® Barrier within a 5 micron of EVOH. However, the company has discontinued this technology and transferred the rights to other company (confidential).	It was expected that O2 Block will be used in Soarnol NC7003, a fully formulated grade based on 29% ethylene content EVOH, but currently the status is unknown
Nanocomposite coatings		
Inmat Inc Nanolok coatings	- Aqueous suspension of nanodispersed silicates in a polymer matrix. - Applied via roll (or dip, or spray) coating process onto a polyester film or other substrate. - Forms a very thin coating (0.25-2 microns) of Nanolok^{TM} on the substrate. - Coatings are transparent, thus useful for see-through packaging applications. - Highly cost-effective: approximately 1-2 microns of Nanolok^{TM} coating can replace 12 microns of EVOH to achieve the same level of oxygen barrier.	Said to be applied in food packaging industry, customers are undisclosed

3.2.3.6 Barrier resins with the unknown development status

The barrier polymer put in this group is liquid crystal polymers (LCPs). Though the results of technology scouting have not found any signs of the continuation of its application in the field of food packaging, there were numerous related mentions previously. In particular, related to its outstanding performance as oxygen and moisture barrier, performing equally to aluminum barrier.

Liquid crystal polymers (LCPs) are a class of aromatic polymers. They can be processed on the conventional film equipment, forming uniform and pin-hole free barrier layers with excellent clarity. It can be used at 2 to 5 micron thickness in

multilayer structures that is up to 10 times thinner than EVOH-based film with the same level of oxygen barrier performance (at 90% relative humidity). (Braun, 2003)
One of the companies that have featured liquid crystal polymers as applied to food packaging was Suprex Polymers Inc. As the results of the scouting have shown Suprex Polymers Inc. was subsidiary of Foster-Miller, which in 2004 changed to QinetiQ North America. Currently there was no information found on LCPs related development at this company. (Advanced polymers for practical use, n.d.).
Other company, still developing LCPs though not for food related purposes is Celanese, previously known as Ticona. Trademarks of the company for LCP is known as such as Vectra®. Several grades of LCP is approved for food contact and the company brochure has stated that these are numerous applications of LCP for food packaging. However, there was no proof found of any food packaging related application apart from medical equipment and electronics. (Vectra Ticona, n.d.)

While there is no clear indication whether LCPs are being developed for food packaging, the research suggests that the attempts were made and the “renaissance” of LCP can be potentially expected.

3.2.4 Summary of passive barrier technologies

For the purpose of comparative graphical understanding of barrier properties, the OTR and WVTR values of passive oxygen barrier materials (where available) have been presented on Figure 14. As have been mentioned earlier, oxygen and moisture permeability are dependent on the thickness of the material, as well as the external conditions such as temperature and humidity. For the purpose of correct representation of the data, all OTR and WVTR values have been calculated with following parameters:

- Thickness of 25 micrometers
- 23°C and 50% RH for OTR
- and 40°C and 90% RH for WVTR

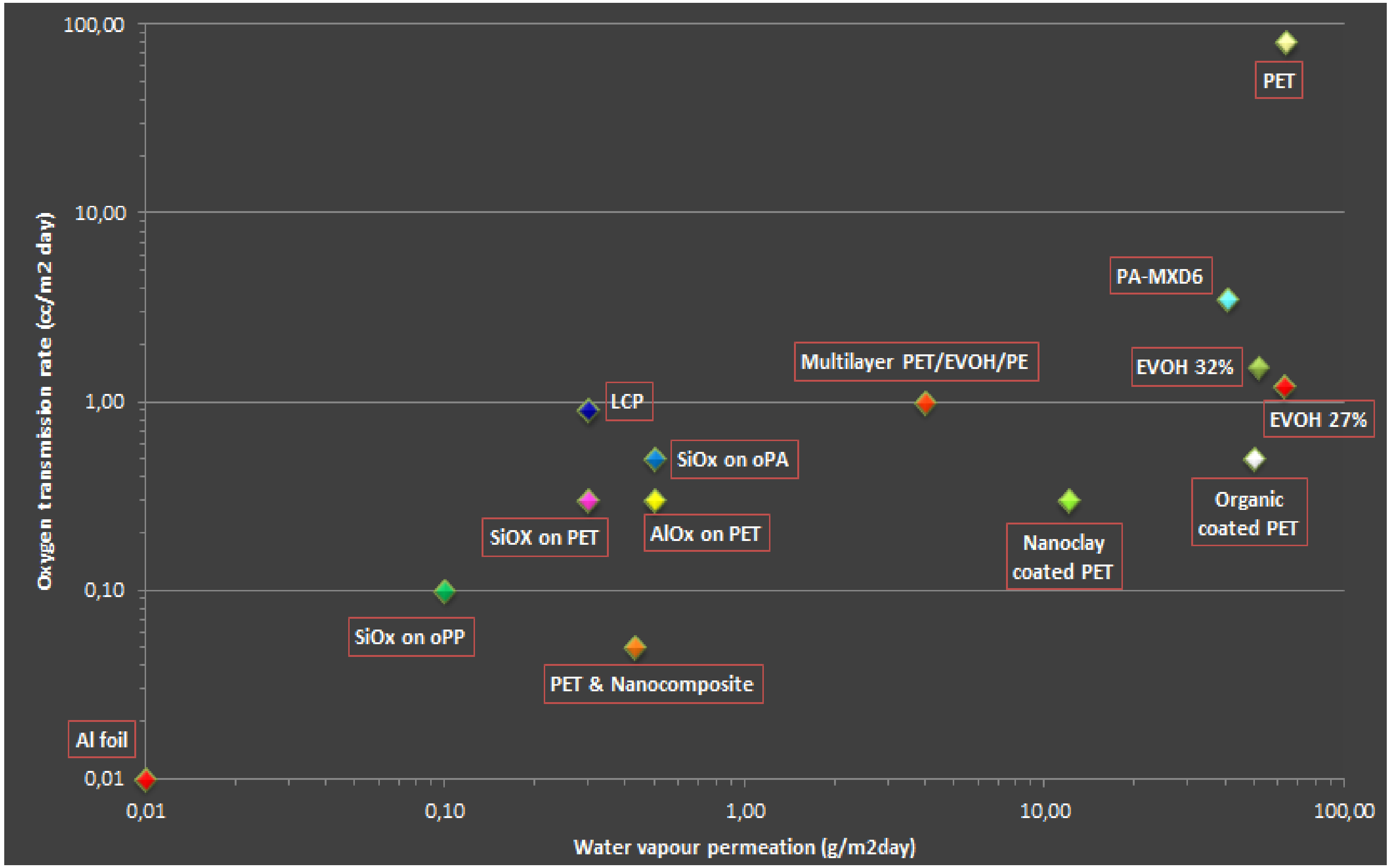


Figure 14. Comparative OTR and WVTR of selected barrier materials

3.3 Active barrier technologies

Active packaging implies that the components of the packaging material will interact with the components of the product inside the package for the purpose of preventing the deteriorative reactions resulting in the loss of product quality. Inhibition of lipid oxidation with antioxidant agents or active packaging is of great importance in protecting foodstuffs with high amounts of unsaturated fatty acids from possible quality deterioration and providing the required shelf life. (Rooney, 2005)
Broadly speaking, oxygen scavenging packaging mechanism can be based on two principles:

- Sachets and pads placed directly into the packaging, containing the components (ex. iron, which absorbs the air). This is an example of external body placed in the package.

- Active ingredients incorporated into packaging material, so the material can release active compounds at controlled rates suitable for reducing the oxidation process in a wide range of foods.

As the food security talks progress, more and more preference is given to the second type of active packaging, where the active components form a part of the packaging material. It helps to minimize the risk of food being contaminated by the components of external agents, such as pads and sachets.
Another option to get rid of the excessive oxygen can be the use of evacuation and inert-gas flushing, such as N_2. However, even after flushing, the residual oxygen remaining after mechanical packaging operation might have the chance to initiate oxidation. (Lee, 2014)
Technology scouting has identified three most noticeable among the commercialized active oxygen scavenging barriers, as shown on Figure 15.

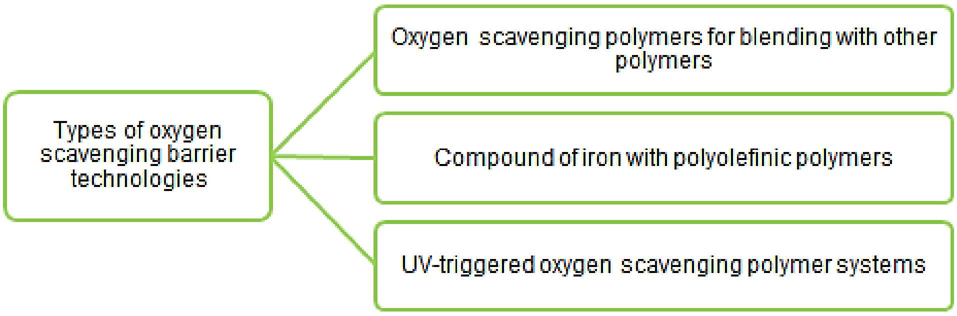


Figure 15. Types of oxygen barrier technologies

3.3.1 Polymers blends with oxygen scavenging properties

Several companies have registered trademarks of polymer blends that exhibit oxygen scavenging activity. As by definition of an active packaging given previously, so the oxygen-scavenging polymer is a polymer that is capable of reacting with the oxygen from air, under ambient conditions and at a controlled rate.

Much interest is given to the development of scavenging polymer systems useful for blending with PET as the latter is considered as a feasible alternative to glass packaging in future. Therefore, there is a need for an improvement of its gas barrier properties. The commercially important oxygen-scavenging polymer systems useful for blending with PET are based on oxidizable olefinic polymers such as a polybutadiene (PBD) block or graft copolymers, oxidizable polyamides, such as PA-MXD6, or oxidizable aliphatic polyether copolymers such as PTMG-b-PET. For the purpose of oxygen scavenging in PET bottles, these oxidizable polymers are always used in combination with a cobalt salt (Co^{2+}) as catalyst, at a level of 50–200 ppm of cobalt. (Akkapeddi., 2014; Honeywell.,2006; (ColorMatrix, n.d.)

Table 10. PA based blends with oxygen-scavenging properties

Company and trademark	***Blend composition and oxygen scavenger***	***Features***	***Packaging type and applications***
Honeywell Aegis® OXCE resin	PA6 or PA6-nanocomposite (ca. 2 % nanoclay, acts as a passive barrier) blended with PA6I/6T and functionalized polybutadiene (PBD, oxygen scavenger) and cobalt catalyst (oxygen scavenger) **Oxidizable polymer:** PBD-g-PA6 + PA6I/6T blend **Catalyst:** Co^{2+}	Recommended ratio in polymers: **5% to 8%** Aegis® for most applications.	- Specifically designed for multilayer co-injection stretch blow-molded PET bottles - Suitable for extrusion molding applications. - Juices and beer packaging, other oxygen-sensitive food and beverages.

Table 11. PBD-b-PET copolymer-based blends with oxygen-scavenging properties

Company and trademark	**Blend composition and oxygen scavenger**	**Features**	**Packaging type and a processing**
PolyOne Corp. Amosorb^{TM} Amosorb^{TM} Plus	PBD-PET block copolymer with cobalt catalyst **Oxidizable polymer:** PBD-PET block copolymer **Catalyst:** Co^{2+}	Used at 1–5 wt% to blend with PET Shelf-life target 6-12 months for non-carbonated beverages	Injection-stretch blow molded PET bottles Suitable with any of PET base resin Suitable for mono-layer and multi-layer containers as well as thermoformed sheet applications Bottles must be filled fresh as molded, as the scavenging activity deteriorates with time
PolyOne Corp. Amosorb^{TM} SolO$_2$	Blend of PBD-b-PET with PA-MXD6	Used at 2–3 wt% to blend with PET Shelf life target 9-18 months for non-carbonated beverages	

PA-MXD6 is an oxidizable polyamide because of the reactive benzylic groups in its structure. The PA-MXD6-Cobalt catalyst-based oxygen scavenger system was initially commercialized in multilayer, barrier PET bottles. However, because of the cost of multilayer co-injection equipment, there has been a significant interest in recent years for developing monolayer barrier PET containers based on PET/PA-MXD6 blends. (Akkappeddi, 2014; M&G Poliprotect,2013; Solovyov, 2008; Wikiinvest,n.d.; Packworld., n.d.)

Table 12. PET/PA-MXD6 Oxygen-Scavenging Blends

Company and trademark	Blend composition and oxygen scavenger	Features	Packaging type and a processing
M&G USA Corp. PoliProtect™ APB	**Oxidizable polymer:** PA-MXD6 **Catalyst:** Co^{2+}	Combines active oxygen scavenger and a passive barrier. The passive barrier is protected via BicoPET™ technology, which incorporates the passive barrier into the core compartment of the pellets.	Injection molding Stretch blow molding Monolayer barrier PET, Packaging of O_2 or CO_2 sensitive foods and drinks and carbonated liquids
Invista Corp.	**Oxidizable polymer:** PA-MXD6 **Catalyst:** Co^{2+}	Provides exceptional oxygen and good carbon dioxide barrier	Blends can be processed on standard PET preform and bottle manufacturing equipment.

3.3.2 Compound of iron with polyolefinic polymers

Initially, iron was used as an oxygen scavenger in package inserts. Its success has encouraged a further research into the potential use of iron in plastic-based compositions. In the early 1990s, several companies launched products based on compounds of iron with polyolefin polymers. These were launched in Japan (Toyo Seikan's Oxyguard) and the USA (Amoco Chemicals' Amosorb 1000 and 2000). The latter became Shelfplus when bought by Ciba Specialty Chemicals.

These resins are extrudable under normal conditions of temperature and used in oxygen-barrier laminations to packages. (Han, 2005)

Table 13. Iron based polyolefinic oxygen scavengers

Company	**Nature of Oxygen Scavenger**	**Features**	**Packaging type and a processing**
ALBIS PLASTIC GmbH Shelfplus® O_2 2710 Shelfplus® O_2 2600 Shelfplus® O_2 3200	**Compound of iron with polyolefin polymers** **Base Polymer:** PP **For use** in PP, PE **Base Polymer:** PE **For use** in PP, PE	Additive batch with oxygen scavenging properties **Maximum O_2 absorption:** 35 cm^3 O_2/first 7 days/1 gram Shelfplus® O_2 Can be adjusted to suit the individual needs. Absorbs the oxygen in the: -Packaging head section -Product itself. In addition, it reduces the extent to which oxygen penetrates the packaging.	It can be integrated into the established production processes. Can be used: Flexible foils Sealed covers Rigid packaging Caps and closures
Toyo Seikan Co., Ltd. Oxyguard	Compound of iron with polyolefin polymers	Film with an oxygen absorbing a property is built into the inside of the barrier foil to absorb residual oxygen in the pouch.	Oxygen-barrier laminations to packages.

