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List of abbreviations

CO2TR	Carbon dioxide transmission rate
EMAP	Equilibrium modified atmosphere packaging
LDPE	Low density polyethylene
MAP	Modified atmosphere packaging
MFC	Microfibrillated cellulose
OPP	Oriented polypropylene
OTR	Oxygen transmission rate
PET	Polyethyleneterephthalate
PHA	Polyhydroxyalcanoate
PP	Polypropylene
RTE	Ready-to-eat
WVTR	Water vapour transmission rate

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Executive Summary

This document reports on the shelf-life assessment of a selection of packaged food products within the substitution Work Package (WP4) in the project R3PACK. The selected foods represent different product categories with specific requirements for packaging: dry and fatty snack foods, dairy products and ready-to-eat fruits and vegetables. These products and their shelf life requirements are assessed qualitatively and quantitatively using a combination of experimental characterization, literature search and shelf life simulations. This document can also serve as a starting point to design storage tests for the products described within and similar products.

Introduction

Packaging fulfils many functions: among others, it provides a display for information and advertisement, a convenient way to control the amount of the packaged product and a speedy checkout. Perhaps the most important function of packaging, at least on a macroeconomic and ecological scale, is the protection it provides for the packaged good, not just from dirt, but also from the atmosphere. It is this function, which extends the shelf life of the product compared to the unpackaged version, facilitating logistics and preventing food losses. On the downside, many food products are packaged in fossil based materials ("plastics"), which come with a host of environmental issues, chiefly their persistence in the environment if they end up there and their often limited recyclability.

The packaging materials developed within WP4 of R3PACK, paper-based packaging with preferably bio-based functionalization, are intended to be used for food packaging as more sustainable substitutes. With this intended transition, the protection of the packaged food has to be ensured for sustainability to be upheld. To this end, the packaging requirements of the respective foods need to be understood.

The purpose of this task and this document is to illuminate the packaging needs of some selected foods in case studies and to provide guidelines on how changes in packaging may affect the shelf life of the packaged food. The primary tool used to this effect are shelf life simulations. In these simulations, the most relevant spoilage mechanisms of the packaged food are described mathematically. Prerequisites for this are the identification of the relevant spoilage mechanisms and the determination of the corresponding parameters. This report follows different products through the assessment, parameter determination and shelf-life simulations with variations in the packaging and storage scenarios to provide some insight into potential substitutions of the established, fossil-based packaging materials.

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1. Initial Data Collection and Qualitative Assessment

The initial step of any shelf life study is the identification of the main spoilage mechanisms. The case studies in this work package were set up to represent a range of products with different requirements on the packaging, which were determined by interviews with the producing companies and a qualitative classification of the products.

1.1 Selected Food Products for Case Studies

The food products for the case studies were chosen to represent different types of food, requirements for the respective packaging and the food producers in the consortium. The chosen foods fall into three categories: snack foods (two variants of crackers, peanut flips, a pea-based snack and a puffed potato-based snack), dairy products (butter, shredded Emmental cheese and crème fraîche) and prepared produce (pineapple wedges and bagged lamb's lettuce). These selected foods will be described further below.

1.2 Company Interviews

Initial Interviews were conducted with the producing companies to establish the basics for the shelf life assessment. In these interviews, the following data were collected: the current shelf life of the packaged product, how the shelf life is determined, the current packaging setup (material, barriers, modified atmosphere) and the main factors considered to be shelf life limiting. Apart from preparing the following studies, the interviews also served to align the experience between the companies and the researcher.

1.3 Qualitative Assessment of Requirements for Packaging

Based on the conducted interviews and general experience on the respective food category, the following initial assessment can be made:

- The snack foods are likely susceptible to the uptake of water vapour, leading to a loss of the desired crunchy texture, and the uptake of oxygen through the oxidation of unsaturated fatty acids. In addition, their high fat content necessitates a grease/oil barrier.
- The dairy products can likewise be somewhat susceptible to fat oxidation, though generally not strongly. They are also subject to more specific processes. In the case of crème fraîche, whey separation can occur; this is an intrinsic process, which cannot be mitigated by packaging, and will not be considered in the shelf life studies. Since the crème fraîche is pasteurized, microbiological spoilage is not a common issue. The shredded cheese on the other hand is susceptible to microbiological spoilage.

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This is addressed by using a low oxygen modified atmosphere (80% N_2, 18% CO_2, 2% O_2). Thus, the oxygen content in the package can be used as a shelf-life limiting criterion (the goal is 2% O_2, 6-8% are the maximum range). The dairy products also have a significant fat content (especially the butter), and thus require a grease/oil barrier.

- Finally, the packaged lamb's lettuce and pineapple wedges are metabolically active. Thus, they breathe, ripen and are susceptible to microbiological spoilage. These products benefit from an equilibrium modified atmosphere packaging (EMAP) approach, with the goal to keep the steady-state atmosphere at a favourable level to both slow down the produce's metabolism and suppress harmful microorganisms while preventing anoxic conditions, which can cause the produce to perish and fermentation processes to start. For the pineapple wedges, an equilibrium O_2 content of 10% is commonly observed, with a varying CO_2 content. For the bagged lamb's lettuce, which is packaged in a closed bag, the end of shelf life usually occurs when the headspace oxygen is consumed.

This initial assessment informs the food characterization experiments to be conducted and the setup of the respective shelf-life models. Table 1 contains an overview of the anticipated shelf-life criteria and characterizations as well as the established shelf life of the different products.

Table 1 Overview over the selected foods for case studies, the anticipated spoilage factors and criteria for the shelf life assessment as well as the established shelf life as given by the respective producer.

Category	Food product	Water vapour	Oxidation	MAP	Other	Shelf life
Snacks	Peanut flips	✓	✓			6 mo
	Puffed snacks	✓	✓			6 mo
	Pea-based Snack	✓	✓			6 mo
	Emmental Crackers	✓	✓			8 mo
	Pizza Crackers	✓	✓			8 mo
Dairy	Butter		✓			75-90 d
	Shredded cheese		✓	✓	Microbiology	2 mo
	Crème fraîche		✓		Whey separation	40 d
RTE Produce	Bagged lamb's lettuce			EMAP	Microbiology	10-12 d
	Pineapple wedges			EMAP	Microbiology	6-8 d

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2. Characterization of Food Products and Literature Survey

Prior to performing shelf life simulations, it is necessary to obtain sufficient information on the food products to be analysed. For this purpose, the previously determined spoilage factors need to be quantitatively characterized. Samples of the snacks and dairy products were provided by the respective producer and analysed as described below. Were necessary, the analysis was supplemented by a brief literature review. For the produce, respiration data was collected from the scientific literature.

2.1. Water Vapour Sorption Characteristics

The water vapour sorption characteristics of the snack foods were determined experimentally using a vapour sorption analyser (proUmid SPSx-1μ). In this device, the samples are subjected to a predetermined temperature-humidity profile and weighed at regular intervals. In this case, a constant temperature and a humidity profile going from 0% to 90% relative humidity in steps of 10% were applied. Each step is held until the weight of the samples is stable over a sufficient time to determine the equilibrium weight. From the collected data, the sorption isotherm (i.e. the equilibrium water content at a given humidity) and the sorption kinetics were determined. The device and the used samples are shown in Figure 1. To prevent interference from other factors, the chamber is held under a nitrogen atmosphere.

Figure 1 Samples in the vapour sorption analyser. The snack food samples are in positions 5 through 9. Positions 1 through 4 have been blurred.

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The conversion from the dynamic measurement to the sorption isotherm and kinetics will be briefly discussed for the puffed snacks. Figure 2 shows the humidity profile and the corresponding weight change during the measurement. As can be seen, the puffed snacks initially respond quickly to the changes in humidity at each step. Afterwards, the weight change slows down, until a stable weight is reached. At this point, the water content in the sample is in equilibrium with the humidity in the measurement chamber. At a relative humidity of 80%, a small drop in weight can be seen, which points to the occurrence of some structural changes in the matrix and can be linked to a possible significant change in texture. While the isotherm can be derived directly from the equilibrium weight, the following procedure is applied to the raw data in order to extract the full information required for modelling: for every segment of the results (as defined by the steps in the humidity profile), a fit is applied on the recorded weight. This fit provides the initial and final weight of that segment as well as a rate change parameter (i.e. a kinetic constant). From the equilibrium weight of the initial segment at 0% relative humidity, the dry weight of the analysed product is determined. The equilibrium weight of the subsequent steps relative to the dry weight provides the water content. To verify the fitting procedure, the sorption model implemented in the modelling framework is applied to reproduce the sorption experiment with the derived parameters. Figure 3 shows the simulated reproduction in comparison with the measurement. Model and experiment agree well, showing that the fitting procedure delivered suitable parameters for further simulation.

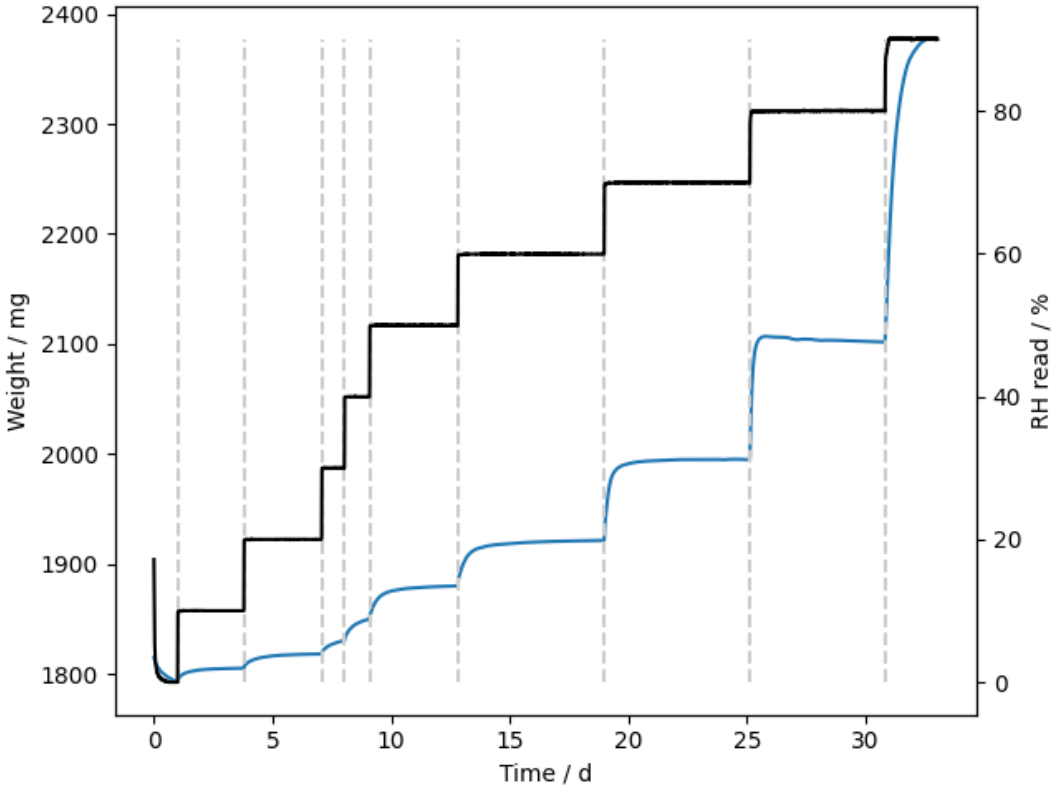

Figure 2 Dynamic weight change (blue, left axis) in response to the pre-determined humidity profile (black, right axis) for the puffed snacks. The dashed vertical lines highlight the steps in the humidity profile.

