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Influence of gases on the integrity of packaging materials upon high pressure treatment

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Scientific contributions

Full Papers

The following peer reviewed publications were generated in the period of this work and are related to the topic of the thesis (publications which are part of this thesis are indicated in bold).

The doctoral candidate is the main author of three out of the four publications presented in this thesis and shares in the fundamental and major part of conception, idea and execution of all scientific experiments as well as the data analysis. The subsequent writing of the manuscripts was exclusively her product. To the review paper about the effect of high pressure processing on the integrity of polymeric packaging (Chapter 3) the doctoral candidate contributed in form of a relevant co-authorship.

1. **STERR, J.; FLECKENSTEIN, B. S.; LANGOWSKI, H.-C. (2017): The theory of decompression failure in polymers during the high-pressure processing of food. In *Food Engineering Reviews.* Published online: 13. October 2017. DOI: 10.1007/s12393-017-9171-9**
2. **FLECKENSTEIN, B. S.; STERR, J.; LANGOWSKI, H.-C. (2014): The effect of high pressure processing on the integrity of polymeric packaging - Analysis and categorization of occurring defects. In *Packaging Technology & Science* 27 (2), pp. 83–103. DOI: 10.1002/pts.2018.**
3. **STERR, J.; FLECKENSTEIN, B. S.; LANGOWSKI, H.-C. (2015): The effect of high pressure processing on tray packages with modified atmosphere. In *Food Engineering Reviews* 7 (2), pp. 209–221. DOI: 10.1007/s12393-014-9081-z.**
4. **STERR, J.; RÖTZER, K.; WECK, K.; WIRTH, A. L. K.; FLECKENSTEIN, B. S.; LANGOWSKI, H.-C. (2015): In-situ measurement of oxygen concentration under high pressure and the application to oxygen permeation through polymer films. In *Journal of Chemical Physics* 143 (11), p. 114201. DOI: 10.1063/1.4931399.**

5. FLECKENSTEIN, B. S.; STERR, J.; LANGOWSKI, H.-C. (2016): The influence of high pressure treatment and thermal pasteurization on the surface of polymeric packaging films. In *Packaging Technology & Science* 29 (6), pp. 323–336. DOI: 10.1002/pts.2213.
6. RICHTER, T.; STERR, J.; JOST, V.; LANGOWSKI, H.-C. (2010): High pressure-induced structural effects in plastic packaging. In *High Pressure Research* 30 (4), pp. 555–566. DOI: 10.1080/08957959.2010.531722.
7. STERR, J. (2013): Konfokale Raman-Spektroskopie - ein nützliches Tool auch für die Getränkeindustrie. In *Der Weihenstephaner* 81 (3), pp. 127–129.
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Further full papers and scientific contributions

1. GEBHARDT, R.; STEINHAUER, T.; MEYER, P.; STERR, J.; PERLICH, J.; KULOZIK, U. (2012): Structural changes of deposited casein micelles induced by membrane filtration. In *Faraday Discussions* 158, pp. 77–88.
2. STRIXNER, T.; STERR, J.; KULOZIK, U.; GEBHARDT, R. (2014): Structural study on hen-egg yolk high density lipoprotein (hdl) granules. In *Food Biophysics* 9 (4), pp. 314–321.
3. ZHUANG, Y.; STERR, J.; KULOZIK, U.; GEBHARDT, R. (2015): Application of confocal Raman microscopy to investigate casein micro-particles in blend casein/pectin films. In *International Journal of Biological Macromolecules* 74, pp. 44–48.
4. ZHUANG, Y.; STERR, J.; SCHULTE, A.; KULOZIK, U.; GEBHARDT, R. (2016): Casein microparticles from blend films forming casein/α-tocopherol emulsion droplets in solution. In *Food Biophysics*. DOI: 10.1007/s11483-016-9446-3.

Oral presentations with first authorship

1. STERR, J. (2008): Verpackungen für hochdruckbehandelte Lebensmittel. Anforderungen, Risiken, Chancen. Hochdrucktagung. Universität für Bodenkultur Wien. Wien, Austria, 9/16/2008.
2. STERR, J. (2009): Characterization of crystallinity of polymers using Raman Spectroscopy. Confocal Raman Imaging. Ulm, Germany, 9/29/2009.
3. STERR, J. (2012): The effect of high pressure on the morphology of polymers – a Raman spectroscopic study. 7th International Conference on High Pressure Bioscience and Biotechnology (HPBB2012). Otsu, 11/2/2012.
4. STERR, J. (2013): Raman spectroscopic study of high pressure induced structural changes and defects in polymer films. European High Pressure Research Group International Meeting (EHPRG 51). Queen Mary, University of London. London, UK, 9/6/2013.
5. STERR, J. (2014): Possibilities and restrictions for the quantitative measurement of Polyethylene with Raman Spectroscopy. ICORS International Conference on Raman Spectroscopy. Jena, 8/10/2014.
6. STERR, J. (2014): Hochdruckbehandlung und MAP. Stellen Sie sich der Herausforderung. Freisinger Tage - Fokus Fleisch und Wurstwaren – Produkte, Verfahren und Verpackungen. Freising, Germany, 11/25/2014.
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Poster presentations with first authorship

1. STERR, J. (2013): The effect of high pressure processing on tray packages with modified atmosphere. Nonthermal food processing workshop, Florianopolis, Brazil, 09/30/2013.