3.3.3 UV-triggered oxygen scavenging polymer systems

This technology includes the example of one of the pioneers on the market of oxygen-scavenging technology, Sealed Air. The novelty of this process lies in its apparent "tasteless" achievement of oxygen removal. (Han, 2005; Cryovac OS Systems., n.d.; Brody., Strupinsky., Kline., 2001)

Table 14. UV-triggered oxygen scavenging polymer systems

Company	**Nature of oxygen scavenger**	**Features**	**Packaging type and a processing**
Sealed Air (has acquired Chevron Phillips Chemical Co.'s oxygen scavenging (OS) business) Cryovac® OS films - rapid headspace	Autoxidation of unsaturated groups on a polymer Oxidizable part: Cyclohexene (C_6H_{10}) side group bound to the polymer backbone	Scavenging activity is UV activated "on-demand" at the processor´s packaging line **Oxygen scavenging capacity:** Achieving less than ...1% oxygen levels in 3-10 days. Ranged from 45 to 70 ml of O_2/gram of OSP	Available as rollstock, can be used as heat sealing lidding film on thermoformed packages, trays, bowls, cups and tubs.

Cryovac oxygen scavenging system is comprised of two components, where 90% of the blend is the oxidizable ethylene methyl acrylate cyclohexane methyl acrylate (EMCM) resin. The remaining 10% is a concentrate that contains the proper ratio of photoinitiator plus a cobalt salt (transition metal catalyst).

These two resins will be incorporated into a multilayer structure containing the OSP as an individual layer between a passive oxygen barrier, such as nylon, EVOH, or PET, and an inside sealant layer, such as LDPE, LLDPE, or ionomers. At the time of packaging, the OSP layer is exposed to sufficient UV radiation to trigger the scavenging mechanism. Once the package is sealed, oxygen within the package would begin to be absorbed and fugitive oxygen would be absorbed as well. The number of cyclohexene pendant groups attached to the polymer chain determines the scavenging capacity. (Brody., Strupinsky., Kline., 2001)

4. Results and discussion

Before this section, the results of the research have been summarized as the summary of findings on the latest development in field of passive and active barrier technologies. As have been already emphasized by the author, these findings provided a skeleton for the further steps of the project. Secondary findings were evaluated competitively against each other, as well as by their relevance to the current packaging development projects at Nutricia Research. These projects are connected with two main packaging solutions used for Danone Nutricia range of products, that is:

- rigid packaging (bottle)
- flexible packaging (pouches)

Therefore, the study described in this paper covered the investigation and evaluation of barrier materials/technologies as applied to the above-mentioned packaging types.

The results and discussion section will present the evaluative study of prioritized and selected technologies from the part of explorative research. It will mostly be the focus for the flexible packaging, while for rigid packaging the main emphasis will be on EVOH barrier material.

Considering the start phase of the project and mostly theoretical calculations many approximations have been made.

Also, as the data is confidential and belongs to Danone Nutricia, the names of the products have been coded, as well as some values have been altered from the original.

4.1 Flexible packaging

As has been mentioned in the earlier course of this report, most of the barrier packaging is presented by multilayer structures, created by means of lamination or, less often, co-extrusion. So, the resulting film is always a combination of layers of polymer materials, as graphically shown on Figure 16.

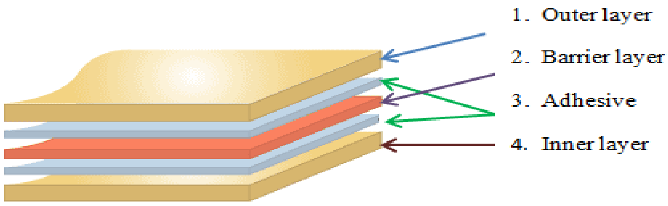


Figure 16. Common composition of multilayer films/laminates

The barrier material is usually "sandwiched" between two layers of other polymer (s). The function of other layers does not only lie in the protection of barrier layer, but other critical functions of the packaging structure. For example the outer layer of the structure (number 1 on the picture) has to be made out of abuse-resistant material, preventing the damage from external forces. The inner layer (number 4 on the picture) is a sealant layer that provides the hermetic seal to protect the product and to bond the layers together. At the same time, each layer of the multilayered structure contributes to the overall barrier performance both against oxygen and moisture ingress. In some cases, such excellent oxygen barriers as EVOH are sensitive to moisture, therefore sealant and outer layers of the package are selected based on their impermeability to the moisture so that the core barrier layer will be protected (Ebnesajjad, 2012).

4.1.1 Flexible pouches currently in use at Danone Nutricia

The above given information is provided in order to understand the current packaging for the flexible pouches of Nutricia products. It is presented by pouch comprised of two different multilayered structures for fronts and sides of the package as shown on the Figure 17.

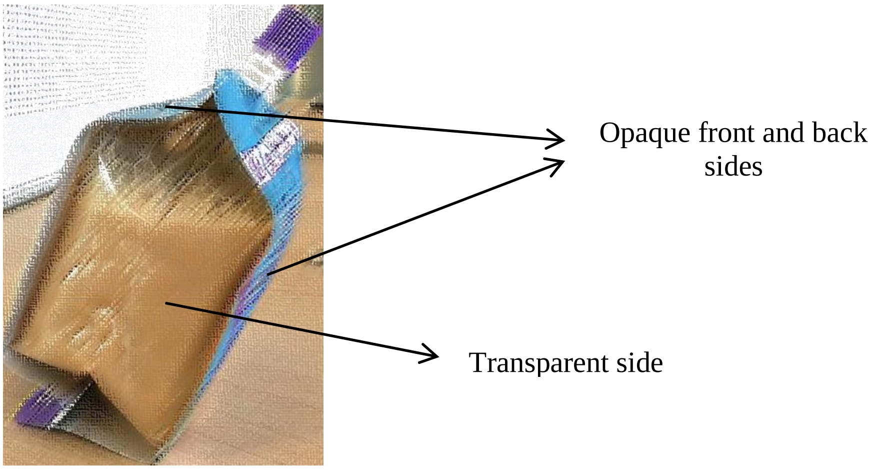


Figure 17. Current flexible pouch for some of Danone Nutricia products
(the image is being smoothed due to the confidentiality of the work)

While front and back of the pouch is opaque, the sides are transparent. For the flexible package considered in this study, the transparency criterion is the pre-requisite. The next Picture shows the concept of the flexible pouch for medical nutrition. Predominantly targeting hospitals' use, it is designed to be placed in upside-down position, connected to the enteral tube. The latter is being directly connected to the patients' stomach. The transparency, especially on the sides of the pouch is necessary to monitor the amount of product consumed.

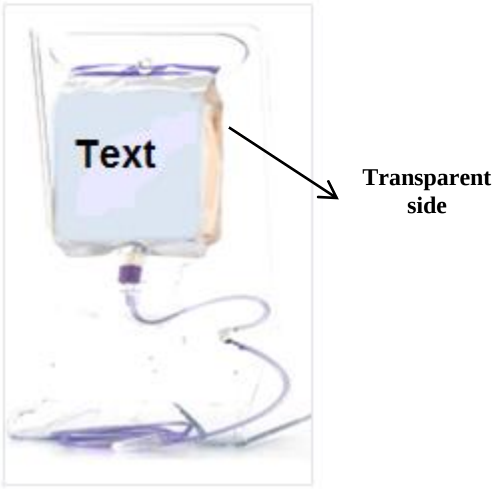


Figure 18. The concept of pouch's use in hospital

Two different multilayer structures used for the pouch design deliver two goals – required barrier protection against oxygen and moisture ingress and transparency. Importantly, it also designed to resist the retort conditions during the package sterilization process. The conditions are of maximum 124 ^{0}C, 3 bars (0.3 MPa) and 20 minutes.

However, dual structure adds to the complexity of the package, including its weight and cost. Therefore, the questions posed by R&D packaging development team in relation to this project were as follows:

- Is it possible to “switch” to the use of one type of multilayer structure instead of two?
- What are the benefits of doing so?

It is absolutely crucial to remember that the design of the package is not only aiming to meet the barrier requirements such as oxygen or water permeation. There are multiple others, including few named below:

- Resist transportation worldwide, avoiding leakage, contamination, damage, etc. Therefore, the package must be resistant to the external factors such as temperature, pressure, etc. For this purpose, usually a drop test from 1 m height is carried out on the final package prototype.

- In case of flexible pouch of Danone Nutricia, the package must resist the retort conditions that are 124 ^{0}C, 3 bars (0.3 MPa) and 20 minutes.

- Also, for this package transparency and good printability are required.

The study performed by the author is completely in the first phase of packaging development project at Danone Nutricia. Also, the project timeline was limited. Therefore, it was not possible to conduct physical evaluations such as drop or retortability test. Also, speaking of barrier performance, no shelf-life tests have been done.

However, it was possible to make a theoretical evaluation of barrier performance based on the external discussion with the suppliers of selected materials. Although, these results can’t be directly correlated to Nutricia product and package, it still gave very good first understanding of the material.

The criterions that formed an evaluation framework for selected materials have included:

- Oxygen barrier performance after retort conditions
- Moisture barrier performance after retort conditions
- Transparency

4.1.2 Evaluation of oxygen and water barrier performance

So, the current pouch is comprised of two different multilayer structures for front/back and sides. The overall thickness of the transparent film is 167 micron (µm), while opaque film is of 146 micron.

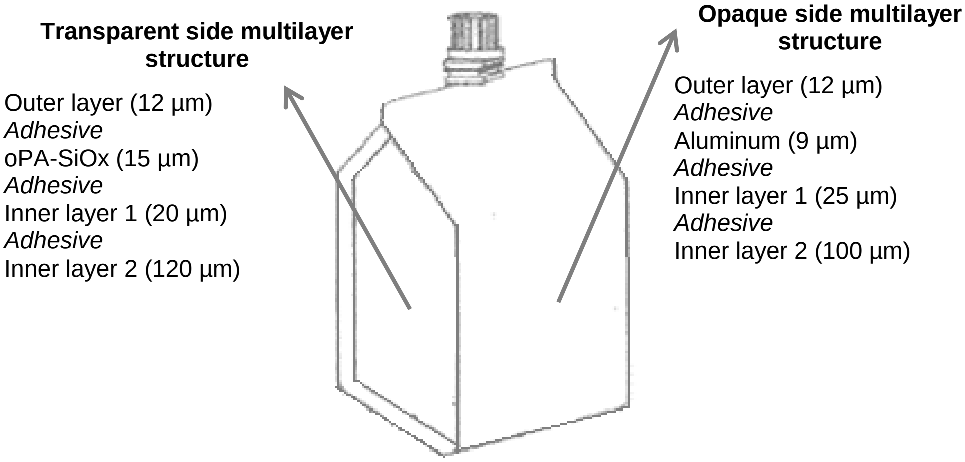


Figure 19. Laminate structure for the current pouch

As put previously, one of the goals was to consider the replacement of dual structure by only one, at the same time getting rid of the aluminum as a barrier layer for the opaque side.

The criterions not to be compromised by the proposed materials are:

- Current oxygen transmission rate (OTR) of 0,03 cm3/pouch/day after retort conditions of 120 ^{0}C, 20 min
- Current water vapor transmission rate (WVTR) performance of 1g /pouch/14 days (500 ml pouch) and 2g/pack/14 day (1000 ml pouch)
- The material must be transparent. At the same time, since front and back sides will bear the information of the product, it has to possess a good printability

Of course, the replacement of the structure is only viable and desirable when there are pronounced benefits obtained. Some of these benefits, outlined at this very explorative stage are:

- replacement of aluminum foil as it is not considered as a sustainable material, as well as subject to physical damage (pinholes, etc.) with drop in barrier performance

- down gauging of the packaging. For example, by reducing the thickness of the layers with potential cost-savings.

- Extension of shelf-life of the product from 12 months to 15-18 months based on the calculation of oxygen ingress over time.

Based on the internal and external discussions, five alternatives have been selected to evaluate against the current packaging structure. The name of the supplier will not be disclosed but the alternatives include previously considered SiOx and AlOx coated films, films with organic coating and hybrid organic/inorganic polymer coating. They are provided in the Table 15 below. All of the alternative multilayer structures are transparent and retortable, as well as easily printable.

Table 15. List of selected alternatives for flexible packaging

Remarks: *oPA - *Oriented* polyamide; ** RCPP - Retort cast *polypropylene;*
****CPP - cast polypropylene ; ****BOPA* - Biaxially *oriented* PA

Code	***Barrier film structure (from outer to inner)***	***Laminate structure tested by supplier***	***Thickness tested (µm)***	***OTR (cm^3/m2/day/atm), WVTR (g/m2/day/atm)***
A	Top coating AlOx PET 12 µm	Barrier film 1 oPA*(15µm) RCPP** (60µm)	Barrier film: 12 µm Laminate: 77 µm	**OTR**: 0.1-0.2 **WVTR**: 0.2
B	Top coating SiOx PET 12 µm	Barrier film 2 OPA(15 µm) CPP*** (50µm)	Barrier film: 12 µm Laminate: 67 µm	**OTR**: 0.2 **WVTR**: 0.2
C	Top coating (Inorg./Org. polymer) PET 12 µm	Barrier film 3 BOPA**** (15µm) CPP (50µm)	Barrier film: 12 µm Laminate: 65 µm	**OTR**: 0.08 **WVTR**: 0.2
D	1 µm organic coating PET 12 µm	Barrier film 4 OPA 15 µm CPP 60 µm	Barrier film: 13 µm Laminate: 78 µm	**OTR**: < 0.5 **WVTR**: 50
E	Inorganic barrier coating Vapour deposition	Barrier film 5	Barrier film: 12 µm	**OTR**: 0.1

	barrier layer PET 12 µm	CPP 60 µm	Laminate: 72 µm	**WVTR**: 0.2

Oxygen and moisture barrier performance have been estimated for each of the alternatives. It is very important to keep in mind, that the following calculations will give only an introductory understanding of package performance. For the complete results, laboratory tests on oxygen and moisture transmission will be needed. Also, shelf-life tests with filled product need to be performed. For the theoretical evaluation, several assumptions have been made, such as listed below.

Assumptions made for the theoretical evaluation:

1. Spout (the cap of the pouch) is not considered separately but as a part of the whole package with the same oxygen and moisture permeation rates as pouch film.

2. The layer thickness of the pouch film is assumed constant throughout pouch surface.

3. Calculations are based on an empty pouch.

4. The barrier performance of the whole pouch structure was compared to the barrier performance of laminate structure with barrier films listed in Table 15.