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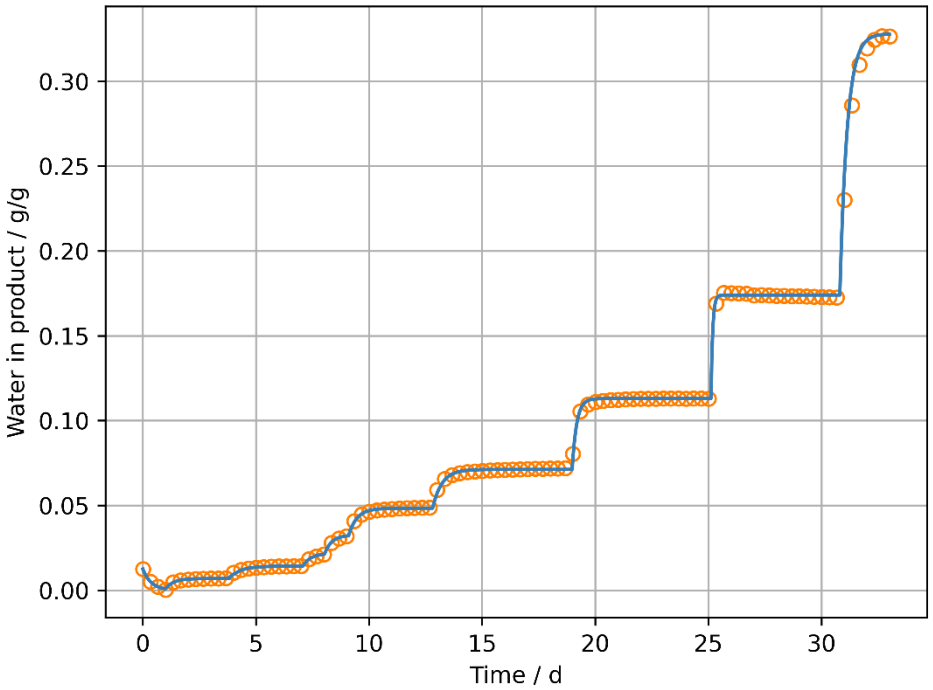

Figure 3 Verification of the fitted model parameters against the measured water content of puffed snacks. The line shows the result of the simulation, circles show the measurement with a reduced number of points for improved visibility.

Overall, the different snack foods show very similar characteristics, as is shown in Figure 4. The isotherms of the tested items lie almost on top of one another over wide ranges of relative humidity. Especially the two cracker variants are very similar to each other overall. The kinetic constants vary somewhat erratically around similar values, with a notable spike at 80% relative humidity for the non-cracker foods. A slight scattering of kinetic constants can often be observed for food samples and can be attributed to the complex nature of such items. The spike around 80% relative humidity coincides with the dropping-off of the measured weight observed at this point. If a deeper relationship exists cannot be categorically stated, but a relationship to some internal changes is very well possible. The similarity between the different products has the great benefit, that few packaging materials can be suitable for all of the studied snack products, and quite possibly many more.

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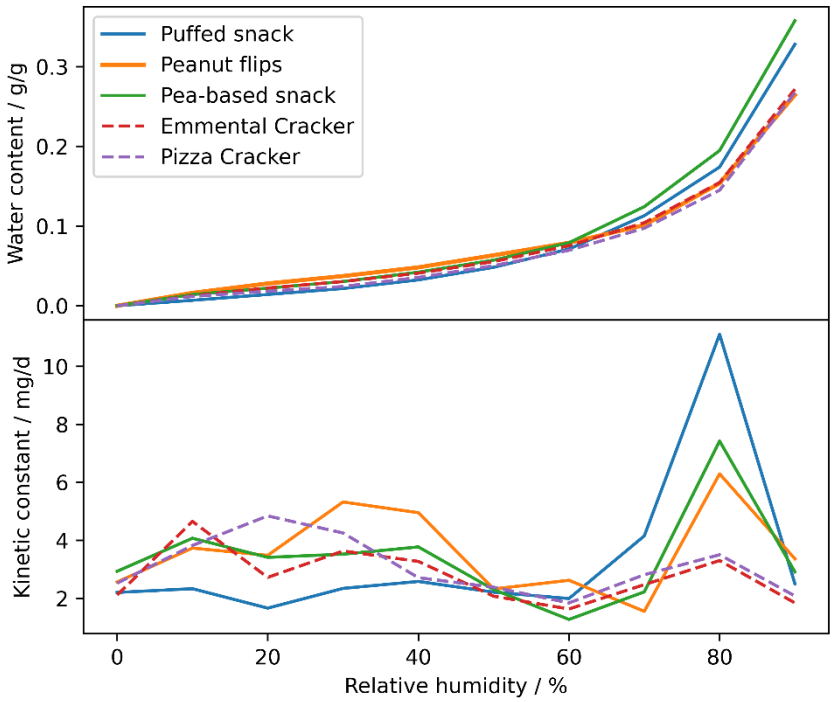

Figure 4 Isotherms (top) and kinetic constants (bottom) of the tested snack foods as derived from the fitting to the experimental data.

2.2. Oxygen Consumption Characteristics

An experimental determination of the oxygen consumption of the products was attempted by placing samples in sealed chambers and monitoring the oxygen concentration inside the chambers. For the cheese and crème fraîche, oxygen consumption was observed, however in conjunction with a rise in carbon dioxide concentration too high to account for regular respiration processes. This combination of trends indicates fermentation, which makes a determination of oxidation characteristics impossible and highlights the importance of good quality sealing. For the butter, no significant oxidation could be observed. Due to butter being rather dense, oxidation rates are limited by diffusion of oxygen through the butter, which occurs very slowly. To mitigate, literature data was collected. While not all processes reported in the literature were used in the analysis, some sources are mentioned exemplarily to provide information on additional aspects of the shelf life of these products.

Oxidation data on butter was collected from Soulti and Roussis, reported as peroxide values, who also studied the possible antioxidant properties of phenolic compounds in butter.[1] They stored the butter at highly elevated temperatures (50 °C and 110 °C) to accelerate the oxidation, which also removes the limitations of diffusion due to the butter being melted. In a similar vein, Gonzalez *et al.* report the correlation of oxidation and texture changes for butter with modified fatty acid profiles.[2] Park *et al.* describe the changes of acidity in butter due to the release of butyric acid, which negatively affects the sensory quality.[3] Based on their criteria, they estimated a shelf life of 22 months at 10

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°C. This time period is much longer than the expected shelf life for the butter studied here. Finally, photooxidation of butter was studied by Emmons *et al.*[4] While butter is photosensitive, it is commonly packaged in opaque packaging material. Thus, the factor of photooxidation is not studied here.

A similar search for crème fraîche, extended to include sour cream as a similar product, produced scant results related to the oxidation of fatty acids or other shelf life limiting processes. As mentioned above, possible whey separation was not included since it cannot be addressed by the packaging. A study by Salem *et al.* includes data on the oxidation of sour cream made from buffalo milk and was used to determine a rate for the oxidation.[5]

For the snacks, the samples were stored at elevated temperature to increase the oxidation speed (30°C for the initial 90 days, corresponding to a factor of two compared to room temperature, 46°C afterwards, corresponding to an acceleration factor of approximately 6). During storage, the pressure was monitored constantly by a sensor in the measurement chamber. Lacking other processes that modify the atmosphere, any decline in pressure is due to oxygen consumption. The sudden step that occurs at the same time of the temperature change is due to the latter. Otherwise, venting of the measurement chambers cause visible fluctuations. Some additional spiked are caused by sensor artefacts. Despite the acceleration, the oxygen consumption by the snacks occurred very slowly. Fat oxidation generally happens in phases: an initiation phase, where oxygen is consumed linearly, followed by an exponential propagation phase, which in turn leads into the termination phase once the amount of oxidisable (unsaturated) fatty acids is consumed. Over the trial period, the oxygen consumption remained firmly in the linear phase (see Figure 5). Converted to oxygen consumption, all samples consumed no more than 0.8 mmol/g. Converted to oxygen consumption per fat, the maximum value lies below 3 mmol/g. This is far below the value of 20 mmol/kg (fat), at which oxidation products become noticeable upon consumption. At the end of the measurement, no rancid smell was noticed.

Due to the accelerated storage, the 180 days measurement correspond to roughly two years of storage at room temperature, far beyond the shelf life of six to eight months for the different snacks. It can thus be concluded, that the studied snacks are not very susceptible to oxidation, especially compared to the sorption of water vapour and consequent loss of texture.