Content

1 Introduction

Throughout the history of mankind people have endeavoured to preserve foods in order to survive winter cold, bad harvests and times of war. Methods such as chilling, drying, salting, smoking and adding preserving agents have been used in the past and are still used today to inhibit the growth of microorganisms. Microbial inactivation is nowadays mostly achieved by heat treatment.

With industrialisation and the increased scientific knowledge in the area of health, nutrition and technology, consumer demands for healthy, minimally processed products have increased. Foods should contain minimal or if possible no synthetic preservatives whilst simultaneously they should have enhanced shelf lives. In developed countries, environmental sustainability as well as ethical criteria are also important for consumers (PARDO, ZUFÍA 2012). For these reasons, innovative technologies for food preservation have been developed in recent years. Besides treatment with for example radiation, pulsed electric fields, pulsed ultraviolet light and non-thermal plasma, high pressure processing (HPP) has become a significant low temperature method for food preservation and microbial inactivation. According to a survey on upcoming trends in food preservation and food processing methods, HPP is viewed as the most important innovative commercial technology for the next ten years (JERMANN ET AL. 2015). More information about alternative non-thermal preservation techniques can be found elsewhere (MORRIS ET AL. 2007; PEREIRA, VICENTE 2010; ZHANG ET AL. 2011).

1.1 The high pressure processing of food

1.1.1 Fundamentals and applications

The principle of preservation using high pressure has been known since the late 19th century (CERTES 1884; HITE 1899). Commercial applications, however, were only developed much more recently when the cost and energy efficiency of equipment and technology became acceptable. Indeed, the first pressurised foods became available 30 years ago in Japan (CHEFTEL 1995; FARKAS 2016) and have been available since 1993 in Europe (KUROWSKA ET AL. 2016). More than 300 high pressure units are now installed in industry worldwide (BROWN ET AL. 2016). In the United States, the estimated volume of sales now amounts to over $2 billion annually (FARKAS 2016). The current estimated price per kilogram of an HPP product ranges from 0.06 – 0.60 US$ (BALASUBRAMANIAM ET AL. 2016b; BROWN ET AL. 2016; MÚJICA-PAZ ET AL. 2011), which is assumed to be about 0.06 – 0.20 US$ more than the costs arising from thermal processing (BALASUBRAMANIAM, FARKAS 2008). A survey by HICKS ET AL. (2009) indicated that consumers are willing to spend more money per item if the process makes the product safer. After a brief explanation of the benefits of high pressure processing, the majority of the persons indicated they would spend $0.25 - $0.50 extra for an HPP product. More information about consumer acceptance of HPP products can be found elsewhere (BRUHN 2016).

Typical goods treated by high pressure treatment to prolong the shelf life are temperature-sensitive foods such as fresh fruit products (smoothies, sauces etc.), cold meats (smoked ham, sausages, etc.) and ready-to-eat meals. In addition, various other applications have been developed in recent years. For example, it was found that the amount of salt in sausages could be reduced and the texture and tenderness of meat products improved by HPP. HPP is also used to open the shell of clams, mussels and oysters and to detach the meat of crustaceans from the skeleton. Good summaries about the influence of pressure on fruit, vegetables, dairy products, meat products and seafood have been given (JOFRÉ, SERRA 2016; MATSER, TIMMERMANS 2016; TABILO-MUNIZAGA ET AL. 2016; TRUJILLO ET AL. 2016). In general, HPP give food producers the opportunity to bring fresh and minimally processed food products to the market which would not be possible with other preservation techniques. The prolonged shelf life and improved sensory, structural and optical qualities make HPP viable for both producers and for customers.

However, the legal framework concerning high pressure technology is still relatively vague as there is no general coverage of food processed by high pressure in EU regulations and there are still ongoing discussions amongst experts as to whether HPP technology and HPP products are part of the Novel Foods Regulation 258/97 (NFR). According to the NFR, a process is novel if it was not used before 15 May 1997 in a significant quantity or if significant negative changes arise in the food (e.g. composition or structure). Some experts are of the opinion that HPP should not be considered as a novel technology because it was already used as a preservation technology before 1997. However, due to the fact that the product itself and not the process must be approved by the regulation, every pressure treated food product should be verified to have no harmful changes. In 1998 a high pressure treated fruit-based preparation of Danone was accepted by the French Food Safety Agency and since that time HPP products have been sold by companies in Europe referring to this decision and without any further authorization. An extensive discussion about regulations for HPP has been given elsewhere (CHOLEWIŃSKA 2010; KUROWSKA ET AL. 2016).