Two pouches with volumes of 500 ml and 1000 ml have been evaluated.
The evaluation has been performed in the following steps:

a. Determination of the surface of the pouches, based on the parameters for the filled pouch. (Appendix B). The Assumption 1 results in neglecting the spout as a separate part.

b. Estimate of the OTR values of the 500ml and 1000ml pouches after retort (120-125 ^{0}C, 20-30 min.). The comparative values for the alternatives have been obtained by the following formulas:

$$\text{OTR per pouch} = \text{OTR } (cm^3/m^2.day.atm) \times \text{pouch surface area}$$

c. Estimate of the WVTR values of the 500ml and 1000ml pouches after retort. The comparative values for the alternatives have been obtained by the following formulas:

$$\text{WVTR per pouch} = \text{WVTR } (g/m^2.day) \times \text{pouch surface area} \times 14 \text{ days}$$

The comparative evaluation results are summarized in Table 16 (the codes are corresponding to those presented in Table 15).

Table 16. Comparative evaluation of pouch alternatives

Remarks: OTR in cc/pouch/day; WVTR in g/pouch/14 days; All values are after-retort conditions in a range of 120-125^{0}C, 30-40 min

Code	*OTR per 500 ml pouch*	*OTR per 1000 ml pouch*	*WVTR per 500 ml pouch*	*WVTR per 1000 ml pouch*
A	0.006-0.0012	0.008-0.016	0.168	0.224
B	0.012	0.016	0.168	0.224
C	0.0048	0.0064	0.168	0.224
D	0.03	0.04	42	56
E	0.006	0.008	0.168	0.224

The calculated values for selected materials, as well as the values of the current performance are presented on the Figure 20.

The latter shows that all options apart from option D are performing better in terms of oxygen and moisture barrier then the current pouch laminate.

Option D is comparable to the current oxygen barrier, however is considerably higher than the requirements for the moisture barrier. The reason to this can be the organic coating of option D barrier film that is very sensitive to water. Based on the talks with supplier, there may be a possibility to improve the water barrier of option D by means of lamination. However, there are no known values of the degree of the expected improvement.

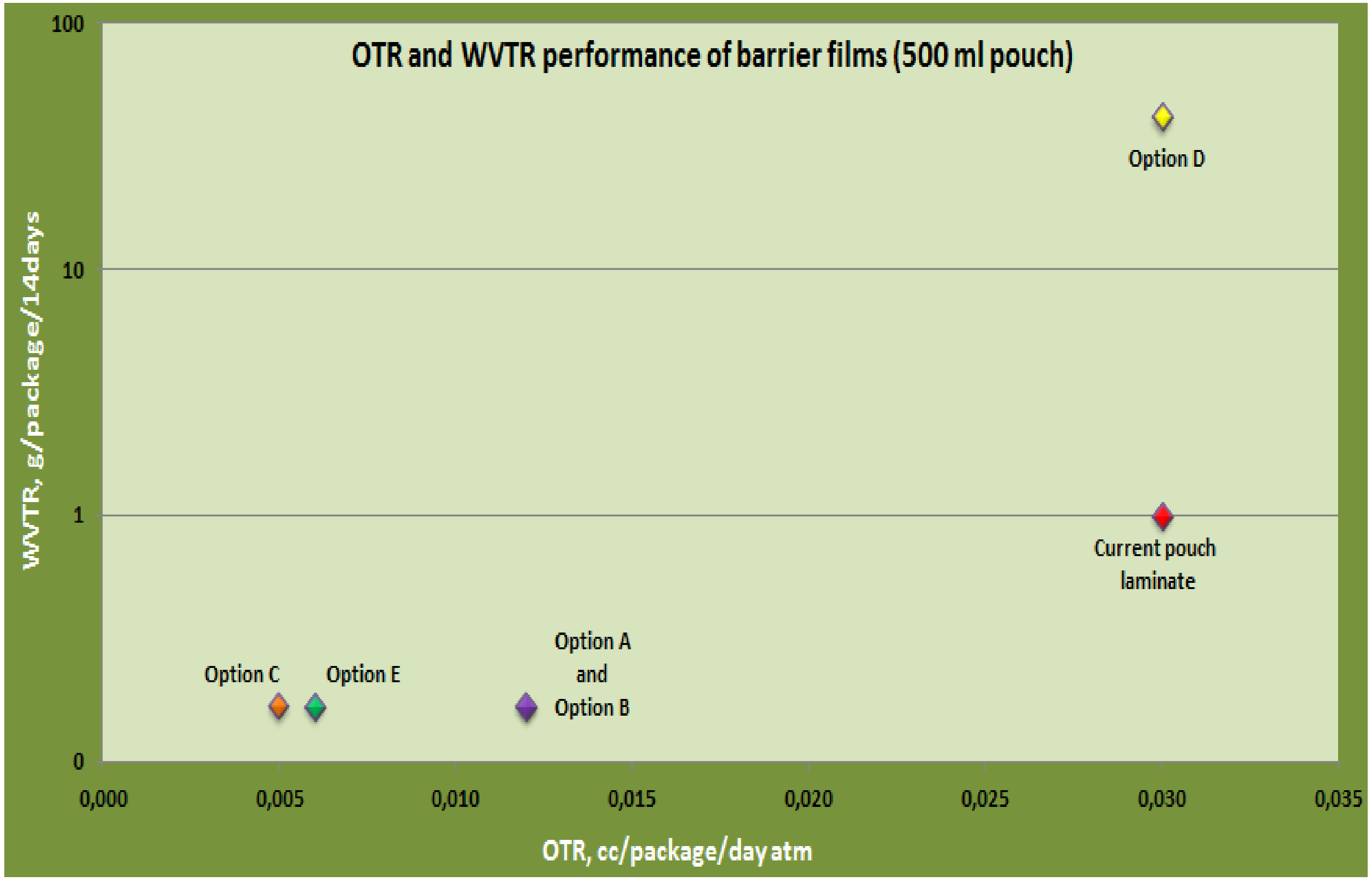


Figure 20. Comparative OTR and WVTR of selected barrier films for pouch

4.1.3 Potential down gauging of the film thickness

Based on the external discussion with the supplier of option B, better oxygen and water barrier performance will allow reduction of the total thickness of the film. The proposed alternative to the current structure in comparison to the current is eliminating the aluminum barrier layer for front/back of the pouch and inner layer 1. The changes of the thickness will result as follows in Table 17.

Table 17. Current film structure versus proposed structure (based on the discussion with supplier)

Transparent sides of the pouch	
Current structure	Proposed structure
Thickness: 167 µm Outer layer (12 µm) *Adhesive* oPA-SiOx (15 µm) *Adhesive* Inner layer 1 (20 µm) *Adhesive* Inner layer 2 (120 µm)	**Thickness: 147 µm** Option B (12 µm) *Adhesive* Inner layer 1 (15 µm) *Adhesive* Inner layer 2 (120 µm)
Opaque sides of the pouch	
Thickness 146 µm Outer layer (12 µm) *Adhesive* Aluminum (9 µm) *Adhesive* Inner layer 1 (25 µm) *Adhesive* Inner layer 2 (100 µm)	**Thickness: 147 µm** Option B (12 µm) *Adhesive* Inner layer 1 (15 µm) *Adhesive* Inner layer 2 (120 µm)

The proposed change to the pouch laminate structure will bring the savings of 19 µm of the film thickness, in case of using the option B.
Considering that the barrier performance of this option is stronger than the current, shelf-life will not be affected.

On the other hand, it is early to speak of other benefits, such as cost savings due to decreased thickness or equally strong mechanical strength of the suggested film structure. Firstly, the total cost will be influenced by many factors, such as new processing equipment needed or different kind of adhesive to be used in new structure. Also, as one of the inner layers is proposed to be eliminated, the puncture resistance of the film may decrease leading to the easier damage of the package during its shelf-life.

4.1.4 Estimation of the shelf-life extension

In reality, to make an estimation of the shelf-life of the product, the understanding of the package environment during filling, processing, distribution and storage is required. Inadequate understanding of the product barrier requirements leads to a distorted prediction of the shelf-life. Extensive shelf-life testing of each product is required to evaluate the barrier requirements for the package.
In case of this study, the shelf-life extension will be only estimated based on oxygen transmission over time. Therefore, the estimation will give only the first picture, but may turn out to be false when tested experimentally.

Shelf life can be estimated as shown in the equation below:

$$t_s = \frac{O_2, \max}{OTR}$$

Where, **t_s** = shelf life, day
O_2, max = maximum allowable oxygen, cm^3 O_2

The current functional requirement to the permeation of the pouch is equal to 0.03 cm^3/package/day. And the shelf life is set on average of 12 months or 365 days.
Therefore, the maximum allowable oxygen ingress for the product will be equal to 10.95 cm^3 /pouch/ 365 days.
Using the value for the maximum allowable oxygen per pouch and with the values of OTR for every of the options discussed above, the shelf life estimation can be made.

Table 18. Shelf-life estimations for pouch

Code	*OTR (cm^3/pouch/day, based on 500 ml pouch)*	*Estimated shelf-life (days)*	*Estimated shelf-life (years)*
A	0.012	912.5	2.5
B	0.012	912.5	2.5
C	0.005	2190	6
D	0.03	365	1
E	0.006	1825	5

Four out of five options of barrier films can theoretically extend the shelf life of the product. However, these calculations are only based on the oxygen ingress over time, no moisture. Again, only shelf-life tests with filled product can give a realistic picture, while this kind of estimations can only provide a comparative understanding of different barrier materials.

4.2 Rigid packaging currently used at Danone Nutricia

As a rigid packaging solution for liquid medical drinks, extrusion blow-molded plastic bottles of 125 and 200 ml are used.

The principle of rigid packaging structure is similar to that of flexibles, described in previous section. (see Figure 16). The main difference, however, is the type of barrier material used. For bottles considered in this study, that barrier is presented by ethylene vinyl alcohol, or EVOH. Its main characteristics and properties are discussed in Section 3.2.2.

The use of EVOH in bottles and not pouches can be attributed to its sensitivity to the retort process, with the latter worsening the barrier properties of EVOH considerably. Bottles, on the other hand, are aseptic filled at a temperature range of 130 ^{0}C to 170^{0}C.

To protect the oxygen barrier properties of EVOH, it is located between two layers of high density polyethylene, or HDPE.

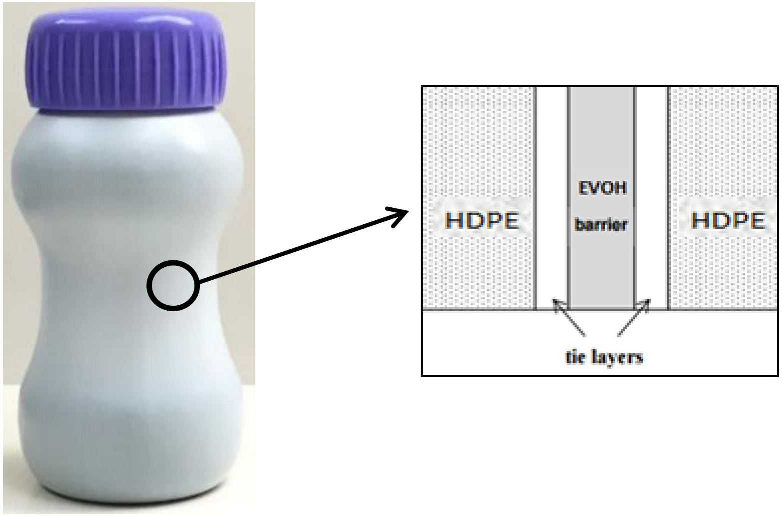


Figure 21. Current rigid bottle and its wall structure

The standard thickness of 20 micron is a widely accepted standard that is used for EVOH in rigid food packaging for the last 20 years. It can be accounted for few reasons, below are just a few of them (*supplier's interview*)

- Easier processing. The thinner the EVOH layer, the harder it is to achieve an even covering of bottle surface.

- The thickness of 20 micron so far has been given the sufficient oxygen barrier required by products contained. Essential to emphasize that this statement will be only reliable in context of food products that have been relevant to this study, such as dairy-based medical drinks. The current shelf-life of Nutricia product is 12 months. Most of the competitors in this market have the similar shelf-life for their products, as well as similar packaging solution.

The research on barrier materials has been conducted with the prioritized focus of Danone Nutricia to optimize the shelf-life of its products from 12 months to 18 months. While other alternative materials rather than EVOH can be considered a possibility, the small changes of the existing structure can be proven more feasible. The obvious advantage is that it takes less time and investment, such as new machinery, etc. So far, no research has been conducted to evaluate the changes in oxygen barrier performance of Nutricia bottle as affected by EVOH. Therefore, to address this gap in knowledge, the questions posed for this study were:

- How the oxygen barrier of Nutricia bottle changes with different EVOH thickness?

- How much stronger the barrier provided by different grade of EVOH?

- Will the position of EVOH in the multilayer structure (closer/further from the inside) have a considerable effect on oxygen permeation?

Apart from that, there was a little research on how the initial oxygen content in package and/or product affects the shelf-life. Therefore, other questions asked were:

- How the headspace contributes to the total oxygen content over shelf-life?

- Can the change in the headspace volume be enough to extend the shelf-life, without changing the packaging structure?

Lastly, so far only the passive barrier solution has been discussed, such as EVOH. As the theoretical part of this report outlines, there are also number of active barrier technologies on the market, where the packaging components can absorb the oxygen throughout the shelf-life of the product.
One of these solutions will be considered for bottles in this section. However, in this case the base polymer of the bottle will be polyethylene terephthalate (PET).

4.2.1 Evaluation of oxygen barrier performance of passive barrier in bottle – EVOH.

4.2.1.1 Influence of EVOH thickness on the oxygen barrier of Nutricia 200 ml bottle

The oxygen transmission rate (OTR) through a permeable package (e.g., a plastic bottle) may be calculated using the equation:

$$OTR = \frac{P \times A \times \Delta \mathrm{p}}{L}$$

Where,
OTR - oxygen transmission rate (cm^3/day)
P – permeability ($cm^3.mm/m^2.day.atm$)
Δp – pressure difference across the barrier
L – layer thickness
A – package area

Therefore, the relation between the thicknesses of the barrier layer, in this case EVOH, will be inversely proportional to the oxygen transmission rate. At the beginning of the study, the main assumption made was that the thinner the EVOH layer, the weaker the oxygen barrier.

The evaluation of oxygen barrier performance has been conducted on Nutricia bottles with 5 different thicknesses of EVOH – 10, 15, 20 (the current thickness used at Nutricia), 25 and 30 micron. (Refer to Appendix C.1). Thus, the difference in EVOH thickness lied in a range of -50% to + 50%. The bottles were tested empty and the tests have been done in three ways:

- Using online oxygen transmission software, provided by Norner Packaging Research Institute, based in Norway. (Refer to Appendix C. 4)

- Internally, at Danone Nutricia Life Science Laboratory, using the oxygen transmission testing system - MOCON OX-TRAN Model 2/21 (Refer to Appendix C.3).