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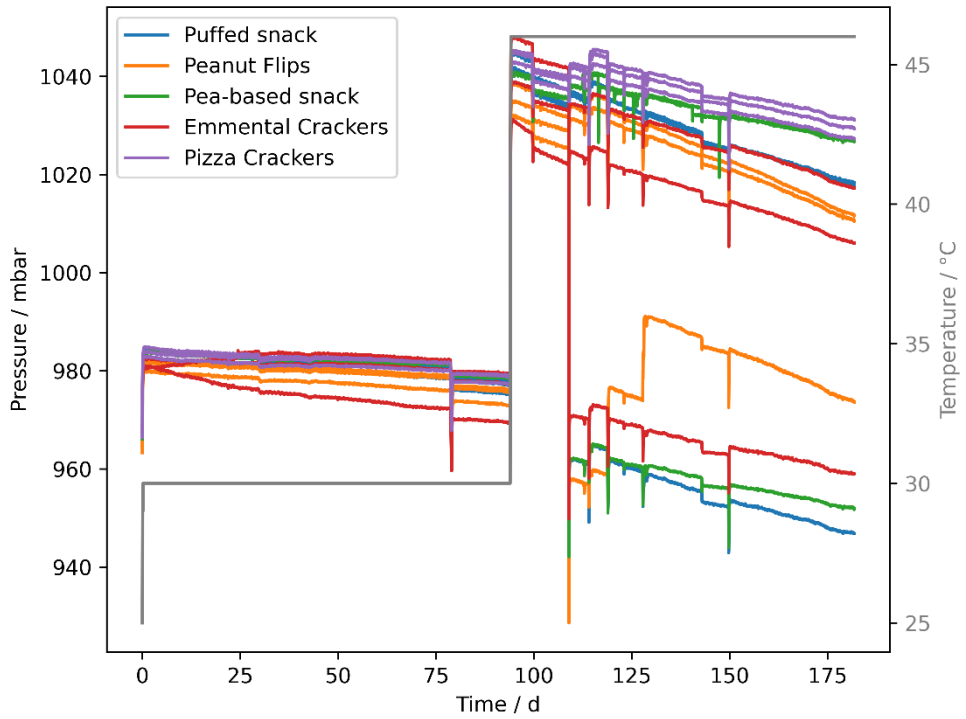

Figure 5 Results from pressure measurements in accelerated storage. The decline in pressure is due to oxygen consumption by the stored samples. Every sample was measured in triplicate. Sudden steps are due to temperature change, venting of the measurement chambers or artefacts caused be the sensor. The temperature is shown in grey.

2.3. Respiration Characteristics

Since they consist of living tissue, fruits and vegetables are complex foods which can undergo a range of changes during storage. This applies to cut fruits, such as pineapple wedges, too, though the cutting process introduces injuries and thus additional stressors, which tend to both increase the metabolism and accelerate further changes. These changes depend on the specific produce, but may affect texture (softening), flavour (sweetness) and colour (browning). Generally, all changes occurring in the produce depend on the headspace atmosphere. A reduced amount of oxygen tends to reduce the rate of most processes contributing to spoilage and is advised. However, anoxic conditions should be avoided since they can give rise to harmful microbial fermentation.

In these case studies, the effect of the packaging on the equilibrium headspace composition is analysed for the pineapple wedges and the lamb's lettuce. The subsequent processes, such as browning, softening etc. are not considered. The relevant information was collected from the literature. A brief overview of some studies may also be useful for additional information to the findings reported below.

For pineapple wedges, respiration rates were taken from a very detailed study by Benitéz *et al.*[6] This study also includes information on the loss of texture and temperature dependence as well as a heat transfer model. For the simplified models used here, only the respiration rate was adapted. It should also be

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mentioned, that the respiration rate can vary between different cultivars and degrees of ripeness, as was explored in a paper by Finnegan *et al.*[7] As shown there, riper pineapples have an increased respiration rate compared to less ripe ones. Another finding from this source was that the respiration rate is highest right after cutting and stabilizes at a lower value over the course of a day. A more recent study by Gomez *et al.* provides a phenomenological model for the changes in firmness and colour of cut pineapple under different EMAP conditions.[8] In contrast to the findings from the simulations reported below, which are based on physiological models, the cited studies used parametric models (e.g. polynomial fits).

For lamb's lettuce, respiration rates were reported by Jacobs together with a detailed analysis of other metabolic changes and spectroscopic characterizations.[9] An additional study on the changes in nutritional value and sensory evaluation has been published by Preti and Vinci.[10]

Spoilage through microbiological infestation (moulds, yeasts and bacteria) is a possibility for all fresh produce. Conditions conducive to the flourishing of microorganisms depend on the species. In general, an elevated partial pressure of carbon dioxide is helpful to suppress the growth of microorganisms. Thus, microorganisms are not considered explicitly in the studies below since they are addressed by the EMAP.

3. Shelf Life Modelling for case studies

Shelf life simulations were performed using the modelling framework and tool developed at Fraunhofer IVV (IVV Shelf Life Modelling Tool, IVVSL). This software allows for the construction of tailor-made models from common components. For the following case studies, the models were constructed based on the initial qualitative assessment and parameterized by values obtained in the characterization and literature search. A brief description of the mathematical makeup of the model components is given in Section 5.

3.1. Snack Foods

Based on the determined characteristics of the snack foods, the corresponding shelf life models focused on the sorption of water and excluded the oxidation. Packaging dimensions were based on the packaging currently in use. A distinction was made between packaging for the crackers and the other snacks (puffed snacks, flips, pea-based snacks). The conventional packaging is made from metallized OPP bags with an OTR of 50 $cm^3/m^2/d$ and a WVTR of 0.5 $g/m^2/d$ for crackers and an OTR of 45 $cm^3/m^2/d$ and a WVTR of 0.25 $g/m^2/d$ for the other snacks. To match the different packaging designs for crackers and other snack foods, the snack foods will be discussed in these two groups,

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referred to as "snacks" and "crackers" from here on. In both cases, a 400 day storage period was simulated, exceeding the established shelf life significantly.

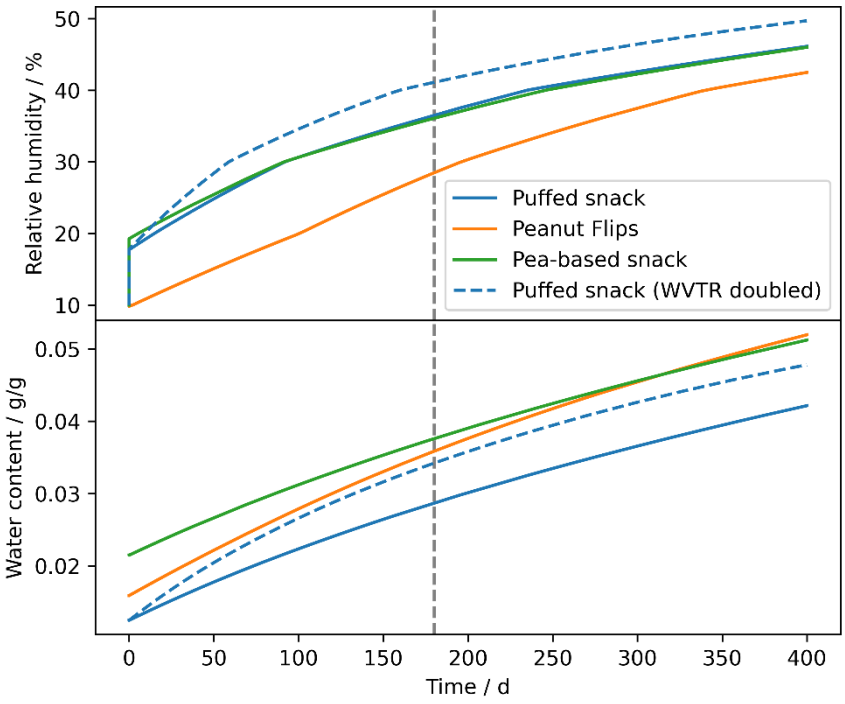

Figure 6 Shelf life simulation results for packaged snacks stored at constant climate conditions. Top: headspace relative humidity, bottom: water content in product. The dashed grey line indicates the established shelf life (six months).

Simulation results for the snacks under constant storage conditions (21 °C, 60% relative humidity) are shown in Figure 6. The initial water content of the snacks was taken from the characterization experiments and an initial headspace humidity of 10% was assumed. Hence, there is a quick equilibration of the relative humidity at the beginning of the simulation in some cases. From the starting point, water vapour slowly permeates into the headspace, closely followed by the increasing water content of the product. The water content at the established shelf life is assumed to be within the acceptable range, though higher values may well be acceptable. For the puffed snacks, a comparison was run with a doubled WVTR of the packaging. This reduces the time until the assumed limiting value of water content is reached. At the conventional shelf life time, the water content is approximately 20% higher compared to the WVTR reference, corresponding to a longer storage time in the conventional packaging.

Results from the corresponding constant storage simulations for crackers are shown in Figure 7. Overall, the findings are similar to those for the snacks. As shown by the characterization, the two cracker variants react like one another and reach an almost identical water content at the time of the established shelf life. Likewise, doubling the WVTR of the packaging for the Emmental crackers leads to the same water content being reached in little more than half the time.

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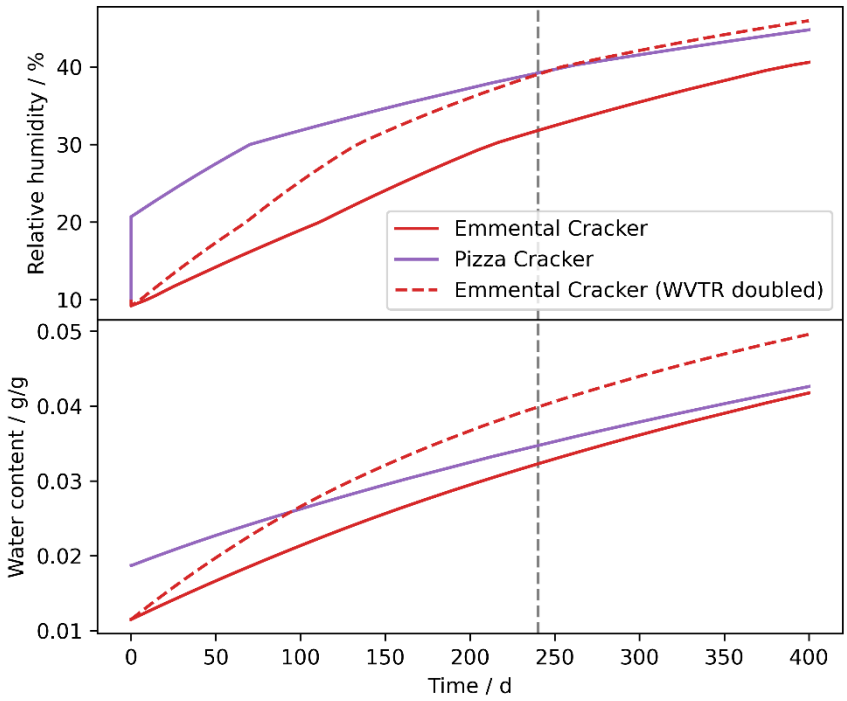

Figure 7 Shelf life simulation results for packaged crackers stored at constant climate conditions. Top: headspace relative humidity, bottom: water content in product. The dashed grey line indicates the established shelf life (eight months).