Some of the most important advantages of non-thermal pressure treatment compared to heat treatment are summarised below:

(1) No significant loss of nutritional or organoleptic value.
(2) The action of pressure is homogeneous and immediate.
(3) The effect is independent of the mass, shape and composition of the product regardless of whether it is liquid or solid and regardless of whether it comes with or without packaging.
(4) Compared to heating methods, the energy consumption is relatively small (PEREIRA, VICENTE 2010; TEWARI 2007). Also, the global warming potential and water depletion are smaller for HPP then for thermal pasteurisation processes (PARDO, ZUFÍA 2012).
(5) The extended shelf life is similar to that obtained by thermal pasteurisation (PARDO, ZUFÍA 2012).
(6) There are opportunities for the development of new products and processes such as the detachment of shells from crustacean meat.

Further information about the high pressure processing of food can be found in the literature (BALASUBRAMANIAM ET AL. 2016a; BALNY ET AL. 1992; HENDRICKX, KNORR 2002; JAY ET AL. 2005; RAY ET AL. 2001; TEWARI, JUNEJA 2007; ZHANG ET AL. 2011).

1.1.2 High pressure processing

Pressures of up to 8,000 bars are usually applied for industrial high pressure processes, along with moderate or chilled temperatures. A typical pressurising process is a batch process and is carried out as follows:

(1) Firstly pre-packed food is placed inside a cylindrical basket and put inside the pressure vessel. The total loading capacity of industrial-scale systems ranges from 35 to 525 litres (BALASUBRAMANIAM ET AL. 2016a).

(2) The vessel is filled with pressure transmitting fluid, which in most cases is water for industrial applications. Some pilot plants in laboratories use glycerol-water mixtures or other low compressible liquids.

(3) Pressure build up is realised with pumps and intensifiers. Typical pressurising rates are 1,000 to 3,000 bar/min, depending on factors such as the number and power of pumps, degree of filling and packaging design, especially if it concerns vacuum packaging or packaging with gaseous headspace (MULTIVAC 10/16/2016; NGUYEN, BALASUBRAMANIAM 2011; SYED ET AL. 2012).

(4) The pressure holding time depends on the product and the desired inactivation rates. Holding times from 2 to 30 min are commonplace.

(5) In most equipment decompression is realised in an uncontrolled way by opening a valve. MULTIVAC HPP machinery utilises a patented method for controlled pressure decrease in defined steps ("soft decompression") (RICHTER 2014).

(6) After reloading the basket, the packaged good is also dried in some applications.

As high pressure equipment is a very cost-intensive investment, the processing time and maximum pressure must be reduced to improve the return on investment. Here, batch processing is one of the biggest disadvantages of the HPP industry due to the fact that the maximum throughput is limited. Even though some semi-continuous and continuous systems have been developed, these processes are only applicable for liquid goods and the required energy is significantly higher than for a batch process (LELIEVELD, HOOGLAND 2016). Other methods such as oscillating pressure treatment are available, where several pressure cycles are realised consecutively. It has been found that this is more effective for microorganism inactivation, but has poor time and cost efficiency for industrial applications (JAY ET AL. 2005; PALOU ET AL. 1998).

The following sections explain the physical and chemical changes that are induced by high pressure and the mechanisms of microorganism inactivation.

1.1.3 Principle of high pressure processing

High pressure processing involves statically determined systems, namely isostatic systems. According to the isostatic principle, "a force transported to the surface of a fluid is equally transmitted through the contact surface" (MARTÍNEZ-MONTEAGUDO, BALASUBRAMANIAM 2016). This means that all fluids are able to transport the pressure homogeneously and almost instantaneously without friction. This also means that the applied force, here the pressure, is transmitted to the packaging and the food in three dimensions, independent of the shape, volume or structure (CHEFTEL 1992).

For further understanding of pressure effects on the products, their constituents and the packaging, the principle of LE CHATELIER must be considered. This principle is a more detailed explanation of the fact that a two-phase system tries to minimise the Gibbs energy and therefore the point of equilibrium of the system exposed to pressure will be shifted to the phase with the lower specific volume (NEVERS 2012). This is clear from Equation 1-1 which shows that the increase in Gibbs Energy G with increasing pressure is reduced if the volume V decreases. Additionally, the principle of microscopic ordering states that at constant temperature an increase in pressure increases the degree of ordering of molecules of a given substance (HEREMANS 1992).

Equation 1-1

$$V = \left(\frac{\delta G}{\delta P}\right)_{T,ni}$$

This principle can explain some of the changes to molecules and structures under pressure. The next section discusses the influence of pressure on chemical interactions.

1.1.4 Influence of pressure on molecules, bonds and chemical reactions

As already mentioned, ordering and volume reducing reactions are preferred under pressure. The concomitant changes to interatomic distances can lead to destruction of bonds if the bond energy is distance-dependent, due to distortion of the balance between repulsive and attractive forces (MARTÍNEZ-MONTEAGUDO, BALASUBRAMANIAM 2016). Based on the interatomic distances of some bonds and interactions, it was expected that Coulomb and van der Waals interactions would be highly affected by pressure (MARTÍNEZ-MONTEAGUDO, SALDAÑA 2014). It was also expected that hydrogen bonding, solvation and hydrophobic interactions would be less affected and that there would be essentially no influence on covalent bonding because this is almost independent of the distance in comparison to Coulomb or van der Waals interactions. Other workers mentioned disruption to salt bridges and deprotonation of charged groups, which also induces the ionisation of water and weak acids, resulting in a decrease in pH (CHEFTEL 1992; EARNSHAW ET AL. 1995; MIN, ZHANG 2007; TAUSCHER 1995).