- Externally, by the supplier of EVOH (name is confidential)

The results obtained are not consistent and noticeable differences exist within and between each of the methods used. Below is the Figure 22, that is demonstrating the OTR fluctuation with differing EVOH thickness obtained from Norner software and supplier’ s laboratory.

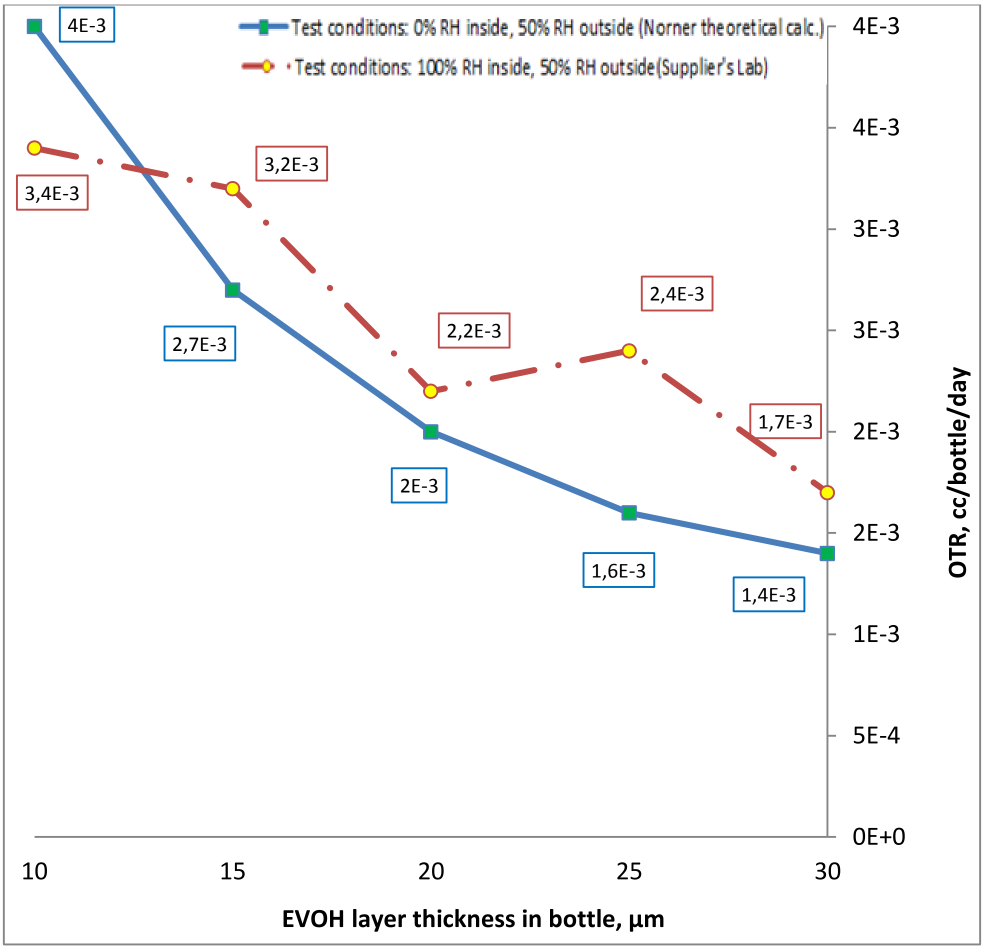


Figure 22. OTR of Nutricia bottles VS EVOH layer thickness

Both theoretical and supplier test confirmed the current OTR for bottle used at Nutricia, that is equal to 0,002 cm^3/bottle/day. However, there are two main differences discoverable from the first look. The possible explanations for these dissimilarities can be formed based on the available data on EVOH behavior VS humidity, as well as the examination of bottle walls’ thickness.

Difference I. Norner software gives a smaller OTR values as compared to OTR values obtained by supplier. It is best explained as caused by moisture absorption or the partial pressure difference across the EVOH layer. Whenever there is a difference in relative humidity between the inside and outside of a package, there will be a difference in partial pressure from one side of the barrier layer to the other. It is best demonstrated on Figure 23.

Norner software does not allow the adjustment of the relative humidity (RH) inside the bottle, therefore it was assumed to be equal to 0%.

On the other hand, supplier's equipment adjusts both internal and external RH. For this test, supplier used the extreme condition of RH inside the bottle equal to 100%. In both Norner and supplier tests, outside RH was set on 50% that is considered as ambient.

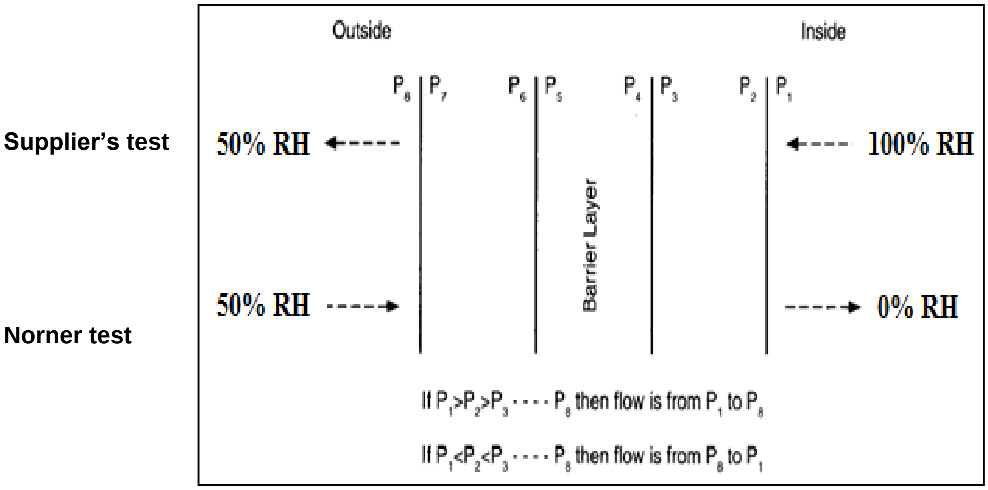


Figure 23. RH effect on EVOH moisture

The more moisture EVOH absorbs as a result of RH inside/outside, the weaker it performs.

In the case of this study, the bottle structure is presented by 5 layers (refer to Figure 21). The formula to evaluate the moisture of EVOH layer for 5 layer structure is as follows below:

$$1/2(P_2+P_3)=P_0\frac{(\frac{t_b}{M_b}+\frac{2t_i}{M_i})+P_i(\frac{t_b}{M_b}+\frac{2t_0}{M_0})}{2(\frac{t_i}{M_i}+\frac{t_b}{M_b}+\frac{t_0}{M_0})}$$

Where:

½ (P_2+P_3) – RH of barrier layer (%)

P_0 and P_I – RH of outside and inside environment (%)

t_b, t_I, t_0 – thickness of barrier, inside and outside layers (mils)
M_b, M_I, M_o – MVTR of barrier, inside and outside layer (g-mil)

The above-given formula was used to calculate the RH of EVOH layer in test conditions provided by Norner and supplier.

Table 19. RH of EVOH layer

Test	*RH outside bottle (%)*	*RH inside bottle (%)*	*RH of EVOH layer*
Norner software	**50**	**0**	**29,9%**
Supplier's lab	**50**	**100**	**70%**

As Table 19 shows, an increase of inside RH led to a considerable spike in moisture level of EVOH layer. In its turn, it resulted in 9-18% weaker oxygen barrier when compared to conditions where inside RH was 0%. (See Figure 22).
One of the questions posed at the beginning was whether changing the position of EVOH in multilayer structure can affect the barrier. The above estimations show that if the product inside the package is of a higher humidity than outside, it makes sense to move the EVOH further from the product. It can be achieved by increasing the layer of HDPE from inside and thinning it on the outside. These kind of bottles have been manufactured on supplier's premise in France, however they are not tested yet. And, in this case, the oxygen barrier test must be done only with the product filled in the package; therefore shelf-life tests are needed.

Difference II. Norner software proofs the assumption that oxygen barrier improves as the EVOH thickness increases. While the tests performed by supplier's laboratory show somehow contradictory results. The barrier improvement can be seen across all thicknesses excluding 20 and 25 micron, with the latter performing worse. This incongruity can be attributed to the EVOH layer distribution across the bottle area.
In ideal conditions it can be assumed that EVOH forms a layer of constant thickness throughout of bottle surface. In practice, however, it is far from the reality. The bottles are extrusion blow molded (Refer to Appendix C.2). In this process, plastic is melted and extruded into a hollow tub that is captured into a cooled metal mold (in this case bottle mold). Air is then blown into the tube, inflating it into the shape of the hollow bottle. There is a very high possibility that plastic is not being evenly distribute across the bottle, because the wider parts of the bottle are stretched more, hence the layer of plastic is thinner. Bottom and narrower parts of the bottle, on the other hand, have a thicker layer. Nutricia bottle is not cylindrical and has both wide and narrow parts (Refer to Figure 21).
The Figure 24 below shows the results of measurements conducted on 5 bottles with different EVOH layer thickness. The same bottles have been tested for OTR

by supplier’s lab. For average thicknesses obtained for bottles refer to Appendix C.1. As can be seen from the Figure 24, the bottle with 25 micron of EVOH has the lower minimum that the bottle with 20 micron of EVOH. The thinner area of EVOH in 25 micron bottle can be a contributing factor to the higher permeation of oxygen. However, it is highly dependent on area and may have a little or no impact if the thin area is small. Other explanation to OTR difference is the variation in measurements itself that can be attributed to the equipment calibration, correct placement of the bottle. Also, as only two bottles per thickness have been measured, more repetitions are needed and it is clearly not enough to draw a conclusion of OTR on the thickness of 25 micron in all bottles.

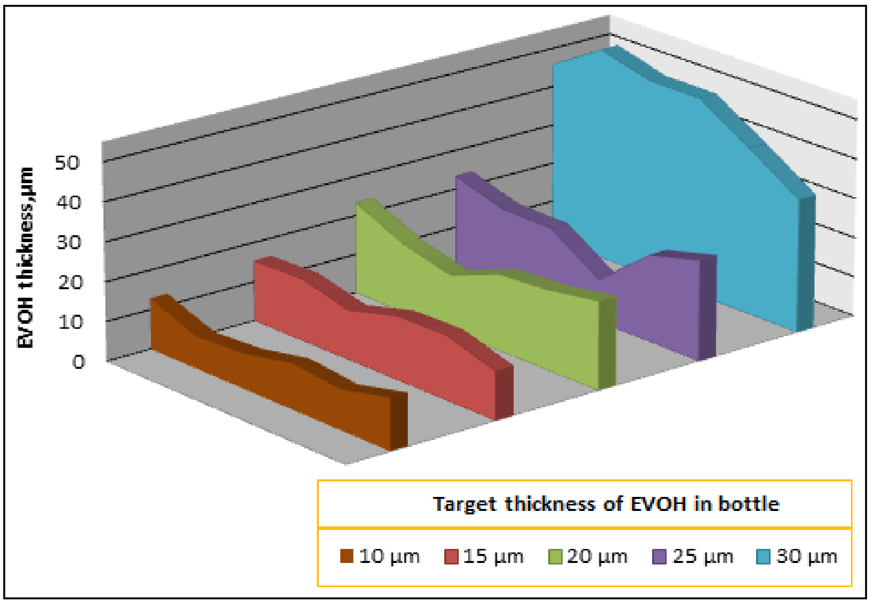


Figure 24. EVOH layer thickness fluctuation across bottle surface

As have been said previously, the OTR tests have been also conducted internally at Danone Nutricia laboratory. Test has been carried out in conditions similar to that of Norner test, with inside RH equal to 0%.The measurements have been repeated three times and have been rather discrepant. This can be attributed to a few factors:

- The equipment has not been calibrated the last few years and may not function properly.

- A human factor as the bottles are mounted manually by gluing on the MOCON analyzer plates (Appendix C.3). During gluing, the bottle may not be attached correctly with micro-holes in glue layer that may contribute to oxygen leakage and higher OTR.

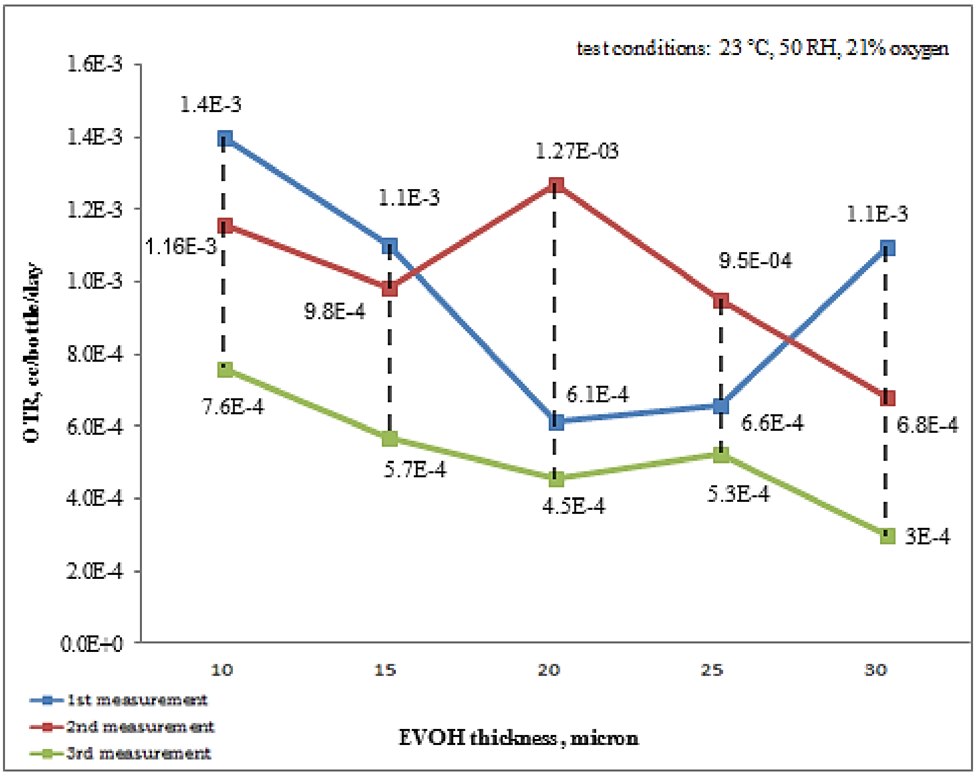


Figure 25. MOCON OTR test, conducted internally

4.2.1.2 Influence of PE content on OTR values. EVOH 32mol % versus EVOH 27mol %

It has been noted earlier in this report, the lower polyethylene content results in the stronger oxygen barrier properties. The drawback is that the lower PE content also makes EVOH more sensitive to moisture. As a result, at elevated humidity the oxygen barrier may weaken remarkably.