The selected storage conditions are a good representation for indoor storage in many parts of Europe. In order to simulate a more stressful environment, additional simulations were carried out with the puffed snacks and the Emmental Crackers as representatives of their respective subcategory stored at 80% relative humidity. The simulation results are shown in Figure 8. The higher humidity leads to a faster uptake of water vapour into the headspace and, consequently, to a faster increasing water content. The reached water content at the established shelf life is less dramatically affected as is the case for the increased WVTR.

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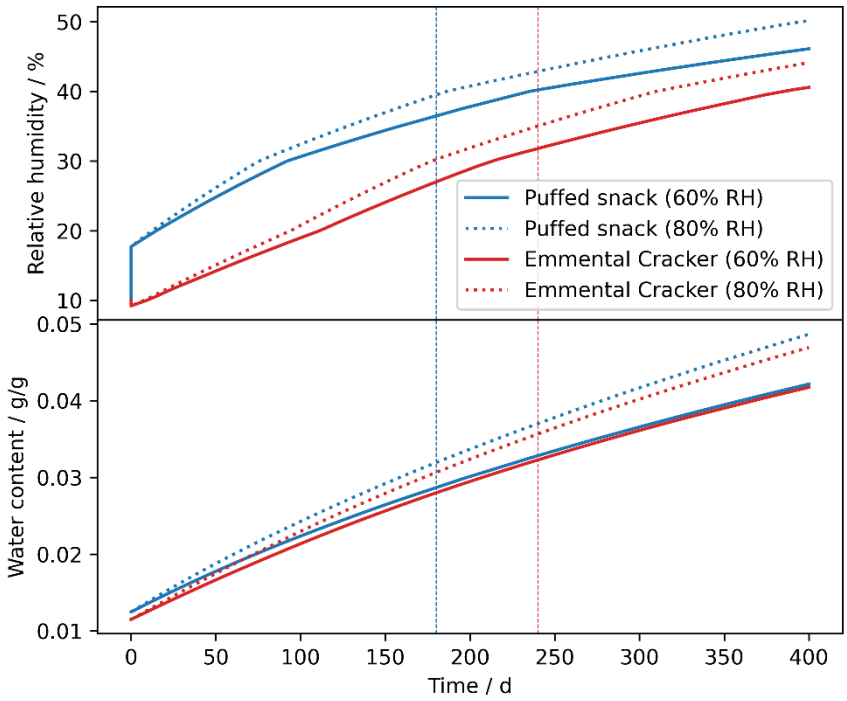

Figure 8 Simulation results for puffed snacks and Emmental crackers stored at 80% relative humidity in comparison to 60%. The vertical lines indicate the respective established shelf life.

Overall, the studies snack foods share common responses to water vapour among themselves. The water content reached at the established shelf life can generally be assumed to be a save value. A constant humidity of 60% at 21 °C is relatively harsh compared to common conditions within Europe (especially in winter, the outside relative humidity may be higher, but with the lower temperatures this translates to a lower water vapour pressure and thus to lower relative humidity at room temperature). Thus, a higher water content, such as that reached in the simulations with heightened humidity or larger WVTR may well be tolerable.

Nevertheless, snack foods such as those studies here, put high demands on the packaging. Possible tolerances notwithstanding, the demands on the water vapour barrier are high. The WVTR values provided by the established packaging are an order of magnitude below the values provided by R3PACK materials so far. Since water vapour barriers are notoriously difficult for bio based materials, non-bio based materials may be required to some degree for this type of product. Compromises on the water vapour barrier may require adaptation of the logistics to compensate. As evidenced by the observations made in the oxygen consumption characterization and the moderate OTR of the established packaging, the demands on the oxygen barrier are much lower. In addition to specific gas barriers, the packaging used for snack foods like flips and chips needs to be gastight, since bags are usually inflated for cushioning, and provide a good barrier to grease.

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3.2. Dairy Products

As discussed above in the initial assessment, the studied dairy products have some distinct characteristics. Despite all of them having a high fat content, oxidation of fatty acids could not be observed experimentally, but is reported in literature. Given their diversity, each of the different dairy products will be discussed separately.

Cheese

For the shredded Emmental cheese, the headspace composition was used as the shelf life limiting criterion, since other criteria could not be determined. Cheese, being produced by microbiological processes, is a fairly complex type of food and its shelf life is strongly affected by its microbiological ecosystem. While this in turn adds to the complexity, it is also controlled by the headspace composition. Combined with the experience by the manufacturer regarding the oxygen content during shelf life, this is a suitable choice for the criterion.

Apart from the oxygen concentration in the headspace (initially 2%, limit 6-8%), the carbon dioxide level is initially at 18%. The remaining 80% are nitrogen which is both metabolically inactive and at atmospheric levels. Thus, nitrogen is not considered in the simulations. Carbon dioxide is relevant, as it acts as a suppressant for a wide range of microorganisms. While a sharp cut-off for its efficacy cannot be categorically given, remaining close to the initial value is generally preferable. Here, an assumption must be made regarding the packaging's permeability towards carbon dioxide, which is not routinely determined for most packaging materials. However, it is usually higher than the oxygen permeability for most materials. For the simulations here, a CO2TR of four times the OTR was assumed. This is a fairly high value, introducing a safety margin into any conclusions drawn from the carbon dioxide concentration in the headspace. OTR values of 1, 5, 10 and 20 $\mathrm{cm}^3 \cdot/(\mathrm{m}^2 \cdot \mathrm{d})$ were applied. Storage at 5 °C under regular external atmosphere was assumed for a simulated storage period of 60 days.

The simulation results are shown in Figure 9. All simulated packaging setups keep the oxygen well within the tolerance over the storage period. This indicates that a well-sealed material with moderate OTR is suitable for the storage of the shredded Emmental cheese. Due to the higher assumed CO2TR, the decline of carbon dioxide concentration is more pronounced than the influx of oxygen. The consequence of this observation cannot be straightforwardly determined since the suppressing effect of carbon dioxide on the growth of microorganisms is species dependent. However, the growth rate of microorganisms generally falls parabolically with increasing concentration of carbon dioxide. Thus, maintaining a higher concentration of carbon dioxide is favourable. A material with an OTR of 10 and a hypothetical CO2TR of 40 would provide a concentration of 15% carbon dioxide (15 kPa) at the end of the targeted shelf life. This modest decay of carbon dioxide can be taken as a safe margin. For materials with a smaller conversion from OTR to CO2TR, the barrier requirements can be assumed to be much less strict. The oxygen barrier requirements are achievable with R3PACK materials.

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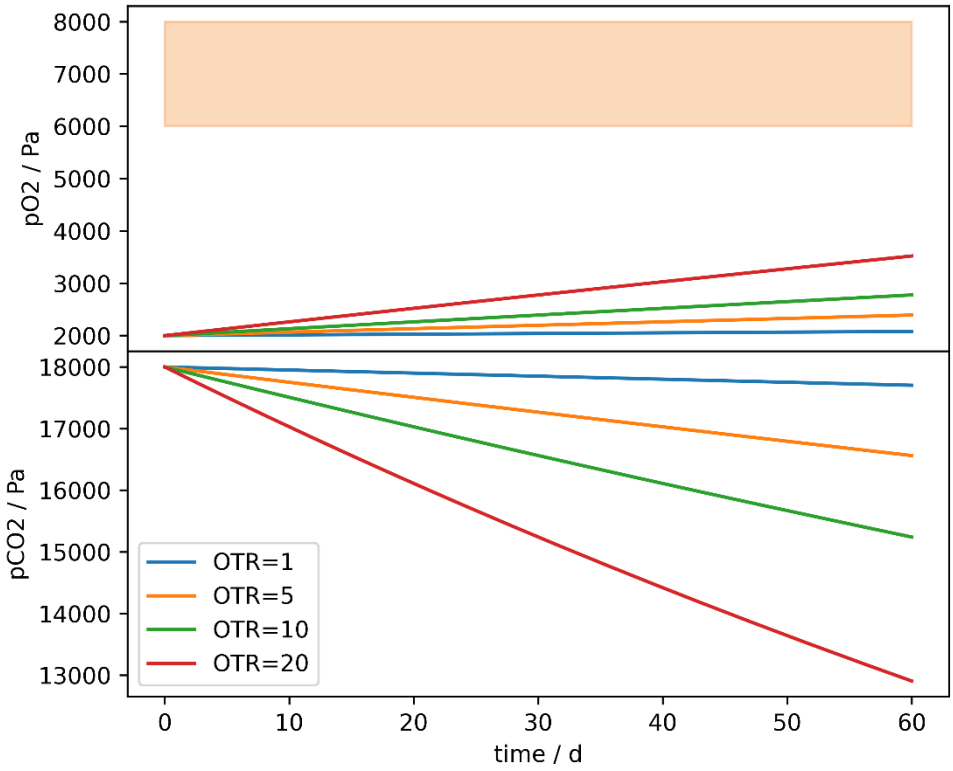

Figure 9 Simulation results for the headspace composition of cheese stored in bags with different OTR values (in cm³/m²/g). The critical oxygen concentration is indicated by the rectangle at the top.

Butter

Based on the oxidation rate gathered from the literature, simulations were performed considering autoxidation of fatty acids and the permeation of oxygen. As a baseline, a package with an OTR of 0.5 cm³/m²/d was assumed. This value is significantly below the values reported within R3PACK so far, which implies that butter may be a very challenging product to package. To represent the PHA based materials developed within R3PACK, OTRs of 5 and 10 cm³/m²/d were considered as well. The simulated temperature was 4 °C.

Figure 10 shows the results from the simulations. The oxygen partial pressure in the (small) headspace decreases rapidly and remains at a low level for all packaging scenarios, indicating that the oxidation occurs faster than the oxygen permeation. The peroxide number rises faster for more permeable materials. While the peroxide number remains well below values considered rancid (20 mmol/kg), this can be misleading: the peroxide value is given for the entire mass of the butter, but the oxidation occurs mainly at the surface. Thus, surface darkening may well be observed under these conditions. Likewise, a rancid flavour at the surface layer is possible. Oxidation deeper in the butter is limited by diffusion, which is a slow process. The exact consequences of switching to a lower oxygen barrier cannot be deduced from the available data and would have to be determined by testing.