All of these changes to intermolecular bonds can explain the conformational changes to the secondary, tertiary and quaternary structures of proteins and other large molecules, in some cases resulting in irreversible unfolding, denaturation, aggregation and gelatinisation under pressure (TAUSCHER 1995). In general, most proteins are denatured at pressures above 4,000 bars, but the denaturation depends on several other factors such as the protein structure, pressure range, pH, temperature and additives, for example salt and sugar (BALNY, MASSON 1993). Enzymes, which are technically deemed to be proteins in most cases, can be activated as well as inactivated by pressure, depending on the reaction volume. Also, the substrate activity can change (CHEFTEL 1992; TAUSCHER 1995). Changes to physical properties such as the melting point, density and viscosity are further consequences of distortion of intermolecular distances (MARTÍNEZ-MONTEAGUDO, SALDAÑA 2014).

In contrast to the marked effect of pressure on proteins, small molecules having covalent bonds such as vitamins and polyphenols mostly stay unaffected. This advantage of HPP is the reason for the minimal changes in flavour, colour and nutritional properties compared to heat treatment. However, in recent studies it has become clear that the stability of bioactive compounds is highly dependent on chemical reactions, and especially on oxidation processes (MAHADEVAN, KARWE 2016). It has, however, already been noted that there is a dearth of relevant scientific studies concerning the in-situ measurement of chemical reactions under pressure (MARTÍNEZ-MONTEAGUDO, SALDAÑA 2014).

1.1.5 Influence of pressure on microorganisms

Vegetative forms of microorganisms are inactivated at pressures ranging from 3,000 to 5,000 bars, whereas spores may survive pressures exceeding 10,000 bars if the processing temperature is not high enough (CHEFTEL 1995; GOULD 1996). A reason for this is the relative low water content of spores and the resulting resistance to solvation and excessive ionisation (EARNSHAW ET AL. 1995; KNORR 1995). It was found that pressure can induce the germination of spores and a subsequent pressure treatment (“oscillating pressure treatment") is able to destroy these germinated spores (KNORR 1995). Besides oscillating pressure treatment, so-called pressure assisted thermal sterilisation (PATS) facilitates the inactivation process at high pressures, especially for spores. Here, high temperatures ranging from 90 to 120°C are employed. The PATS process will not be discussed further in this thesis.

Besides depending on the type and initial numbers of microorganisms, the inhibitory effect of HPP also depends on the physicochemical properties of the product and on the process conditions such as the maximum pressure, temperature and pressure holding time. Bacteria, for example, are more resistant to high pressures than yeast and mould (MIN, ZHANG 2007). The inactivation effect of HPP can in general be improved by higher water activity, by low acidity of the product and/or by adding preservatives (JOFRÉ, SERRA 2016).

In summary, several different and overlapping pressure effects exist for microbial inactivation (EARNSHAW ET AL. 1995; KNORR 1995; MARTÍNEZ-MONTEAGUDO, SALDAÑA 2014; MIN, ZHANG 2007):

- Ionisation and concomitant precipitation of protein complexes
- ATPase inactivation or destabilisation (results in low internal pH)
- Physical modifications to membrane permeability and membrane protein function and stability
- Collapse of intracellular vacuoles
- Separation of cell walls and cytoplasmic membranes
- Ribosomal destruction
- Mitochondrial damage

1.2 The role of packaging with high pressure processing

At every single stage, from harvest to consumption, spoilage of a product can occur. After the food is processed, the packaging undertakes the task of protecting the product against mechanical stress and physical, chemical and microbial contamination in order to maximise the shelf life. Oxidation processes, for example, can be reduced by a good active or passive gas barrier in the packaging film. Negative alterations due to light absorption can be prevented by using opaque materials. More recently, active packaging has provided various additional functions such as humidity regulation and the absorption of ethylene gas produced by fresh fruit. Besides its protective tasks, the packaging acts as a medium for transferring information to the consumer about the ingredients, shelf life and marketing matters. Often the design and appearance of packaging are driving factors for consumer acceptance of a product and the decision to buy that product.

1.2.1 Combined effect of HPP and modified atmosphere packaging

The use of modified atmospheres in packaging technology is a standard method for extending the shelf life and maintaining the quality of food products during storage. Chemical and biochemical reactions are decelerated and so, depending on the gas and food product, oxidation processes are inhibited, microbiological growth is slowed down and colouring agents in fresh meats can be stabilized (MULLAN, MCDOWELL 2003). In many cases, nitrogen also acts as an inexpensive gas for filling and support to prevent collapse of the packaging. Nitrogen has a low permeability coefficient compared to other gases such as CO_2.