The bottles with new grade have been manufactured on supplier's premises; however the OTR tests are still ongoing. Therefore, the modeling of oxygen barrier performance was done using previously mentioned Norner software. Important to note that the results shown can be only true in ideal conditions - the EVOH layer across the bottle surface is assumed to be of a constant thickness and external conditions are stable.

Table 20. OTR properties of two EVOH grades

Grade of EVOH	OTR, (at 20 ^{0}C, RH 50-65%)
PE content 32mol%	0.4 cm^3.20µm/m^2day.atm
PE content 27mol%	0.2 cm^3.20µm/m^2day.atm

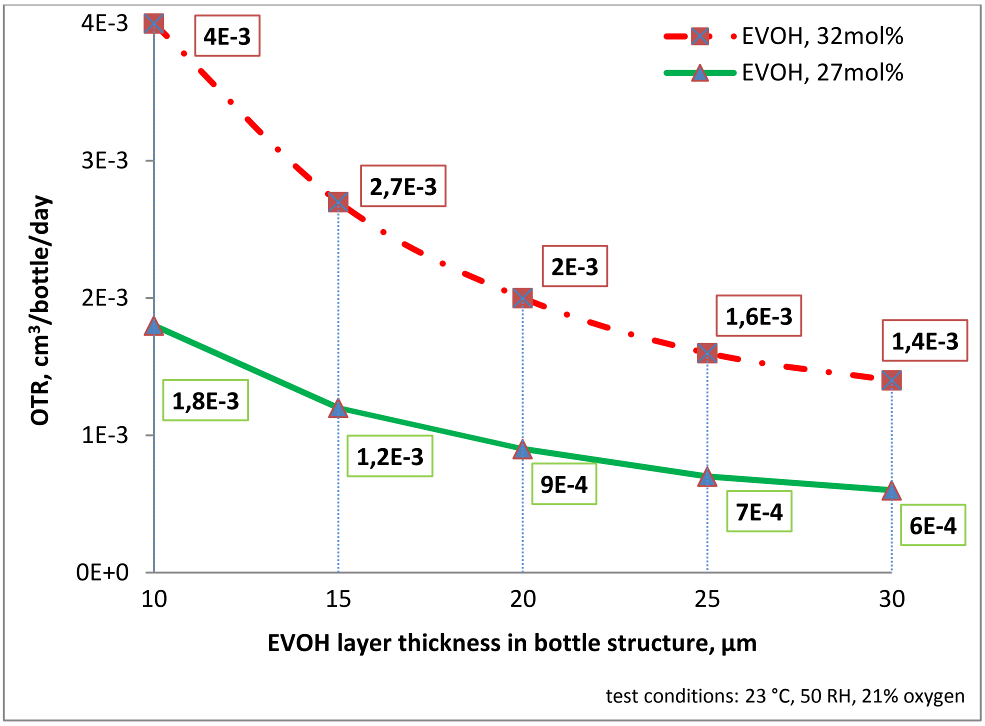


Figure 26. Model of OTR performance in bottles with two grades of EVOH

The theoretical modeling backs up the assumption that bottle oxygen barrier is stronger with EVOH 27%mol. Further in the study, the experimental testing is imperative to confirm the theoretical results.

4.2.2 Shelf-life extension via modification of EVOH and headspace

The current shelf-life of Nutricia medical drink is 12 months that is provided by a bottle with 20 micron EVOH as a barrier. As the goal is shelf-life extension to 18 months, it is logical to study how the change of EVOH thickness and type influence the shelf-life duration. Nonetheless, the exclusive focus on barrier material is not the right approach. It is easy to omit the other, no less important point that is the headspace of the bottle.

Currently at Danone Nutricia, the bottles are flushed with inert gas – nitrogen, before and after filling. It purges the bottle and the product of oxygen. Despite this, there is always residual oxygen content in a headspace, equal to 7-9%. This oxygen, together with the permeating oxygen, contributes to the total oxygen ingress and determines the shelf-life of the product.

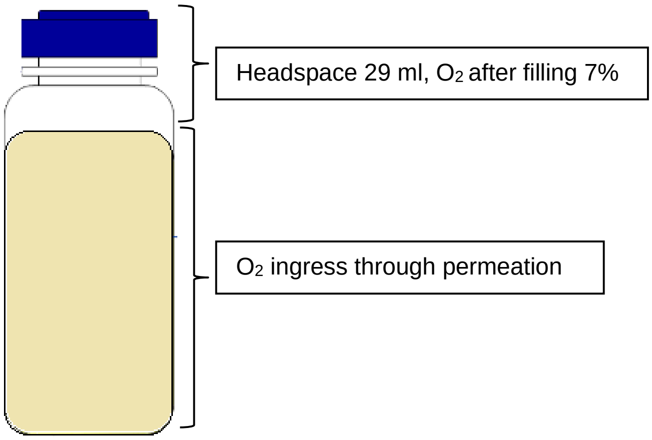


Figure 27. Headspace volume in Nutricia bottle

4.2.2.1 Oxygen ingress during current shelf-life

Before evaluating the potential impact of barrier changes, it is necessary to understand the oxygen ingress in the product for the current shelf-life of 1 year. After that, the several scenarios can be modeled for the possible extension of shelf-life. The below given estimations are provided for the comparative understanding of different approaches. For detailed calculations see Appendix C.5.

Table 21. Oxygen ingress with the current packaging solution

*For oxygen mass calculation from ml, the conversion factor of 1.33 was used. See Appendix C 4.

Initial oxygen (after the filling)	
Bottle volume (total)	229 ml
Headspace	29 ml
O_2 in a headspace	7%
Total O_2 in bottle	2,03 ml
Mass O_2	2,7 mg*
Ingress over 365 days	
Permeation Rate	0,002 cm^3/bottle/day

Thickness of EVOH layer in bottle	20 micron
Grade of EVOH	32mol%
After 365 days' ingress	0,73 ml
Mass of O_2 ingress	0,959 mg*
Total O_2 in bottle after 365 days – initial plus ingress	
3,6 mg (2.76 ml)	

Assumption made for shelf-life calculation:

A. If the shelf-life is purely determined by the amount of the oxygen ingress, then in order to extend the shelf life by 6 months (550 days), the total oxygen load shall remain the same as during the 12 months (365 days) of shelf-life.

B. Based on the above, the **maximum allowable oxygen ingress** for 550 days is assumed to be **2.7 ml O_2** in 200 ml, **or 3.6 mg O_2** in 218, 5 mg of product

4.2.2.2 Scenarios of shelf-life extension

Two scenarios where considered where either the barrier material or headspace is modified.

Table 22. Scenarios for shelf-life extension

*Values obtained by Norner software (see Figure 22)

Scenario A: Modification of barrier material								
	Initial oxygen			Oxygen ingress, after 550 days				Total O_2, mg
Type of modification	Headspace, ml	Headspace O_2, %	O_2, mg	OTR* cm^3/bottle/day	EVOH grade	Thickness, µm	O_2, mg	
Change EVOH thickness	29	7	2,7	0,0016	32mol%	25	1,2	3,8
Change EVOH thickness	29	7	2,7	0,0014	32mol%	30	1	3,6

Change EVOH grade	29	7	2,7	0,0009	27mol%	20	0,65	3,3
Change EVOH grade and thickness	29	7	2,7	0,0012	27mol%	15	0,87	3,5
Scenario B: Modification of headspace volume and O_2%								
Decrease headspace volume	See Figure 28	7	1,3-2,5	0,002	32mol%	20	1,4	2,7-3.9
Decrease headspace O_2 %	29	See Figure 30	0,4-2,67	0,002	32mol%	20	1,4	1,4 - 4

In Scenario A, the headspace volume and oxygen percentage are not changing. In this case, the change that can lead to a smaller OTR and hence longer shelf-life is the modification of barrier material. Either increasing the thickness of EVOH or changing the grade of EVOH can be applied. While new grade can deliver the superior oxygen barrier over the old grade, even at lower thickness, the risks needed to be evaluated. EVOH is an expensive material and decrease of material use is much welcomed. However, the proposed new grade of 27mol% must be subjected to repeated factory trials to prove its machinability and processability.

Any scenario considered here is purely theoretical calculation and it is required to be supported by actual shelf-life tests. However, based on this first estimation, shelf-life gains for Scenario A can be summarized as shown in Table 23.

Table 23. Achievable shelf-life for Scenario A

Scenario A	**Estimated shelf life, days**
EVOH 32mol% thickness of 25 micron	456
EVOH 32mol% thickness of 30 micron	550
27mol% EVOH, 15 micron	608
27mol% EVOH, 20 micron	811

In Scenario B, the barrier material is not changed anyhow, while the headspace volume and oxygen content are the main focus. Figure 28 and 30 are representing the dependency of shelf-life based on these factors. Faster to implement, such change as decrease of headspace may lead to such undesirable consequences, as overfilling.

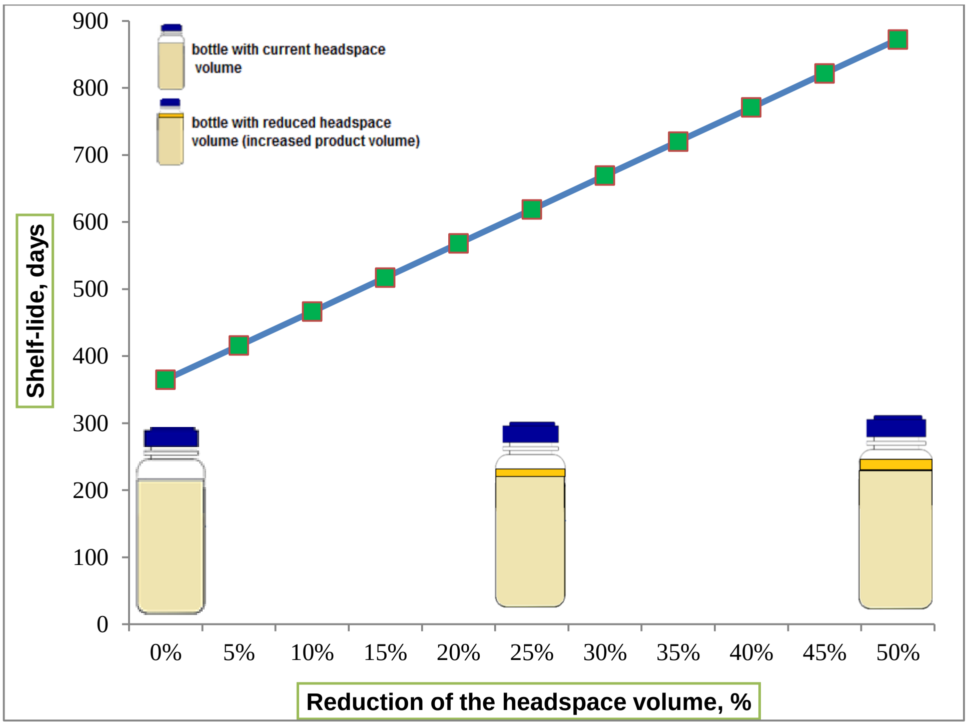


Figure 28. Reduction of headspace volume VS shelf-life

To avoid this, the decrease of the oxygen % in headspace volume seems to be a feasible option (Figure 30). Currently, it is equal to 7%, but reduction as small as by 2% can give the shelf-life even longer than the desirable 550 days. However, the amount of oxygen in a headspace is hard to control even on the same filling head. There is always a slight variation in oxygen %, as affected by filling process. It is best demonstrated on Figure 29, where oxygen in headspace was measured in bottles filled on 20 different filling heads. Three measurements were done in three different weeks on the same 20 filling heads. It can be seen that the oxygen content varies not only between the different filling heads (that is designed for the same bottle volume and product), but within one filling head at different times.

Below, as Figure 30 demonstrates, even a small variation in headspace % O_2 can have an impact on subsequent shelf-life of the product.

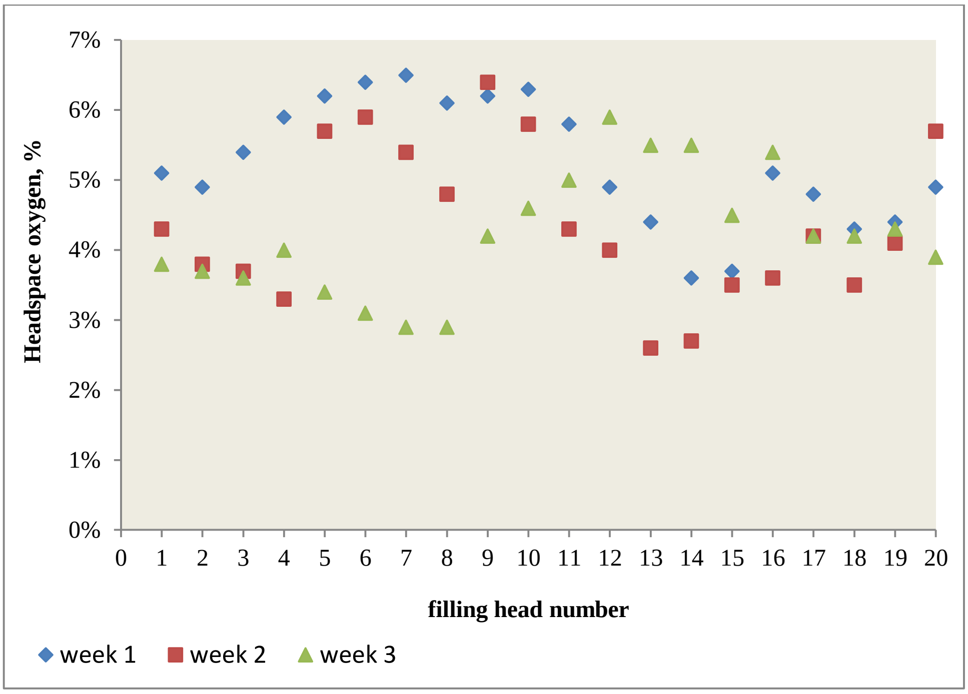


Figure 29. Headspace oxygen% fluctuations per filling head

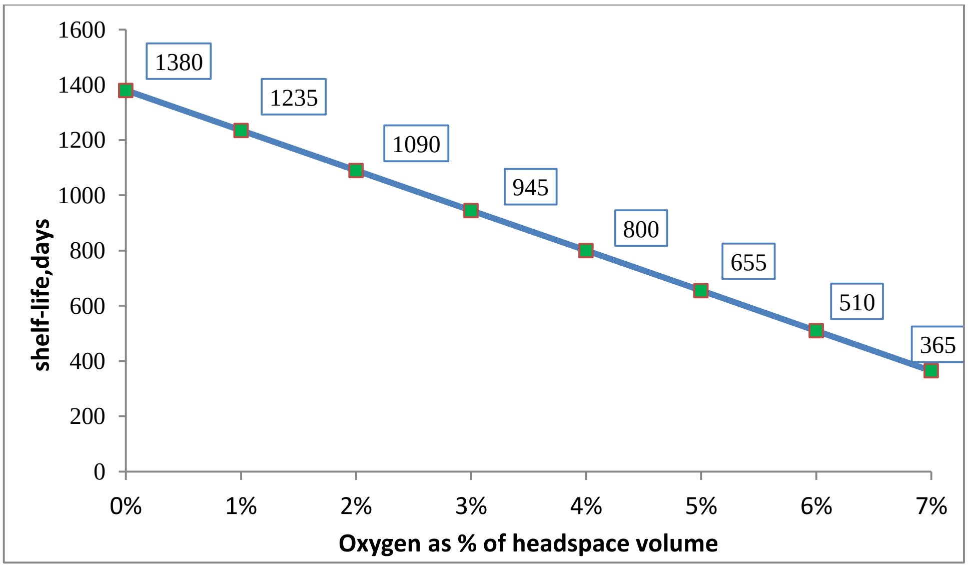


Figure 30. Oxygen % in a headspace versus shelf-life

4.2.3 Evaluation of oxygen barrier performance of active barrier – oxygen scavenging PET bottle

Earlier in this report numerous technologies on the market of oxygen scavenging packaging have been outlined. Most of the oxygen scavenging packaging is designed to be used with PET as a base polymer.