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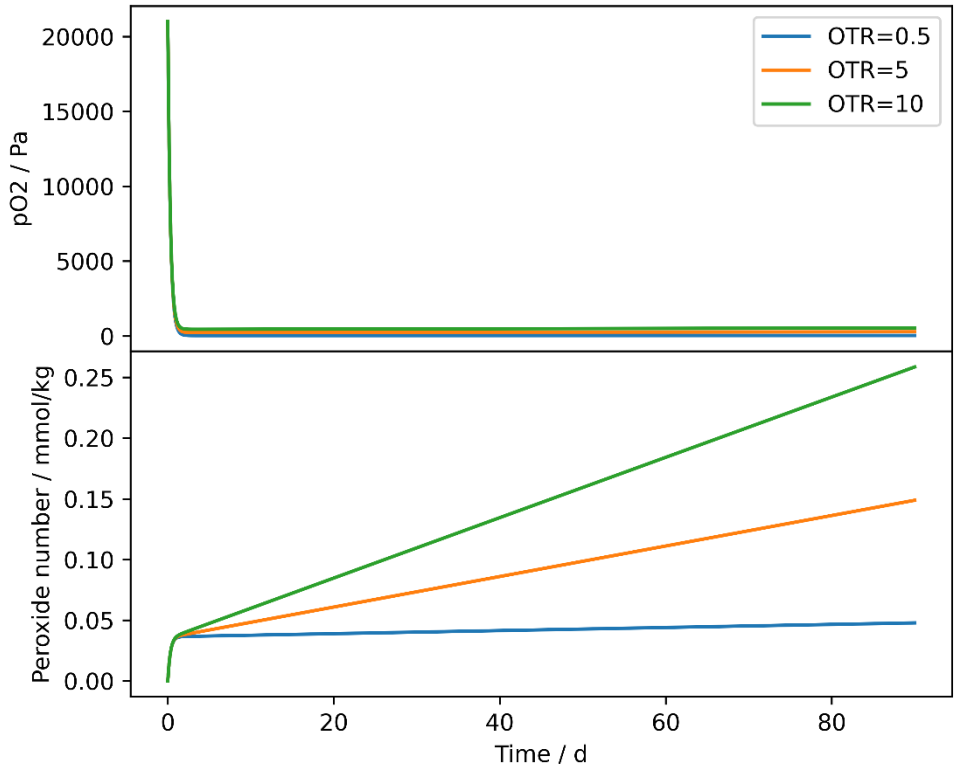

Figure 10 Shelf life simulation results (oxygen partial pressure and peroxide number) for packaged butter with different OTR values (reported in cm³/m²/d).

Additional processes, like acidification and microbiology were not considered for this case. The same applies to photooxidation, which can easily be mitigated by using an opaque packaging material. Regarding the other previously mentioned points, a brief, qualitative discussion is in order. Butter contains a certain amount of butyric acid as fatty acids, which is released via hydrolysis over the storage period and a common contributor to the rancidity of butter. Thus, butter becomes more acidic over time. As mentioned previously, this process occurs over times much longer than the known shelf life of the butter studied here. Hydrolysis also cannot be mitigated by the packaging. Since butter contains some amount of moisture, it is a possible breeding ground for microorganisms. However, the high fat content and typical cold storage conditions reduce the risk of microbiological spoilage.

Crème fraîche

For crème fraîche, storage at 4°C in a PP cup according to specifications provided by the producer was simulated. For the reference, an OTR of 500 $cm^3/m^2/d$ was assumed to account for the low oxygen barrier provided by PP and the thickness of the cup. For comparison, an OTR of 50 $cm^3/m^2/d$ was applied, which is a value attainable by the starch based and PHA based materials produced within R3PACK. The results are shown in Figure 11. The oxygen partial pressure remains at somewhat stable levels dictated by the OTR of the packaging. Oxidation occurs faster for the higher OTR, of course, but the peroxide number remains below noticeable values at the end of shelf life. There is some tolerance for higher transmission rates, as far as oxidation is concerned.

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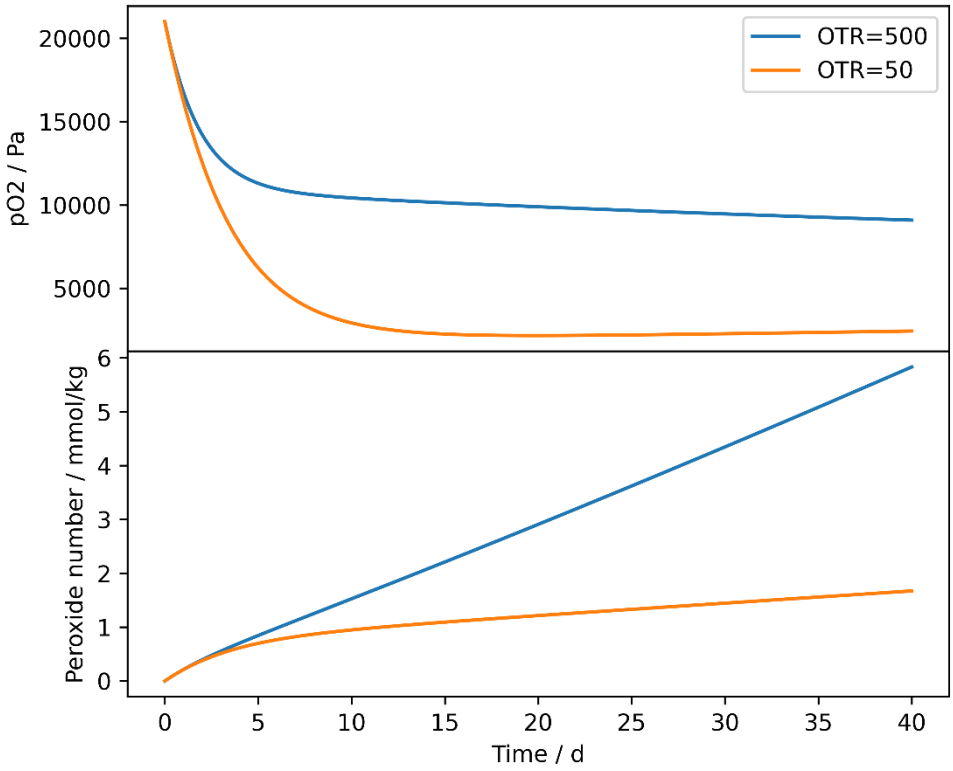

Figure 11 Shelf life simulation results (oxygen partial pressure and peroxide number) for crème fraîche in cups made from materials with different OTR (given in cm³/m²/d).

3.3. Ready-to-eat Fruit and Lettuce

Both fruit and lettuce are living tissue and as such respire even after harvest and, in the case of the pineapple wedges, processing. Separated from the rest of the plant and external sources of nutrients, however, the plants' immune systems and longevity are compromised. Decay processes can be delayed by slowing down the metabolism of microorganisms and the plant itself. This is achieved by limiting the available oxygen through packaging: the respiration rate depends on the oxygen partial pressure and can be lowered by reducing the same. In the case of the pineapple wedges, an EMAP approach is used, where perforations in the lid control the influx of oxygen such, that the respiration rate matches the oxygen replenishment rate at an equilibrium value. For the lamb's lettuce, a closed bag is used, so that the available oxygen is depleted over time. In this case, anoxic conditions are reached at the end of shelf life, leading to the occurrence of fermentation.

Pineapple

The pineapple wedges are packaged in a PET cup with a LDPE lid, with two available sizes, 230 and 400 g. The lid contains three or four perforations with a diameter of 90 µm each for the 230 g pack and five to ten perforations for the 400 g pack, leading to a commonly observed equilibrium headspace oxygen content of 10%.

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The perforations dominate the gas exchange compared to the permeation through the material. This has the benefit that the gas barrier requirements placed on the material are relatively lax. Of course, the material needs to be resistant to liquid water to prevent leakage. Simulations that include perforations need to track the full atmosphere, i.e. also nitrogen, since the perforations enable both diffusive (i.e. partial pressure dependent) and advective (total pressure dependent) gas exchange. Due to it not being relevant for respiration, the nitrogen partial pressure will not be reported in the following.

Simulation results for the headspace composition for both sizes of packaged pineapple wedges are shown in Figure 12. Since natural, minimally processed foods are highly variable, respiration rates are taken from a standard distribution and averaged over a series of 100 simulations. This leads to a corresponding variability in the resulting headspace composition, as indicated by the shaded areas in the plot. The smaller package size - with three perforations - equilibrates after approximately two days, which is faster than the larger package with five perforations, which takes about twice as long to reach equilibrium for oxygen. The oxygen equilibrates at 10 kPa for both packages, which is at the experience value (10% with a total pressure of 100 kPa). The agreement is almost astonishing given that literature values were used for the respiration rates, which generally depend on a variety of factors, such as the cultivar and ripeness of the fruit.

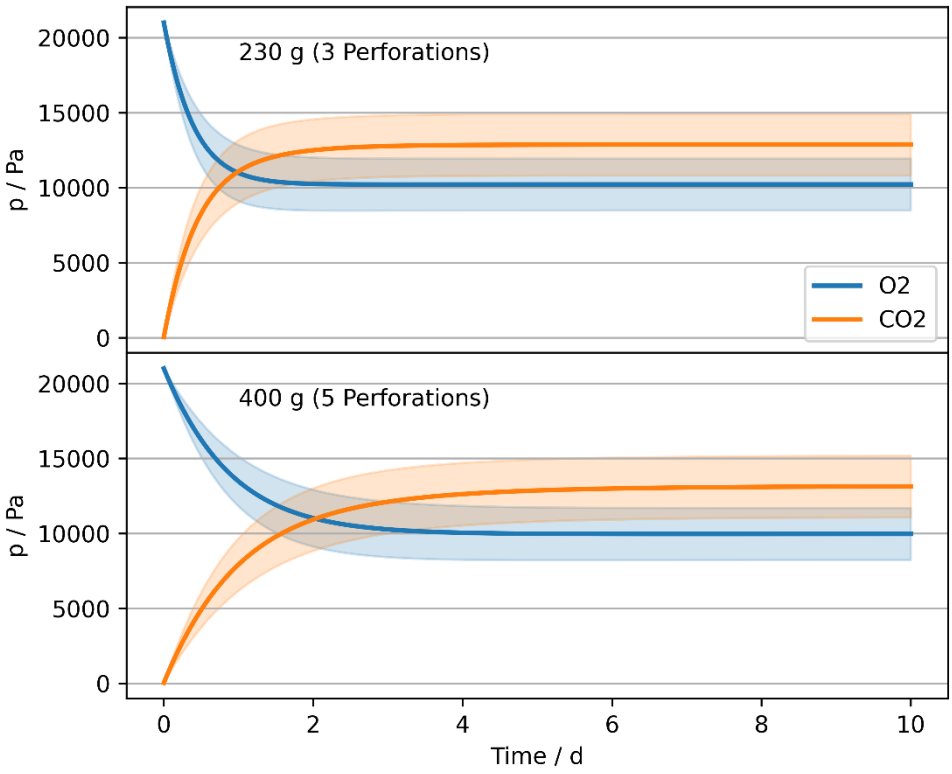

Figure 12 Simulation results for different amounts of pineapple wedges in cups with packaged lids. The lines represent an average over 100 simulations each, the shaded areas the corresponding standard deviation.