Modified atmosphere packaging (MAP) often includes CO_2 for preservation. The gas acts as a weak acid and dissolves in the food matrix, forming amongst other things bicarbonate anions. A decreased internal pH in vegetative bacteria is a tentative explanation for the observed inhibition of microorganism growth. However, the exact mechanism is still not yet fully understood. It has, however, become clear that the growth of aerobic bacteria, especially Gram-negative bacteria, is slowed down and that the inhibiting effect increases at lower storage temperature (GOULD 1996; JAY ET AL. 2005; MULLAN, MCDOWELL 2003). Clostridia seem to be the most resistant to CO_2. At high pressures it was found that the antimicrobial effect of CO_2 is improved by the additional extraction of intracellular substances such as phospholipids, which is enhanced due to the increased solubility of the gas in the membrane (EARNSHAW ET AL. 1995; KAMIHIRA ET AL. 1987). Regarding HPP, the effect of CO_2 on the inactivation of living cells was found to be dependent on the kind of microorganisms, the water content, the state of CO_2 and the addition of ethanol or acetic acid as an entrainer to CO_2 (KAMIHIRA ET AL. 1987).

It must be understood that the application of modified atmospheres, and especially CO_2, in combination with HPP is part of a hurdle concept, with synergistic interactions improving the quality and safety of the pressurised products. MAP also provides benefits from an environmental perspective because the energy requirements are very low (energy is only required for the packaging and gas injection process) compared to thermal processing (PARDO, ZUFÍA 2012).

1.2.2 Influence of pressure on polymeric packaging

For high pressure processing, the food products are packed prior to treatment in flexible, polymeric based pouches, trays or bottles. The ability to treat ready packed food is a further advantage of HPP, avoiding contamination with pressure transmitting fluids and costly aseptic filling. However, it must be ensured that the packaging still fulfils all necessary requirements for food protection and has acceptable optical properties after processing. Selection criteria for packaging materials are the barrier properties (O_2 and water vapour permeation), mechanical properties, structural characteristics (crystallinity, density etc.), conformity with food contact regulations with respect to migration of packaging constituents into the food and the overall integrity of the packaging (e.g. delamination).

The focus here will be on the use of polymer based materials for HPP. Further information about the use of paperboard as an HPP packaging material can be found elsewhere (CANER ET AL. 2004; OCHIAI, NAKAGAWA 1992).

For a better understanding of all the effects which take place in packaging during and after high pressure treatment a schematic classification (Figure 1-1) has been developed (FLECKENSTEIN ET AL. 2014; RICHTER ET AL. 2010). These were differentiated into direct and indirect effects. Direct effects are induced by the high pressure and indirect effects are caused by compressed headspace gases or food.

Pressure induced damage includes reversible as well as irreversible structural changes to the polymers. Delamination phenomena are due to large differences in the mechanical properties of the materials. Indirect effects on the polymer packaging in the form of crystallisation, plasticisation and macroscopic damage such as blistering and delamination are induced by the rapid compression of gases accompanying high heating rates and increased solubility of gases in the matrices. The increased solubility also facilitates possible extraction of polymer components and the devolatilisation of volatile food components. The solubility was also identified as being the main factor causing decompression failure ("explosive decompression failure" XDF), accompanied by the development of bubbles and blisters in oversaturated materials.