PET presents many advantages to be used in food packaging – it is clear, unbreakable and inexpensive. Most importantly, it is monolayer material that is easily recyclable. However, its barrier properties are not strong enough for PET to be considered as an option for long shelf-life products. The situation started to change when the commercially important oxygen-scavenging polymer systems have been introduced. Some of these oxygen scavengers intended for blending with PET are based on oxidizable olefinic polymer such as a polybutadiene (PBD) block or graft copolymer used in combination with a cobalt salt as a catalyst.

The current structure of Nutricia bottle is multilayer with EVOH as a barrier material.

For the purpose of research, the following questions were asked:

- How would the shelf-life be affected if the packaging would be changed to oxygen-scavenging PET bottle?

- What are the other benefits rather than shelf-life extension?

One of the suppliers of this kind of oxygen scavenging PET bottle has modeled the package incremental oxygen ingress over time for Nutricia bottle 200 ml. In Figure 31 below, PET bottle is compared to PET bottle with mixed oxygen scavenging PBD-PET block copolymer with cobalt catalyst. The incremental oxygen ingress rate in the bottle decreases as the dissolved O_2 content increases towards saturation.

Where oxygen scavenging additive is used, the initial incremental ingress rate is negative as oxygen is absorbed from the headspace/product by the active scavenger additive.

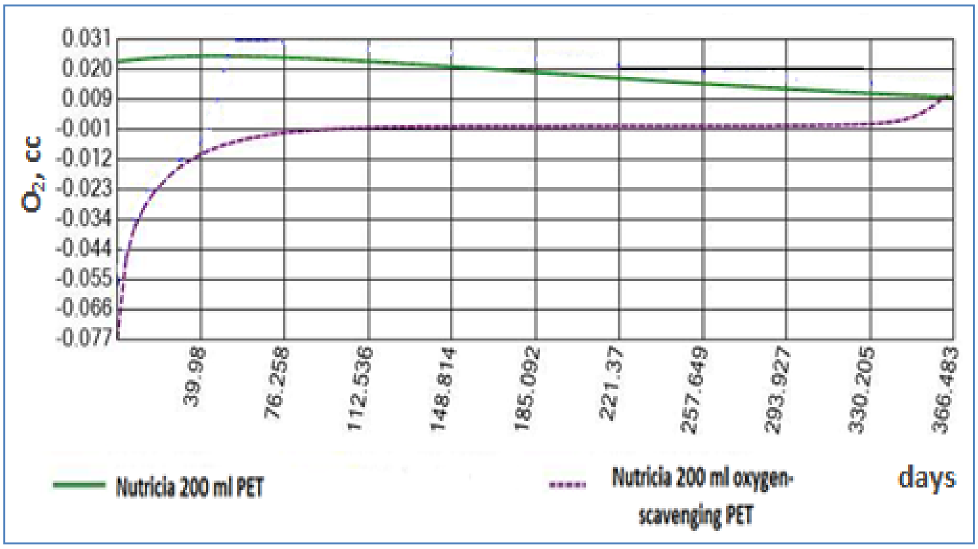


Figure 31. Incremental ingress of O2 in PET and oxygen scavenging PET

In case of oxygen scavenging PET, the oxygen ingress only starts after approximately 330 days, as the scavenger absorbs the permeating oxygen all time before that. Though, based on only this estimation it is challenging to predict the possible shelf-life, the active packaging definitely bears a tremendous potential.
Important to bear in mind, that PET bottle offers both the options of multilayer and monolayer packaging structure. The oxygen scavenging additive described in this case is 100% recyclable with PET that makes it an environmentally more favorable choice when compared to multilayer bottle.

5. Conclusions and further research

Packaging considerations are closely integrated with the evaluation of product shelf-life. There are numerous functions that packaging fulfills, such as the containment of the product, mechanical resistance, protection against physical and chemical degrading agents, etc. The prioritization of these functions is done based on the nature of the product, its shelf-life requirements and distribution conditions. In this study, the focus has been given primarily to one of the limiting factors of products' shelf-life – oxygen. With regard to that, the study has been carried out to examine the commercially available high barrier materials for both rigid (bottles) and flexible (pouches) packaging portfolio of Danone Nutricia.

5.1 Flexible packaging – pouch

Among the latest developments for high barrier flexible packaging, thin barrier coatings on polymer base represent the significant part (Section 3.2.3.3). Based on the findings on the materials found in this niche, a comparative study has been performed versus the current pouch laminate, though limited to the evaluation of oxygen and water barrier characteristics. It allowed to form the first understanding of the benefits that these options may bring if used as an alternative to current packaging material. These benefits include but not limited to the shelf-life extension and the downgrading of the packaging structure.

The first estimations led to the conclusion that most of the considered alternatives exhibit stronger oxygen and water barrier properties when compared to the current pouch structure (Section 4.1.2). However, based on the values given by suppliers, it can be observed that most of these materials have the similar OTR and WVTR performance. Therefore, it is hard to identify what material shall be prioritized. For that, the further evaluations must be scheduled by Nutricia, both for OTR and WVTR, as well as other tests such as drop test. OTR measurements are advised to be carried out over an extended period of time and with a high number of repetitions. The reason is that due to the factors such as equipment failure or incorrect manual handling of the samples, the results are easily distorted, as an example of OTR analysis for rigid packaging (Section 4.2.2.) demonstrates. Moreover, any of the tests must be performed on a sample as similar to the current pouch as possible, meaning the same volume and dimensions. So far, all OTR and

WVTR values received from suppliers, are obtained on the evaluations of pouches significantly smaller in size comparing to Nutricia pouch.

The study has also revealed a necessity to conduct the product shelf-life tests with any of the packaging considered. Only with the product inside the package and in conditions close to that of distribution chain the reliable conclusion can be drawn.

5.2 Rigid packaging

Speaking of the optimization of oxygen barrier performance in Nutricia bottles, the main objective pursued was the extension of shelf-life. Several options have been proposed for this purpose, with the main focus being on the modification of barrier material (EVOH) thickness, based on the assumption of higher thickness leading to an improvement of barrier strength. (section 4.2.2.2). . As theoretical and experimental evaluations have shown, there is an effect of the thickness. However, more measurements must be scheduled due to the high inconsistency of results between three ways of measurements – theoretical modeling via Norner software, experimental measurement by EVOH supplier and experimental measurements performed at Nutricia facility. The theoretical prediction was not supported by experimental data, therefore no conclusion can yet be done. Reasons for that are in detail given in Section 4.2.1.1. The recommendations are as follows:

- Maintenance check on the oxygen analyzer equipment. There were no consistent checks the last years and there is a high possibility of its malfunctioning.

- Continuation of measurements, at least from supplier side. Higher number of repetitions per bottle batch that will allow to see the standard deviation in measurements. The last measurements received were done only in two repetitions and can’t be taken as reliable.

Other than the modification of thickness, the other possible scenarios are the change of EVOH material grade, the modification of bottle headspace volume and residual headspace oxygen content. Any of these scenarios must be considered within a defined range of requirement and affecting factors, some of them given below.

The decrease of the empty headspace volume implies two approaches:

1. Filling the bottle with more product
2. Changing the size of the bottle.

Both of these approaches must be investigated in depth to understand the required investment and possible consequences. One assumption is that the first approach with more product may require the optimization of the filling process to avoid the risk of overfilling with subsequent negative impact on bottle sealing. Secondly, the consumer category as vulnerable as medical patients has many restrictions to comply with. Medical nutrition is characterized by a meticulously planned content and strictly defined consumption limits. The consequences of adding the excessive volume of product are not known and must be investigated. The slight modification in product volume may bring on negative health effects. The second approach is to change the size of the bottle mold in extrusion blow molding machine. This solution can require large capital investments and the separate study must be scheduled to investigate the benefits and drawback of such change.

While options given above are based on the changes in existent material structure, the active packaging will require the change of bottle material. (Section 4.2.3) For example, the PET bottle with oxygen scavenger offers the “environmental” benefit of easily recyclable monolayer material, with oxygen protection and shelf-life comparable with currently used multilayer materials. From other side, the amount of capital investment shall be investigated together with machinery changes it may entail. Any of the active packaging must be tested extensively in shelf-life product tests.

Much focus is given to the barrier material of the bottle, be it EVOH or PET with scavenger, so that the permeating oxygen can be reduced and shelf-life extended. At the same time, most of the oxygen responsible for limiting shelf-life is in the headspace of the bottle. What can be the solution where the headspace oxygen can be removed effectively without changing the structure of the bottle, as well as its volume?

Bottle closures with oxygen-scavenging sealing layer can be one of the promising options to investigate deeply. It was not considered in this study, but it is strongly recommended for further research. Based on the same principle, as any of the oxygen scavenging packaging (see Section 3.3), the closures of this type remove the oxygen out of the headspace right after the filling process. Its consumption by scavenger can bring the expected shelf-life extension, with no further modifications required to headspace volume or packaging material. Therefore, it may be a good way for shelf-life optimization without significant packaging changes. There are many suppliers of this kind of closures already on the market, the most widely known include, BERICAP, GCP Applied Technologies with its CELOX® range and ACTEGA with SVELOX® range.

Lastly, as has been already emphasized numerous times, this study has considered only one aspect contributing to product shelf-life – its packaging. But it does not give the complete picture and must be studied together with range of other factors. The absolute pre-requisite is to know the nature of food product’s interaction with oxygen, as well as the environment in which the product is stored and distributed. As these factors are differing, there can’t be assumptions made. Without a well-formed knowledge of these interactions, there is a risk of selecting the material with inadequate barrier properties, based only on one requirement such as OTR.

The recommendation for the further course and continuation of herewith discussed study is to start a close collaboration with Product Development team, so to understand the nature of the product.

References

Advanced polymers for practical use. (n.d.) Retrieved February 5, 2016, from http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20020063434.pdf

Akkapeddi., M.., (2014) Chapter 19 - *Commercial Polymer Blends. In:* Utracki.,L., Wilkie.,C., (2014) Polymer Blends Handbook (2nd edition)., http://dx.doi.org/10.1007/978-94-007-6064-6

Alpha Marathon. Retrieved February 5th, 2016, from http://www.alphamarathon.com/index.php?option=com_content&view=article&id=210&Itemid=199)

Amcor (n.d.) Ceramis Brochure. Retrieved February 4, 2016, from http://www.amcor.com/CMSPages/GetFile.aspx?guid=807a2197-b14d-4d61-adeb-a0b004efec85

BASF (n.d.) Combined power for sustainable innovation – multi-layer film by BASF Solvent-free and compostable technologies for the flexible packaging industry. Retrieved January 18, 2016, from http://worldaccount.basf.com/wa/plasticsEU~ru_RU/portal/show/content/products/biodegradable_plastics/ecovio_applications_multilayer_films

BESELA Retrieved February 12, 2016 from http://www.abre.org.br/esp/wp-content/uploads/2012/07/secaoE.pdf (n.d.)

BioPlastics. (2015). Compostable, biodegradable barrier coating for biodegradable film for food packaging. Retrieved January 25, 2016 from http://www.bioplasticsmagazine.com/en/news/meldungen/20150113-bioOrmocer.php

Braun.,D. (2003) Chapter 32 – Liquid Crystal Polymers. In: Massey., L., Permeability properties of plastcis and elastomers (2nd edition) New York: Plastics Design Library/ William Andrew Publishing

Chadwick., P. (2014) Greiner aims to reduce food spoilage with barrier technology, Retrieved February 10, 2016, from http://www.packagingnews.co.uk/news/greiner-aims-to-reduce-food-spoilage-with-barrier-technology-09-09-2014

Colormatrix. (n.d.). Amosorb™ , Amosorb™ Plus and Amosorb™ -SolO$_2$. Active oxygen scavengers for product protection and shelf stability in oxygen sensitive beverages and foods packaged in PET. Retrieved February 26, 2016, from http://www.polyone.com/files/resources//ColorMarix_Amosorb_Range_Product_Info_Brochure%2C_July_2013.pdf

Cryovac., (n.d.) Retrieved February 29, 2016, from *http://www.cryovac.com/na/en/food-packaging-products/oxygen-scavenging-headspace.aspx*

DibbioPack. D3.6 Biodegradable and humidity activated antimicrobial devices. Publishable executive summary. Retrieved January 25, 2016, from http://www.dibbiopack.eu/uploads/media/Biodegradable_and_humidity_activated_antimicrobial_devices.pdf

Dual Spiral Systems. (n.d.) Retrieved February 10, 2016, from http://www.dualspiralsystems.com/blown_film_dies.html

DuPont™ Selar® PA3426 Blends With Nylon 6 (2005). Retrieved February 17, 2016, from http://www.dupont.com//content/dam/dupont/products-and-services/packaging-materials-and-solutions/packaging-materials-and-solutions-landing/documents/selar_pa3426_nylon_blends.pdf

Ebnesajjad., S. (2012) *Plastic Films in Food Packaging: Materials, Technology and Applications*. Oxford: United Kingdom/William Andrew

Ecolean® Air Aseptic for ambient distribution (2015). Retrieved January 18, 2016, from https://www.ecolean.com/wp-content/uploads/ecolean-air-aseptic-ru.pdf

EVAL Americas. (n.d.) *Gas barrier properties of resins.* Technical Bulletin No. 110 Retrived: March 20, 2016 from http://www.eval-americas.com/media/36916/tb_no_110.pdf

Farber., B. (2004). The importance of meeting in person. Retrieved April 4, 2016, from https://www.entrepreneur.com/article/72596

Greiner Packaging News (2015). Swiss Packaging Award: Greiner Packaging's innovative packaging technology receives prestigious Swiss packaging award. Retrieved February 4, 2016, from http://www.webpackaging.com/en/portals/greinerpackaging/assets/11124715/swiss-packaging-award-greiner-packagings-innovative-packaging-technology-receives-prestigious-swiss-packaging-award/

Grivory EMS. Grivoty G 21 Natural 6506 (2005). Retrieved February 12, 2016, from http://ems.materialdatacenter.com/eg/en/main/ds/Grivory+G+21

Harrison Hayes, (n.d.).Technology Scouting Overview. Retrieved April 2, 2016, from http:// http://www.slideshare.net/lsakoda/technology-scouting-overview

Honeywell. (2006) Aegis® OXCE resin. Retrieved February 13, 2016, from http://www.honeywell-pmt.com/sm/aegis/documents/PP_Aegis_OXCE_Specification_sheet.pdf

InMat., (n.d.) Nanolok technology for high barrier applications. Retrieved February 27, 2016, from http://www.inmat.com/upload/files/packaging_brochure_0308_a.pdf

Järrehult., B. (2011). Two mindsets in one company. *Applied Innovation Management*, 2011 (1), 10-27

KHS Plasmax GmbH (2015). 1_InnoPET Plasmax, Optimum protection of sensitive products

KHS Plasmax press-release (2011). Amcor Confirms InnoPET Plasmax Coating as a Barrier Solution in North America. Retrieved February 4, 2016, from http://www.khs.com/nc/en/press/press-articles/press-releases/press-release/pressrelease/amcor-confirms-innopet-plasmax-coating-as-a-barrier-solution-in-north-america.html?type=98&print=1

Kim., L.Y. (2009). *The wiley encyclopedia of packaging technology (3rd edition)* New Jersey: John Wiley & Sons, Inc.