Since they play a major role in establishing the EMAP, it is instructive to analyse the effect of variations of the size and number of perforations. Variations of both approaches have been studied for the 230 g cup.

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The simulation results for two, three (default) and four perforations are shown in Figure 13. As can plausibly be expected, the more perforations are present, the less the EMAP differs from the external atmosphere, though each case is clearly different from the standard atmosphere. With fewer perforations, the oxygen partial pressure drops to a lower level. If taken to the extreme, very low oxygen levels can be harmful, but this is not to be expected for the values reached in this simulation. A fourth perforation raises the equilibrium partial pressure of oxygen to the level slightly higher than observed in in-company tests. The carbon dioxide values change accordingly. Here, a higher value has an increased potential to hamper the growth of microorganisms, but also has the risk of increasing the acidity of the product (since pineapple is naturally acidic, this may not be an issue in this specific case).

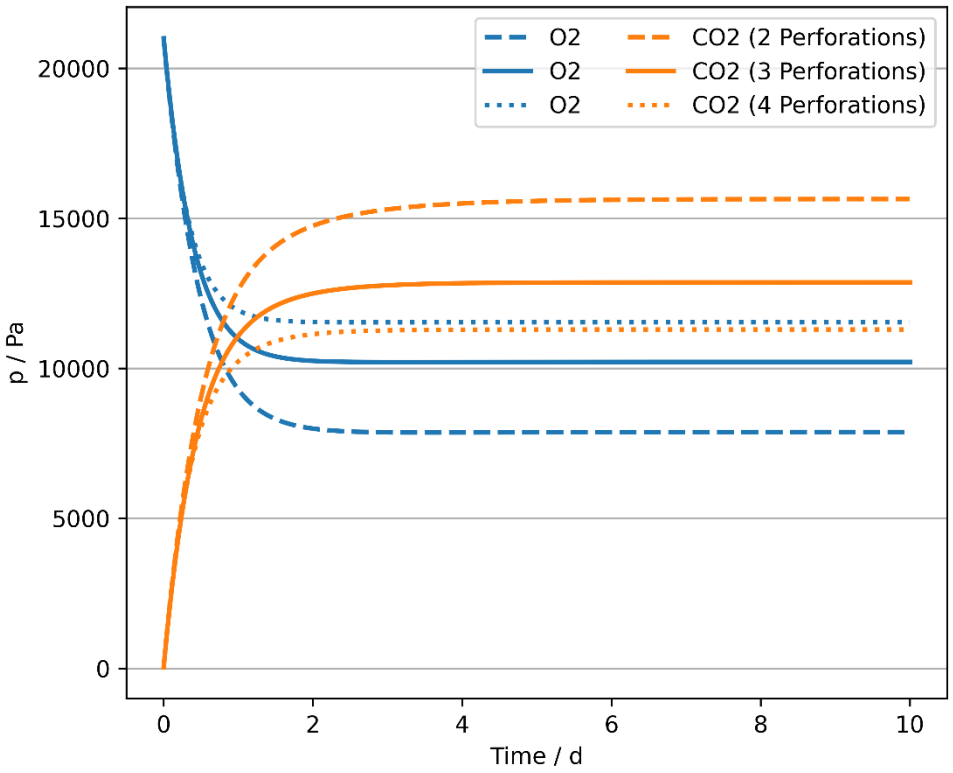

Figure 13 Simulation results for 230 g of pineapple wedges stored in containers with different numbers of perforations with a diameter of 90 µm each. The averages of 100 simulations each are shown. For the sake of clarity, the representation of the standard deviations has been omitted.

To test the variation of perforation size, simulations were performed with the usual diameter of 90 µm varied by 10 µm in either direction. The results are shown in Figure 14. The variation of equilibrium is smaller compared to changing the number of perforations, which is a sensible outcome considering the total exchange area is varied less. In fact, the average values of the partial pressures from the changed cases fall within the standard deviation of the default case (though the spread of the former would extend that of the latter). Overall, in the size range studied here, choosing the number provides the coarse "setting" of the EMAP, whereas variations in the size provide the opportunity for fine tuning.

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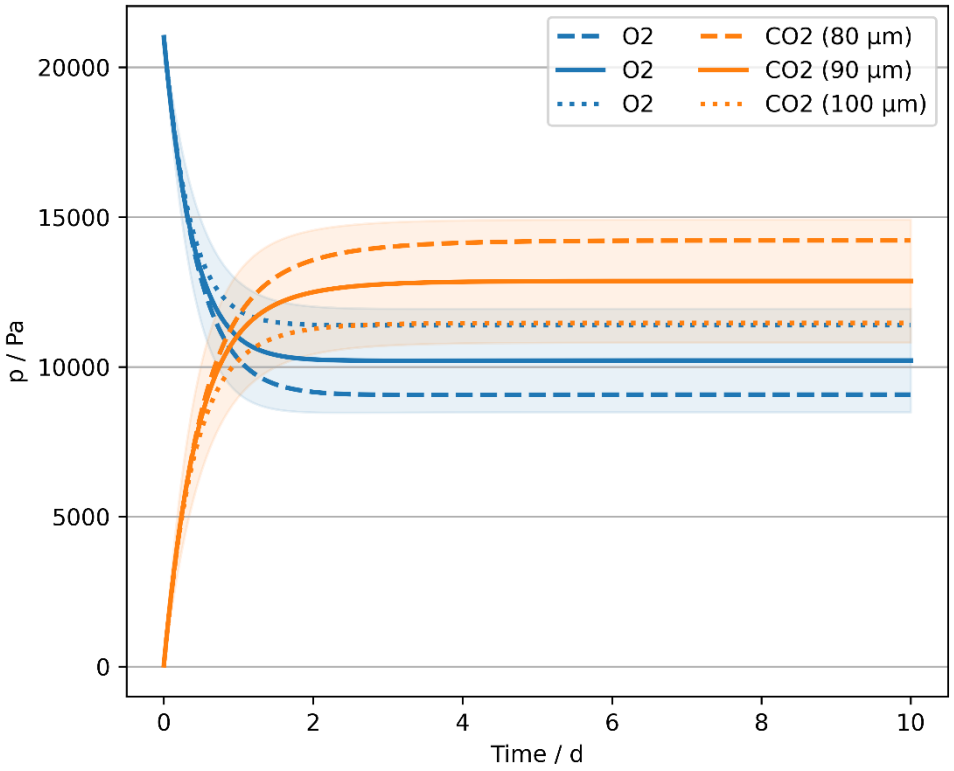

Figure 14 Simulation results for 230 g of pineapple wedges stored in containers with three perforations of different size (lines represent the average of 100 simulations each). For the sake of clarity, only the standard deviations of the default case (90 µm) are shown.

Finally, the impact of the packaging material on the EMAP is shown in Figure 15. The oxygen permeability was varied between 0.1 and $1000\ \mathrm{cm^3 \cdot 100\ \mu m \cdot m^{-2} \cdot d \cdot bar}$ for both cup and lid (which both have a different thickness and thus OTR). For the carbon dioxide permeability, a value of four times that of oxygen was assumed. Thus, the impact of permeability variations is more pronounced for carbon dioxide than it is for oxygen. Overall, the most different EMAP composition from the others occurs for the highest permeability of $1000\ \mathrm{cm^3 \cdot 100\ \mu m \cdot m^{-2} \cdot d \cdot bar}$, but even here, the equilibrium oxygen partial pressure barely differs from that of the higher barrier materials. The differences between the other values are mostly negligible. These observations reinforce the initial statement, that the perforations account for most of the gas exchange. Thus, the gas barrier of the material is not of particular importance, allowing a wide choice of materials to be used for this kind of packaging, as long as they provide a sufficient water barrier. Since pineapples in particular are acidic, the inside of the packaging material should not be sensitive to acidic conditions.

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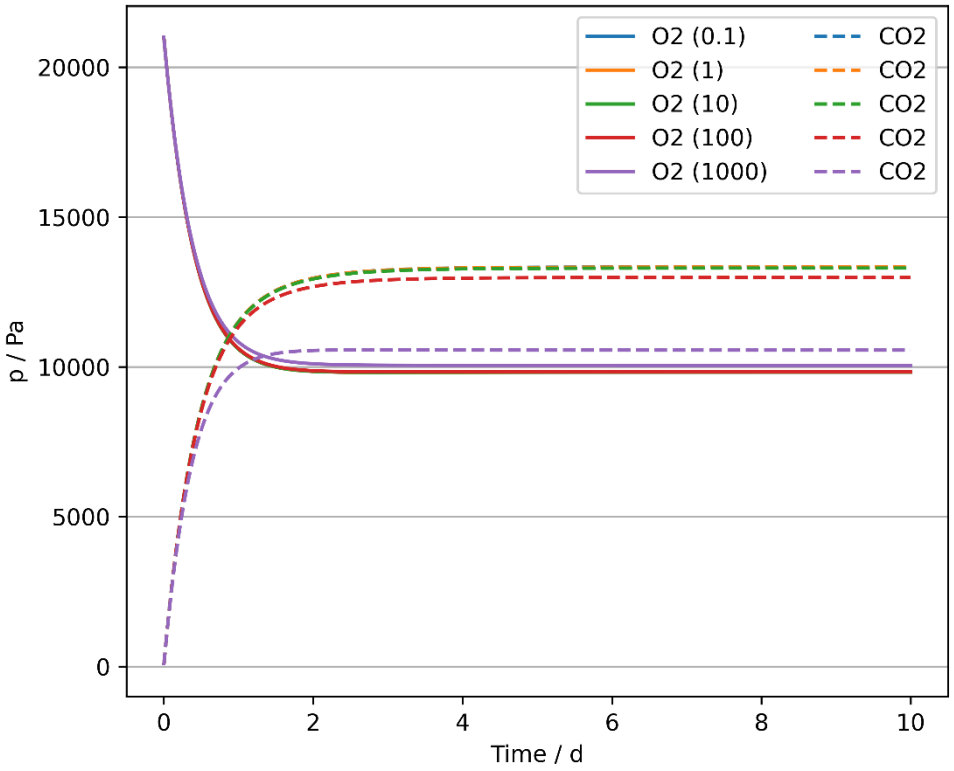

Figure 15 Simulation results for 230 g of pineapple wedges stored in containers made out of materials with different permeability for oxygen and carbon dioxide and three perforations in the lid. The permeability is given in units of $cm^3 \cdot 100\ \mu m \cdot m^{-2} \cdot d \cdot bar$.