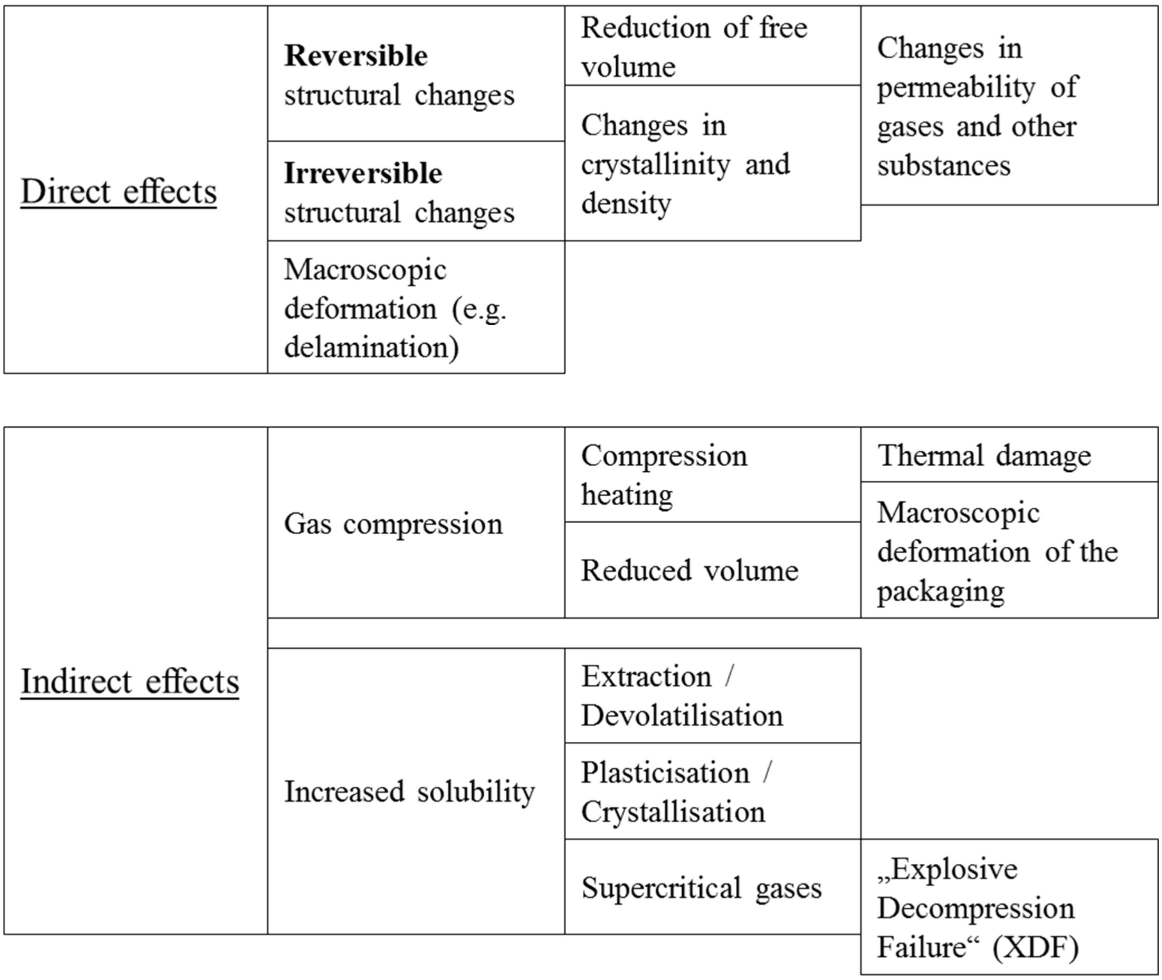

Figure 1-1 Schematic classification of effects on polymeric packaging materials upon high pressure treatment (Fleckenstein et al. 2014; Richter et al. 2010).

The influence of hydrostatic pressure on vacuum packaging has been extensively reviewed (Ayvaz et al. 2016; Fleckenstein et al. 2014; Han 2007; Juliano et al. 2010); see also Chapter 3. Only a short summary of the results will be given here.

Permeability: The oxygen permeability of common polymers was found to resist the process in most cases. Some studies, however, found even improved barrier properties upon pressurisation. Similar results were found for water vapour permeability. Solely inorganic barrier layers showed weak pressure stability and/or film delamination due to large differences in elasticity compared to the adjacent flexible polymers.

Mechanical properties: The mechanical properties were mostly found to be unaffected or slightly improved after pressure treatment. Some samples showed increased tensile strength, indicating higher rigidity. However, these results were without any practical importance for industrial applications due to the low effect in absolute terms.

Structural effects: Comparing the findings about pressure induced structural changes from different research groups it was clear that the findings varied considerably from group to group. In Chapter 3 these differences are put down to the differing physical and chemical measurement principles that were used. Most of the methods (e.g. differential scanning calorimetry DSC) provided only poor spatial resolution of crystallinity measurements. Locally limited changes in crystallinity or density might not have been detected by these methods. Additional information about changes to the surface and surface structure of polymers can be found elsewhere (FLECKENSTEIN ET AL. 2016).

Migration: Only a few migration studies have been performed to investigate the total migration of substances induced by high pressure. Some researchers have found there to be little influence, with all values of total migration conforming to the requirements of EU directive 90/128 for the global migration limit.

Regarding the scientific work on this topic, it can be concluded that common flexible polymers are suitable as vacuum packaging for high pressure processing at moderate temperatures. However, only a small amount of data is available about the suitability of polymers as part of modified atmosphere packaging (MAP) for high pressure treatment. Up until now, scientific information about the indirect effects induced by gases in a supercritical state on polymeric packaging is still lacking. In 1992 authors started mentioning physical damage such as delamination and/or visible changes in the materials (bubbles/blisters) in the presence of headspace gases used for HPP (FRADIN ET AL. 1998; MERTENS 1993; OCHIAI, NAKAGAWA 1992). Since then only a few studies have dealt with possible failure mechanisms of modified atmosphere packaging at high pressures or tried to identify the parameters responsible for packaging failure or shortcomings in the food products.

1.3 Motivation and objective

The use of modified atmosphere packaging for the high pressure processing of food provides benefits in terms of improved product quality and shelf life. As this is already used by industry, the suitability of the packaging and regulatory compliance should also be verified. As already stated by some authors, there is still a lack of information about the influence of headspace gases on the integrity of the packaging at high pressure.

The objective of this work was to provide the necessary information for safe use of polymeric materials as part of modified atmosphere packaging for the high pressure processing of food.

The first part of this work focuses on the mechanisms behind explosive decompression failure. As mentioned previously, bubbles form in highly supersaturated materials on decompression. However, the exact mechanisms are still not clear. A literature study (Publication I, Chapter 2) was necessary to quantify and qualify the key parameters responsible for the formation of bubbles and blisters. The transport properties of gases in the polymers were identified as being the most important parameters, but it also became clear that there is a lack of information about the permeation, solubility and diffusion of gases in polymers during HPP and there were no in-situ measurement systems for high hydrostatic pressure.

Accordingly, a new method for in-situ measurement of the oxygen concentration and oxygen permeation through polymers at hydrostatic pressures up to 2,000 bars was developed based on the principle of fluorescence quenching (Publication III, Chapter 4). A reduction in oxygen permeability through a polyethylene film by a factor of between 35 and 70 at 2,000 bars applied pressure was put down to the reduction in free volume and chain motion.