Lange., J., Wyser., Y. (2003). Recent Innovations in Barrier Technologies for Plastic Packaging – a Review. *Packaging Technology and Science,* 16, 149-158. http://dx.doi.org/10.1002/pts.621

Lee., D. (2014) *Chapter 6 – Antioxidative Packaging System*. In: Han, J.H. (ed.) Innovations in Food Packaging (2nd edition). San Diego: Academic Press.

Loapez-Rubio., A. (2011). *Chapter 10 - Ethylene- vinyl alcohol (EVOH) copolymers* In: Lagaron., J-M.(ed.) Multifunctional and nano-reinforced polymers for food packaging. Cambridge, United Kingdom: Woodhead Publishing Limited

M&G PoliProtectTM APB. (2013) Retrieved February 14, 2016, from http://www.mg-chemicals.com/uploads/media/attachment/0001/01/0f44e234858962b436fbba0d80158f451666104e.pdf

Mitsubishi (2012). High - Speed DLC coating equipment for Improved Gas Barrier Performance of PET Bottles, *Mitsubishi Heavy Industries Technical Review* 49 (4) Retrieved February 6, from https://www.mhi.co.jp/technology/review/pdf/e494/e494070.pdf

Mitsubishi (2015). High-barrier PET bottles are used for beer containers. Retrieved February 6, 2016, from http://www.mpi.co.jp/english/news/201508180801.html

Mitsubishi (n.d.) Retrieved February 5, 2016, from http://www.techbarrier.com/productinfo/search_application.html

Mitsubishi Gas Chemicals., (n.d.) Retrieved February 14, 2016, from http://www.mgc.co.jp/eng/products/nop/nmxd6/bottle.html

Mitsubishi Plastics News Release (2015). Mitsubishi Plastics develops a new high gas barrier SiOx film for retort food packaging. Retrieved February 5, 2016, from http://www.mpi.co.jp/english/news/201501290766.html

Mokwena, K., Tang, J. (2012). Ethylene Vinyl Alcohol: A Review of Barrier Properties for Packaging Shelf Stable Foods. *Critical Reviews in Food Science and Nutrition*, 52 (7), 640–650. http://dx.doi.org/10.1080/10408398.2010.504903

Nanocor., (n.d.) Imperm Grade 103 Superior gas barrier resin. Retrieved February 24, 2016, from http://www.nanocor.com/tech_sheets/i103.pdf

Plastics Technology (2012). 10-Layer, 10-Extruder Nano Blown Film: A Russian First. Retrieved February 10, 2016, from http://www.ptonline.com/articles/10-layer-10-extruder-nano-blown-film-a-russian-first

Plastics. (2014). Inert barrier technology: ultra-thin layer of silicon dioxide extends shelf life. Retrieved February 4, 2016, from http://www.plastics.gl/packaging/inert-barrier-technology-ultra-thin-layer-of-silicon-dioxide-extends-shelf-life/

Reger., G. (2010) Technology Foresight in Companies: From an Indicator to a Network and Process Perspective. *Technology Analysis & Strategic Management,* 13 (4), 533-553 http://dx.doi.org/10.1080/09537320127286

Reynolds., P. (2012) Chinese dairy introduces a new kind of aseptic pouch. Retrieved January 18, 2016, from http://www.packworld.com/package-design/structural/chinese-dairy-introduces-new-kind-aseptic-pouch

Rohrbeck.,R. (2006) Technology Scouting – Harnessing a Network of Experts for Competitive Advantage. *4th Seminar on project and innovation*. Retrieved April 24, 2016, from https://www.researchgate.net/publication/202288895

Rooney., M. (2005) *Chapter 8 - Oxygen-scavenging packaging*. In: Han, J.H. (ed.) Innovations in Food Packaging (1st edition). San Diego: Academic Press.

Rotstein., L., Singh.,P., Valentas.,K., (1997). *Handbook of food engineering practice*. New York: CRC Press

Schmid, M. (2010). *Whey protein-based coatings as sustainable barrier material in food packaging applications*. In: Singh., J. (ed.) 18th IAPRI World Packaging Conference. San Luis Obispo, CA: DEStech Publications,Inc..

Shohet, S. (2008). Using technology scouting as part of open innovation. Retrieved April 2, 2016, from https://www.frost.com/prod/servlet/cpo/142130204

Sidel (n.d.) Sidel's ACTIS Coating Economical Barrier Option for PET Bottles Retrieved February 15, 2016, from http://www.packagingnetwork.com/doc/sidels-actis-coating-economical-barrier-optio-0002

Solovyov., S., Goldman.,Y. (2008). *Mass Transport & Reactive Barriers in Packaging: Theory, Applications, and Design.* DEStech Publications, Inc

SpecialChem., (2012) NIPPON GOHSEI to Introduce its Latest Series of EVOH/Specialty Clay Composites at NPE 2012. Retrieved February 19, 2016, from http://polymer-additives.specialchem.com/news/industry-news/nippon-gohsei-to-introduce-its-latest-series-of-evoh-specialty-clay-composites-at-npe-2012

Struller., C., Kelly P., Copeland., J., V. Tobin, Assender.,H., Holliday.,C. & Rea., S. Aluminium oxide barrier films on polymeric web and their conversion for packaging applications. *Thin Solid Films* 553 (2014) 153–156. http://dx.doi.org/10.1016/j.tsf.2013.10.091

Strupinsky., G., Brody., A., L.,(1998). *A twenty-year retrospective on plastics: Oxygen barrier packaging materials.* Polymers, laminations & coatings conference. Book1. California: Tappi Press. http://www.gbv.de/dms/tib-ub-hannover/25315670X.pdf

Toppan Printing. GL film. (n.d.) Retrieved February 26, 2016, from http://www.toppan-usa.com/products/barrier_film/

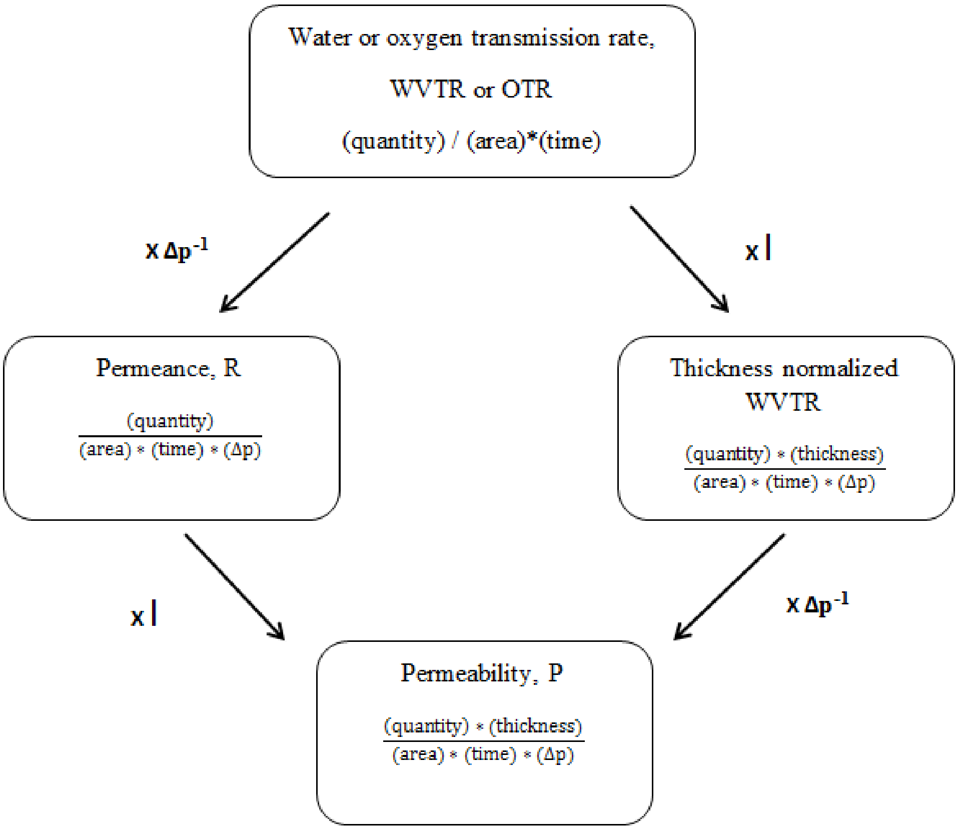
Toyo Seikan (n.d.) retrieved February 15, 2016, from https://www.toyo-seikan.co.jp/e/technique/petbottle/barrierbottle/

Vectra Ticona., (n.d.). Retrieved February 23, 2016, from http://www.hipolymers.com.ar/pdfs/vectra/diseno/Vectra%20brochure.pdf

Weissmann., D. (2015). The search for block..*Plastics in Packaging.* 22-23 Retrieved February 15, 2016, from http://www.cavonic.com/fileadmin/platzhirsche/mitglieder/4/4370/article.pdf

WikiInvest., (n.d.). Retrieved February 9, 2016, from http://www.wikinvest.com/stock/Constar_International_(CNST)/Proprietary_Technologies

Appendix A OTR and WVTR



Relation between WVTR, OTR, permeance, thickness normalized WVTR, and permeability coefficient

The permeability is the intrinsic characteristic of the polymeric material. It characterizes the volume of gas or mass of moisture passing through a certain thickness, per certain area and time, under unit partial-pressure difference between the two sides of the material. One of the common units used in packaging industry for oxygen permeability are **cm^3.mm/m^2day.atm**, for water permeability **g.mm/ m^2day**.

Transmission rate, on the other hand, is used to describe the barrier properties of the packaging material, not separately considered polymer.

Oxygen (OTR) or moisture transmission rate (WVTR) gives an understanding on the total volume of oxygen that passes through the polymer packaging. Especially, when multilayer structures are considered, OTR or WVTR is the preferable way of characterizing its barrier properties.

Appendix B Pouch evaluation

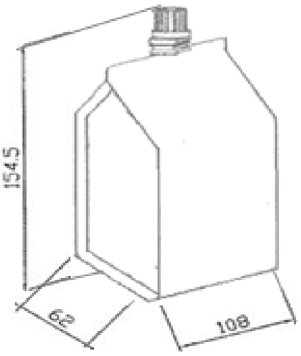
Pouch area calculations

Pouch with 500 ml volume:

Dimensions expressed in square meters
(in picture on the right values are in mm):

(0.108 x 0.1545) x2 = 0.033372m²
(0.062 x 0.1545) x2 = 0.019158m²
(0.062 x 0.108) x 2 = 0.006696m²

Total surface of the pouch = +/- 0.06m²

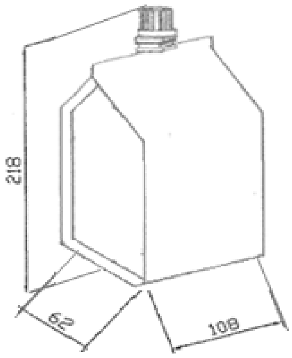


Pouch with 1000 ml volume:

Dimensions expressed in square meters
(in picture on the right values are in mm):

(0.108 x 0.218) x2 = 0.047088m²
(0.062 x 0.218) x2 = 0.027032m²
(0.062 x 0.108) x 2 = 0.006696m²

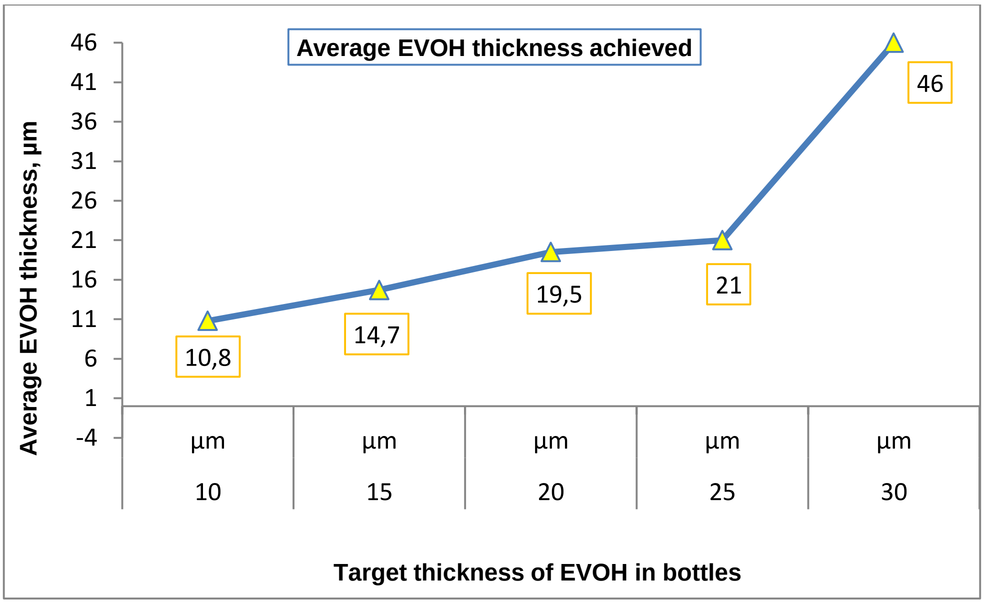
Total = +/- 0.08m²



Appendix C Bottle evaluation

C.1 Bottles used for measurements

Nutricia bottles measured by supplier and at Nutricia laboratory. 5 different thicknesses of EVOH – 10, 15, 20, 25 and 30 micron