Lamb's lettuce

The lamb's lettuce is packaged in sealed OPP bags with no perforations. In-company storage tests show, that the oxygen is consumed at end of shelf life and that humidity builds up inside the package over time. For the transmission rates of the packaging, a range of values is given in the technical data sheet provided by the producer of the lamb's lettuce (for 40 µm: WVTR 2.5-3.5 g/m²/d, OTR 950-1450 cm³/m²/d, calculated CO2TR 2700-4200 cm³/m²/d). To account for variations in the respiration rate and for the range of transmission rate, all these values are varied randomly over 100 simulations. For the respiration rate, a variance of 15% was set. For the transmission rate, the values were drawn from a standard distribution centred at the middle of the given range (WVTR 3±0.5 g/m²/d, OTR 1200±250 cm³/m²/d, CO2TR 3450±750 cm³/m²/d).

The simulation results are shown in Figure 16. The oxygen partial pressure drops to a final value of 5 kPa instead of being fully consumed as observed in in-company trials. This deviation can be explained by the dependence of the respiration rate on the oxygen and carbon dioxide being unknown in detail (values for the corresponding parameters were estimated) and the model not accounting for possible changes in the respiration rate due to internal changes in the lamb's lettuce. In addition, the simulation showed some accumulation of water vapour, which remained below the saturation water pressure (815 Pa at 4 °C). Since the model only accounts for water as a by-product of respiration, not from transpiration, the water production is underestimated.

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The initial bump in the partial pressure of carbon dioxide and water vapour is due to the respiration rate being initially higher and falling with the consumption of oxygen and the production of carbon dioxide.

Regardless of the deviations between the model and in-company observations, the effect of adding microperforations to the packaging has been studied. Since the lamb's lettuce is stored in a bag, additional considerations to the EMAP concept must be made. Specifically, bags of lettuce or salad are typically inflated for protection against squashing, which would not be the case for perforated packaging. Thus, incorporating perforations may require a different packaging concept with otherwise identical barrier. The micro perforations were kept to a very small diameter of 50 µm, which keeps the barrier of the material relevant, and up to three perforations were added in the simulations. Simulation results are shown in Figure 17. With an increasing number of perforations, the equilibrium oxygen level is raised. The same applies to the carbon dioxide and water vapour levels due to the increased respiration. These observations suggest, that an EMAP approach with the use of perforations needs to be carefully balanced: while the increased availability of oxygen may ward of fermentation processes, the increased respiration rate and general metabolic activity of the lamb's lettuce may well lead to a faster spoilage of this product. However, with the available data, this question cannot be conclusively answered.

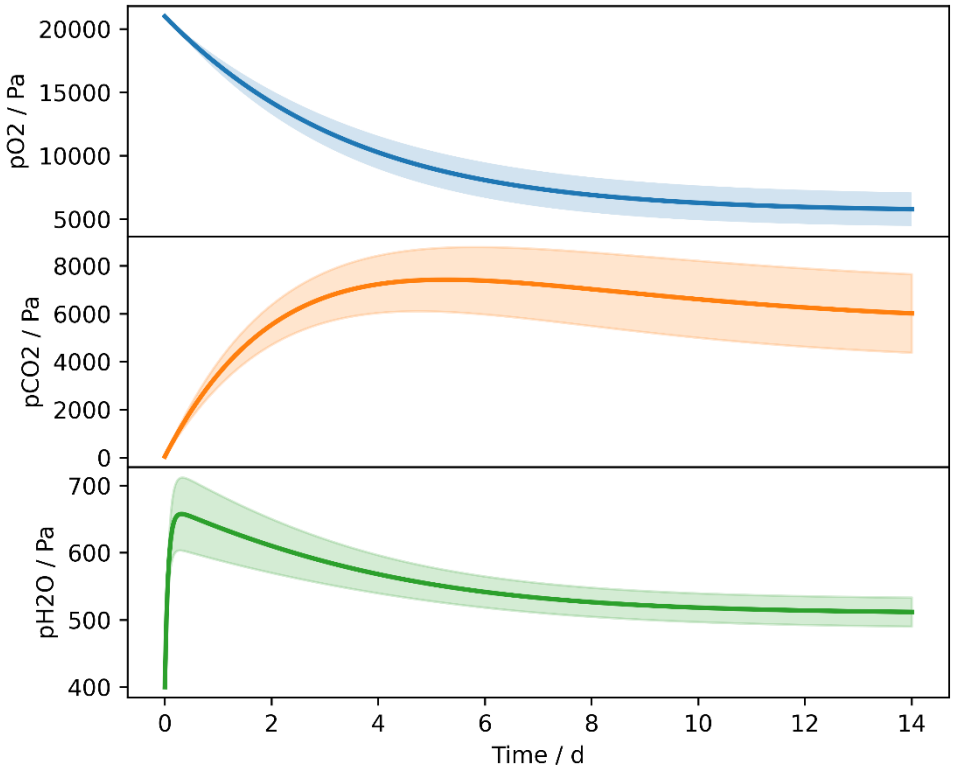

Figure 16 Shelf life simulation results for 265 g of bagged lamb's lettuce. The lines show the average values for the resulting partial pressures and the shaded areas indicate the standard deviation. Variations were included for the respiration rate and for oxygen, carbon dioxide and water vapour permeability.

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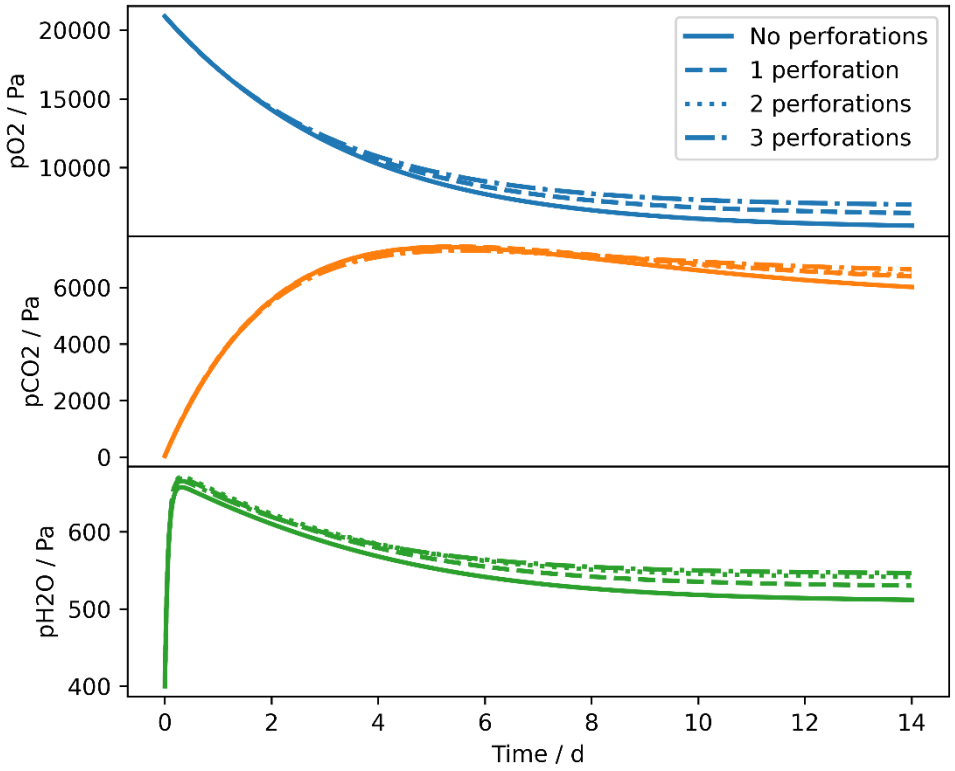

Figure 17 Shelf life simulation results for 265 g of lamb's lettuce in a microperforated (50 µm diameter) bag with the non-perforated bag for comparison. For clarity, only the mean values are shown.

While the introduction of perforations may not be the best choice for bagged lamb's lettuce, among others due to the loss of cushioning, choosing a different packaging material is a viable option. The used OPP provides a good water vapour barrier, but only a low barrier against oxygen and carbon dioxide, which allows for some gas exchange to occur. The PHA based materials developed within R3PACK are an interesting candidate, since they achieve a similar WVTR (3-7 g/m²/d) and a much lower OTR (1-90 cm³/m²/d) compared to OPP, depending on the application strategy (see deliverable 4.2[11]). Assuming a paper coated with MFC and laminated with PHA, a WVTR of 5±1 g/m²/d and an OTR of 60±10 cm³/m²/d are used for the simulations. From the OTR, a CO2TR of 180±30 cm³/m²/d is estimated for the sake of this study. Simulation results are shown in Figure 18 with the reference for comparison. Due to the limited influx of oxygen through the material, the oxygen content drops significantly lower than in the OPP bag. At the same time, more carbon dioxide accumulates in the headspace. As a consequence of the reduced respiration rate and the higher WVTR, less water vapour is present in the headspace. The stronger drop in oxygen content indicates that fermentation-furthering conditions are reached earlier in this alternative packaging, which may reduce the shelf life. At the same time, the increased carbon dioxide content can have two different effects: an increased suppression of microorganisms, but also a higher acidity of the lamb's lettuce. An alternative material for this particular product might benefit from a higher OTR to extend the period in which oxygen is available. Alternatively, a suitable perforation can be a good choice to establish EMAP conditions conducive to the shelf life of the lamb's lettuce, at the expense of losing the cushioning effect provided by a fully closed bag.