Besides the formation of bubbles, many other effects are possible when using modified atmosphere packaging for HPP. A review article was prepared, classifying effects and identifying missing but relevant criteria (Publication II, Chapter 3). Direct effects induced by high pressure and indirect effects caused by the combined use of headspace gases and pressure on monolayer films and multi-layered packaging were categorised (Figure 1-1). Aspects such as sorption induced crystallisation and plasticisation, local thermal effects, solution and extraction effects and decompression failure were discussed. In summary, it was concluded that there was a lack of information about irreversible structural changes induced by supercritical gases. Studies on plastic constituent migration due to supercritical CO_2 could not be found in the literature. The influence of parameters such as headspace volume, film thickness and depressurisation rate on the packaging integrity and migration properties was also unclear (JULIANO ET AL. 2010).

Based on these summarized findings, experiments were undertaken to investigate important factors such as the material properties, packaging design, process parameters and migration processes (Publication IV, Chapter 5). The extraction potential of headspace gases such as supercritical CO_2 to the overall and specific migration of certain substances under high pressure processing was also part of the study. Changes in the oxygen permeability of organic and inorganic barrier layers were analysed after pressure treatment. The influence of pressure on polymer structure in combination with and without use of supercritical gases in monolayer and multilayer films and trays was investigated using Raman spectroscopy. This non-destructive method is based on detection of the inelastic scattering of monochromatic light due to molecular vibrations and allows qualitative and quantitative analysis of structural changes. The method has very high spatial resolution and allowed determination of the crystallinity and density of different polymers in monolayer and multilayer packaging and films. The emphasis was put on polyethylene due to the fact this polymer is widely used in the food industry and for HPP applications, but was also the polymer experiencing most decompression failure. Not only the crystalline content but also the amorphous content of polyethylene could be distinguished and so crystallization as well as plasticization could be identified.

This thesis is structured as follows:

1. Critical review of the mechanisms of bubble formation based on explosive decompression failure.
2. Critical review of damage mechanisms and pressure induced effects on polymeric materials and packaging.
3. A new methodology for measuring oxygen permeation through polymers under high hydrostatic pressure.
4. Measurement of the influence of headspace gases on the integrity and crystallinity of polymers and the migration potential of supercritical CO_2.

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2 The theory of decompression failure in polymers during the high-pressure processing of food

This review article is dealing with the influence of gases on polymers (thermoplastics, elastomers etc.) under very high pressures up to several thousands of bars and subsequent decompression. This topic is an important and crucial part of several current application and research areas like in petroleum industry (“explosive decompression failures” XDF), in fuel cell vehicles in hydrogen infrastructure, the foaming of polymers, in high pressure processing of packed food (HPP) or even in diving (decompression sickness). In all of these mentioned areas the formation of bubbles and blisters in matrices after a sudden pressure drop is a well-known phenomenon and part of important research work. It is known that the phenomenon is based on the supersaturation of gas in the polymer and the accompanied thermodynamical imbalance, hence an increase in free energy in the system at rapid decompression. The expansion of gas leads then to the mostly unwanted blistering effect.

Only the exact mechanisms of the formation of bubbles are still topic of current research. Especially at HPP of food, where pressures of up to 6,000 bars are reached at moderate temperatures only very few data is available. Considering relevant literature it could be shown that especially the solubility but also diffusion and permeability coefficient of gases in polymers under high pressures are the most important factors influencing the formation of bubbles. Therefore the first part of the review is dealing with the solution and transport properties of gases in polymers under pressure. In a second part it is concentrated on the theory of bubble nucleation and the influence of other parameters like material properties, gas nature and process conditions (e.g. temperature, decompression rate etc.) on bubble density and/or bubble growth. Scientific gaps, especially concerning very high pressure conditions are highlighted.

The theory of decompression failure in polymers during the high-pressure processing of food

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ABSTRACT

The occurrence of blistering and the formation of bubbles in matrices after a sudden pressure drop is a well-known phenomenon in many fields, including in the petroleum industry ("explosive decompression failure"), in diving (decompression sickness), in the infrastructure of hydrogen fuel cells, in the foaming of polymers, and in the high pressure processing of food (HPP). This usually undesirable effect is caused by the increased absorption of gas in the polymer under high pressure conditions and the subsequent supersaturation and increase in free energy on rapid pressure release. The exact mechanisms of the resulting expansion of gas, and hence the formation of bubbles, are not fully understood. Regarding the high pressure processing of food where pressures of up to 6,000 bars are reached at moderate temperatures, little information is available about the key factors involved in decompression failure. This review summarises results and findings from relevant research areas to understand polymer decompression failure. The first part of this review describes the transport properties of gases in polymers under high pressure (sorption and desorption, diffusion coefficient and permeability coefficient). The second part focuses on damage mechanisms and discusses parameters such as material properties, the nature of the gas and process conditions (e.g. temperature, decompression rate). Knowledge gaps and proposed research are highlighted.