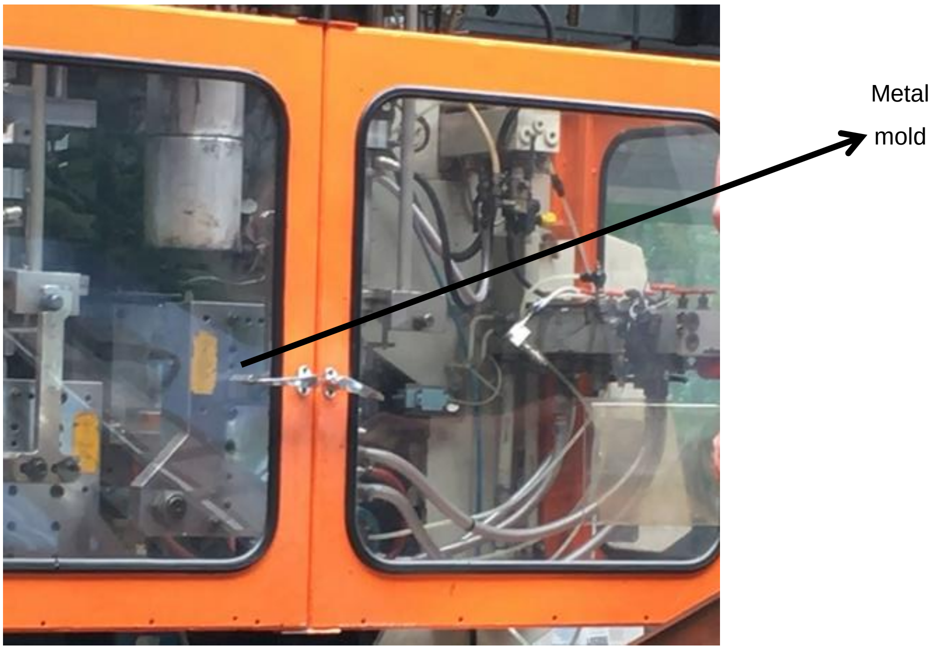


Average achieved EVOH thickness in bottles versus the target thickness.

C.2 Extrusion blow-molding

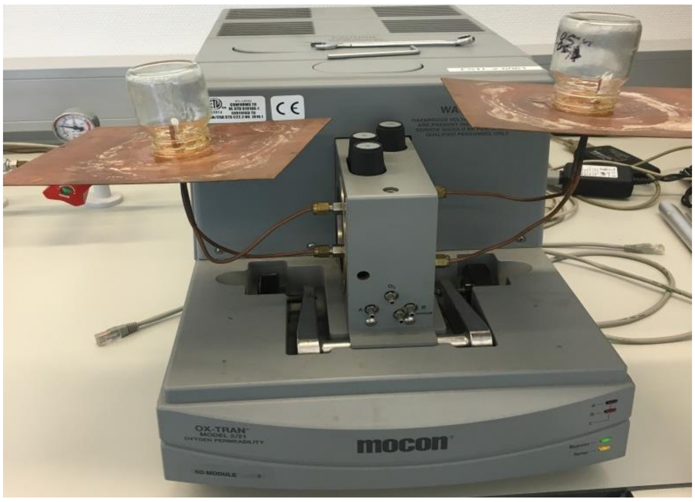
Extrusion blow-molding machine for plastic bottles

Plastic is melted and extruded into a hollow tub

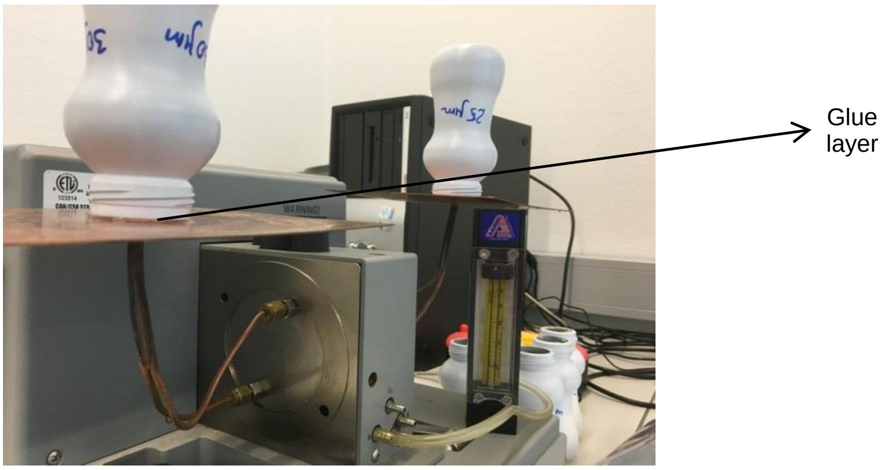


It is captured into a cooled metal bottle mold.

C.3 Mocon analyzer for OTR

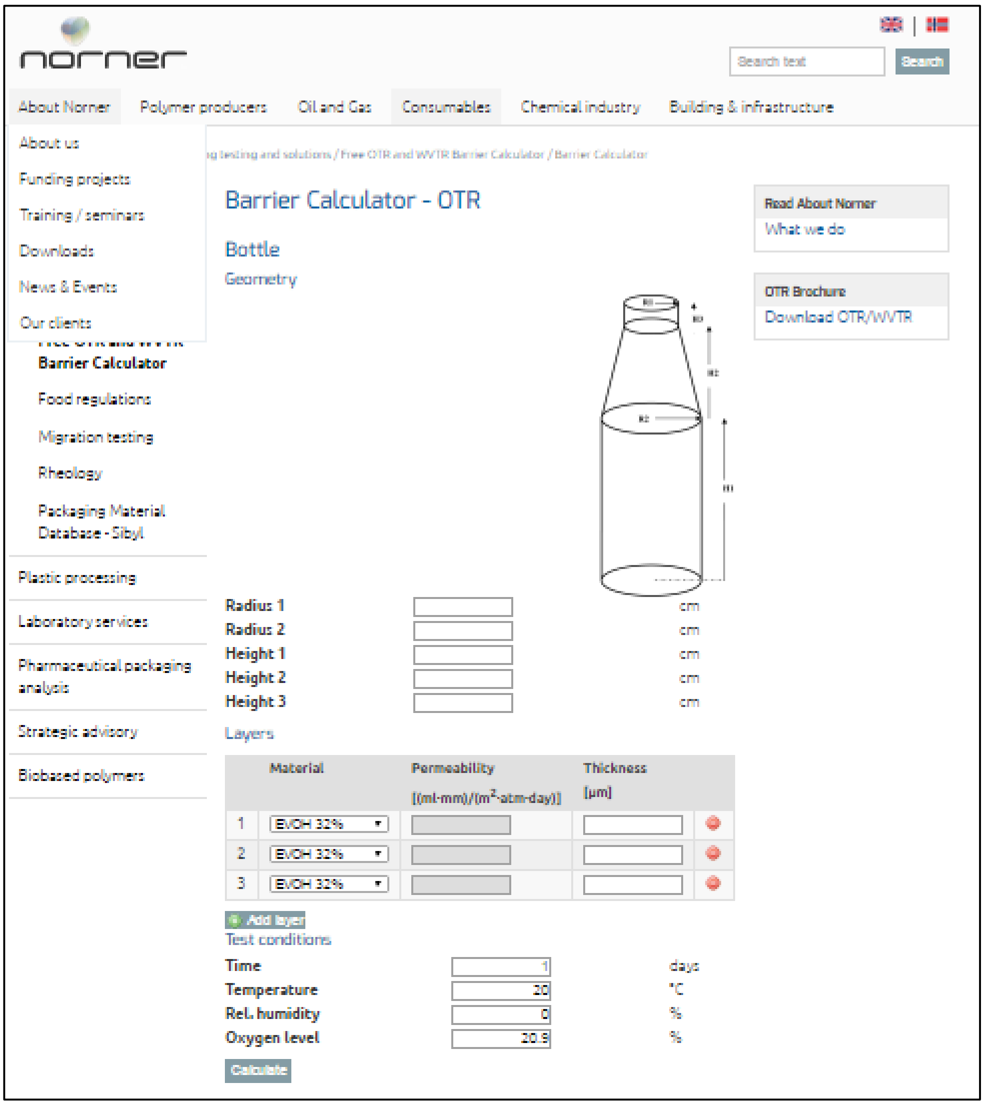


MOCON OX-TRAN Model 2/21, used to perform OTR measurements at Nutricia laboratory



Bottles glued on Mocon analyzer’s plates

C.4 Norner software



Barrier Calculator - OTR

Bottle

Geometry

Radius 1		cm
Radius 2		cm
Height 1		cm
Height 2		cm
Height 3		cm

Layers

	Material	Permeability [(ml-mm)/(m^2-atm-day)]	Thickness [µm]
1	EVOH 32%		
2	EVOH 32%		
3	EVOH 32%		

Test conditions

Time	1	days
Temperature	20	°C
Rel. humidity	0	%
Oxygen level	20.9	%

Screenshot of online Norner software, used to estimate the performance of EVOH barrier in Nutricia bottle

C.5 Oxygen ingress in bottle during current shelf-life

For the calculations of mass ingress of oxygen out of its volume, the **gas law formula has been used**, as follows:

$$P \times V = n \times R \times T$$

For the purpose of these calculations, it was modified as:

$$n = \frac{P \times V}{R \times T}$$

Where:

P – pressure, atm

V - volume, L

n - moles of gas

R- gas constant, 0.0821 L*atm/mol*K

T - temperature in Kelvins, 293 K

Further, mass of oxygen has been found by the formula:

$$m = n \times M$$

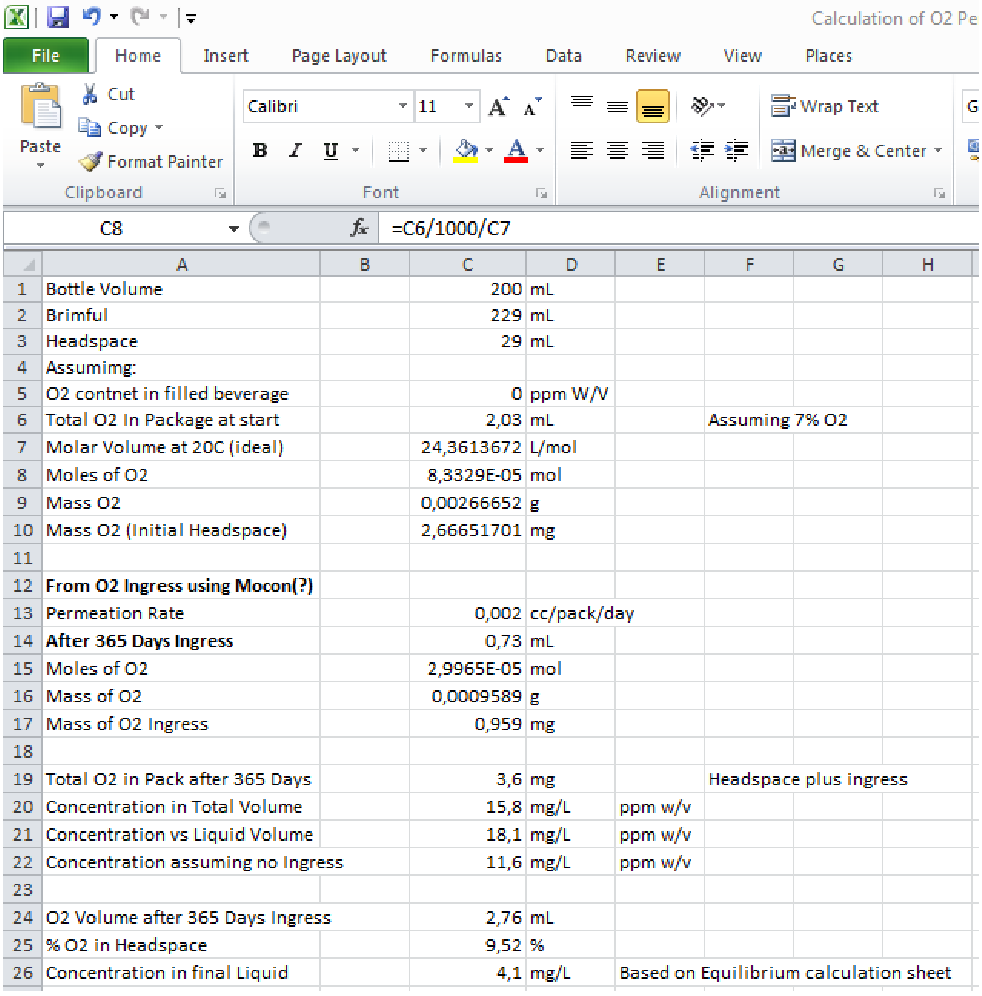
Where:

m – mass, g

n – moles of O_2

M – molar mass of O_2, 32g/mol

The conversion factor for oxygen mass from volume has been found to be 1,33. The excel sheet has been done for the purpose of fast calculation and comparison of different scenarios of material permeability (resulted due to the thickness change), headspace volume and/or oxygen content.



C8 =C6/1000/C7

	A	B	C	D	E	F	G	H
1	Bottle Volume		200	mL				
2	Brimful		229	mL				
3	Headspace		29	mL				
4	Assumimg:							
5	O2 contnet in filled beverage		0	ppm W/V				
6	Total O2 In Package at start		2,03	mL		Assuming 7% O2		
7	Molar Volume at 20C (ideal)		24,3613672	L/mol				
8	Moles of O2		8,3329E-05	mol				
9	Mass O2		0,00266652	g				
10	Mass O2 (Initial Headspace)		2,66651701	mg				
11								
12	**From O2 Ingress using Mocon(?)**							
13	Permeation Rate		0,002	cc/pack/day				
14	**After 365 Days Ingress**		0,73	mL				
15	Moles of O2		2,9965E-05	mol				
16	Mass of O2		0,0009589	g				
17	Mass of O2 Ingress		0,959	mg				
18								
19	Total O2 in Pack after 365 Days		3,6	mg		Headspace plus ingress		
20	Concentration in Total Volume		15,8	mg/L	ppm w/v			
21	Concentration vs Liquid Volume		18,1	mg/L	ppm w/v			
22	Concentration assuming no Ingress		11,6	mg/L	ppm w/v			
23								
24	O2 Volume after 365 Days Ingress		2,76	mL				
25	% O2 in Headspace		9,52	%				
26	Concentration in final Liquid		4,1	mg/L	Based on Equilibrium calculation sheet			