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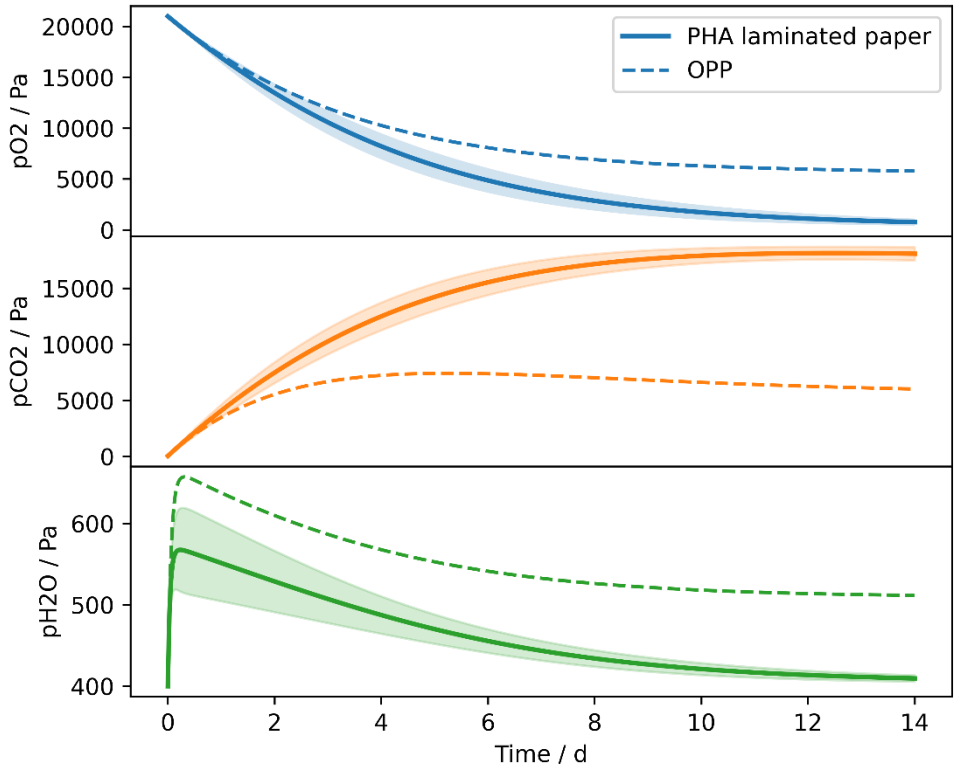

Figure 18 Shelf life simulation results for lamb's lettuce bagged in PHA laminated paper (with MFC coating) in comparison to the OPP reference. The lines indicate the mean results from 100 simulations with random variations in respiration rate, WVTR, OTR and CO2TR. The shaded areas indicate the standard deviation (only for the alternative packaging).

To summarize the findings on RTE produce: The challenge with packaged produce, RTE or otherwise, is to provide the right conditions to extend its shelf life, without suffocating it. If the packaging is perforated, as is the case for the pineapple wedges, the perforations make the biggest contribution to the total gas exchange. The permeation through the material can safely be ignored, unless the barrier is very low. If the materials barrier is indeed low, as is the case for the bagged lamb's lettuce in its established packaging, perforations may not be necessary. In addition, not using perforations allows for the possibility to inflate the bag for a cushioning effect. In cases where EMAP conditions are to be used, they need to be tailored to the respective product.

4. Conclusion and Perspectives

The shelf life studies described in this deliverable provide some guidance on the packaging requirements of the foods studied in the case studies and prospective applications of the materials developed in WP 4. From the studied food types, the snack foods could be characterized the most thoroughly: They are susceptible to absorb water vapour and fairly resistant to oxidation. They put high requirements upon the water vapour barrier of their packaging, which requires further modifications of the R3PACK materials. The dairy products were more resistant to characterization but could be analysed with the aid of literature data and boundary values provided by the producer in the case of shredded cheese.

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Their requirements for oxygen barriers are moderate and well within reach of the R3PACK materials. Finally, the ready-to-eat produce is packaged either using the EMAP concept, which does not require a high barrier due to the presence of perforations, or in material with a low oxygen barrier. In both cases, R3PACK materials can reach the required barrier taken into account in these studies.

There is one aspect that has so far been excluded from the deliberations described here: aroma barrier. "Aroma" covers a cornucopia of different compounds, which introduces a high degree of complexity at the first glance. However, these compounds tend to be quite large and are either polar or nonpolar. The latter aspects indicates that the transmission rate of aroma compounds correlates strongly with either the OTR (for nonpolar compounds) or the WVTR (for polar compounds). The size of the molecules can be expected to lead to a lower transmission rate compared to small molecules like oxygen or water. This aspect is mostly important for products which rely on keeping volatile aroma compounds or are good absorbers of external aromas.

Given the findings from the case studies presented herein, the materials developed in WP 4 of R3PACK are suitable candidates for the packaging of a variety of foods, with some additional improvements required for more demanding products. The actual usability of the materials depends on additional factors, such as machinability and sealability, and can only be proven in packaging trials.

The parameters have been saved as presets in IVVSL for further use. The tool and the parameters are available upon request.

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5. Appendix: Mathematical Foundation of the Shelf Life Model

The shelf life models are composed from tracked variables and processes that change these variables and are also affected by them. The variables can be the partial pressures of gases in the headspace or properties of the stored food, such as its water content. The latter include permeation through the packaging or perforations, respiration and sorption as well as others. The purpose of this appendix is to give an overview over the equations that describe the processes as implemented in IVVSL. In general, every process is represented by a differential equation which yields the rate of change of one or several variables under certain conditions. Process parameters have to be derived experimentally or taken from literature.

All processes can generally be scaled with temperature using Arrhenius scaling. In practice, a rate constant k_{ref} is determined at a reference temperature of 21 °C. The rate constant at another temperature is then given as $k_T = k_{\mathrm{ref}} \cdot \exp\left(-\frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right)$. Here, E_a is the activation energy and R is the universal gas constant. If the temperature dependence is not explicitly known, an activation energy of $50\ \mathrm{kJ/mol}$ is assumed, which corresponds to the (empirical) van't Hoff rule, stating that reaction rates typically double when the temperature is increased by 10 °C.

Starting with gas exchange processes between the headspace and the external atmosphere, permeation through the packaging material is the most common process and occurs in almost every packaging scenario. For package with surface area A and thickness d made from a material with permeability P_i (for permittent i), the rate of change of the volume is described by

$$\frac{\mathrm{d}V_i}{\mathrm{d}t} = \frac{P_i \cdot A}{d} \cdot \left(p_{i,\mathrm{in}} - p_{i,\mathrm{out}}\right),$$

where $p_{i,in}$ and $p_{i,out}$ are the internal and external partial pressure of the permittent, respectively. If the permeability is replaced by the diffusion coefficient, this equation describes Fickian diffusion. Thus, it can also be applied to diffusion through perforations, if the area and thickness are replaced by the area and length of the perforations (the latter of which is generally identical to the thickness of the packaging).

The total gas flow through perforations cannot be described by diffusion alone. Diffusion occurs due to partial pressure differences. If a total pressure difference is built up by the total gas balance, an additional advective flow has to be considered. The total volumetric flow is described by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = N \cdot C_d \cdot \pi \cdot r^2 \sqrt{\frac{2 \cdot \left(\sum_i p_{i,\mathrm{in}} - \sum_i p_{i,\mathrm{out}}\right)}{\rho}}$$

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Here, *N* and *r* are the number and radius of the perforations, C_d is the flow coefficient (set to 0.62) and ρ is the density of the gas. The volumetric flow of the individual gases is proportional to the mole fraction of the respective gas.

Simulating sorption of water vapour requires information on the isotherm (i.e. the water content at equilibrium with the vapour pressure in the headspace) and the kinetics (i.e. the water uptake/release rate). Both pieces of information are included in the rate equation:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k \cdot f(\mathrm{RH}) \cdot (n_{\mathrm{iso}} - n_{\mathrm{sol}}(t))$$

Here, k is the mass exchange rate constant, which is scaled by a humidity dependent factor $f(\mathrm{RH})$. The equilibrium water content from the isotherm n_{iso} and the actual water content n_{sol} control the sorption rate based on the distance to the equilibrium. This equation can model both absorption and desorption of water vapour.[12]

Radicalic autoxidation of unsaturated fatty acids is a highly complex process, which is represented in s strongly simplified model. The oxidation is represented by a third order reaction between oxygen, oxidizable double bonds (representing the unsaturated fatty acids) and free radicals. In addition, radicals can react with each other in a termination reaction. The amount of oxygen ($n_{\mathrm{O_2}}$), double bonds (n_{DB}) and radicals (n_{rad}) changes according to

$$\frac{dn_{\mathrm{O_2}}}{dt} = \frac{dn_{\mathrm{DB}}}{dt} = -k_{\mathrm{Ox}} \cdot n_{\mathrm{DB}} \cdot n_{\mathrm{rad}} \cdot n_{\mathrm{O_2}}$$

$$\frac{dn_{\mathrm{rad}}}{dt} = 2 \cdot k_{\mathrm{Ox}} \cdot n_{\mathrm{DB}} \cdot n_{\mathrm{rad}} \cdot n_{\mathrm{O_2}} - k_{\mathrm{Term}} \cdot n_{\mathrm{rad}}$$

The rate constants k_{Ox} and k_{Term} control the rate of the oxidation and termination reaction, respectively. For the reactions to progress, an initial amount of free radicals needs to be set.

Respiration of produce is described by the Michaelis-Menten equation with competitive inhibition, expressed as mass of consumed oxygen:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = m_{\mathrm{Prod}} \cdot r_{\mathrm{max}} \cdot \frac{p_{\mathrm{O_2}}}{\left(1 + \frac{p_{\mathrm{CO_2}}}{K_I}\right) K_m + p_{\mathrm{O_2}}}$$

with the product mass m_{Prod}, the maximum respiration rate r_{max}, the Michaelis-Menten constant K_m, which scales the respiration rate with the available oxygen, and the inhibition constant K_I, which dampens the respiration rate with increasing carbon dioxide partial pressure.

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