Content Publication I

2.1 Abbreviations

APET	Amorphous polyethylene terephthalate
BD	Bubble density = bubbles/blisters per volume of the matrix
BS	Bubble size, volume or diameter
DCS	Decompression sickness
EPDM	Ethylene propylene diene, M-class
GR	Bubble growth rate
HPP	High pressure processing
MAP	Modified atmosphere packaging
NBR	Acrylonitrile butadiene rubber
PA11	Polyamide 11
PC	Polycarbonate
PEEK	Poly(ether-ether-ketone)
PE-HD	Polyethylene high density
PE-LD	Polyethylene low density
PET	Polyethylene terephthalate
PGA	Poly(glycolic acid)
PLLA	Poly L-lactic acide
PLG	Copolymer of D,L-lactide and glycolide (varying content)
Pmax	Maximum applied pressure in the system
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PSS	Supersaturation pressure
PSU	Polysulfone
PTFE	Polytetrafluorethylene (Teflon)
PVAc or PVA	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
scrCO_2	Supercritical carbon dioxide
SRR	Supersaturation ratio
STP	Standard temperature (273 K) and pressure (1.013 bar)
TiO_2	Titanium dioxide
Tg	Glass transition temperature
Tm	Melting temperature
VMQ	Vinyl methyl polysiloxane
XDF	Explosive decompression failure

2.2 Introduction

High pressure processing (HPP) is an innovative and increasingly used technology for prolonging the shelf life of temperature-sensitive food. In industry pressures up to 6,000 bars are reached and temperatures between 5 and 40°C are common. Under these conditions most bacteria and fungi are inactivated. To avoid recontamination via cost and time consuming aseptic filling after HPP, the food is packed and sealed before treatment. In many cases vacuum packaging is used. Increasingly, however, modified atmosphere packaging (MAP) with gases such as nitrogen (N_2), carbon dioxide (CO_2) and oxygen (O_2) is being utilized in order to use the synergistic effect of high pressure and CO_2 against certain enzymes and microorganisms (Al-Nehlawi et al. 2014, Corwin and Shellhammer 2002).

The negative side effect of using gases in the headspace of packaging is the expansion of gases during (fast) pressure release and the accompanying formation of bubbles, blisters or foam like structures in the polymer and food (Bull et al. 2010, Fairclough and Conti 2009, Fleckenstein et al. 2014, Götz and Weisser 2002, Koutchma et al. 2009, Masuda et al. 1992, Richter et al. 2010, Richter 2011, Sterr et al. 2015a). This phenomenon of decompression failure is also well known in other fields such as decompression sickness (DCS) for divers at pressures up to 10 bars or as "explosive decompression failure" (XDF) in the petroleum industry where polymers are used as seal barriers in flexible pipes for petroleum transportation processes with CO_2 ($P < 1{,}000$ bars and $70 < T < 130°C$) (Baudet et al. 2009, Boyer et al. 2007, Grolier and Boyer 2007). A similar effect also arises in the area of hydrogen fuel cells working with pressures up to 1,000 bars (Barth et al. 2013, Koga et al. 2013). In the food packaging industry the formation of bubbles and cracks is an undesirable effect as it negatively affects the overall packaging integrity, barrier properties or leads to film delamination (Fleckenstein et al. 2014, Götz and Weisser 2002, Sterr et al. 2015a). The exact mechanism of the decompression failure is still not fully understood and is the subject of ongoing research. This is particularly so for food packaging applications. This review therefore collates data and information from other research areas and considers their relevance to HPP. The first part of this review discusses the dissolution, diffusion and permeation of gases in and through polymers under high pressure conditions. This review focuses primarily on gases appearing in MAP including O_2, N_2 and CO_2 and on common polymers used in the food industry such as polyethylene

(PE), polyethylene terephthalate (PET), polypropylene (PP), polyamide (PA) and polystyrene (PS). Other gases and polymers are considered only if important for further understanding of decompression failure induced by high pressure. Differentiation is made between results derived from experiments working with high gas pressures (i.e. two-phase systems) and experiments working with high isostatic pressures, where the pressure is transmitted by an incompressible fluid (i.e. three-phase systems). The second part of the review discusses the theory of bubble formation and options for reducing decompression failure. The transport properties of gases in polymers, the mechanical properties of polymers and the process conditions such as the temperature and the pressure profile are taken into account.

2.3 Solution, diffusion and permeation of gases in polymers under pressure

The formation of bubbles and the amount and growth rate of bubbles are strongly dependent on the amount of gas that is able to dissolve in the polymer (solubility or sorption coefficient *S*) and the speed at which the gas diffuses through the polymer film (diffusion coefficient *D*) (Flook 2000). Different methods have been used for measuring the solubility, diffusion and permeability coefficient of gases through polymers under pressure (Flaconnèche et al. 2001b). These differing measurement methods can result in different outcomes. Further discrepancies arise in the application of "open" and "closed" pressure cells, with a dynamic gas flow with unlimited access of the polymer to gas in the former and a limited access to gas in the latter. The applied pressure in open systems gives a constant high partial pressure difference on the upper and bottom side of the polymer (flow-method), whereas the applied pressure in closed systems is uniform over the whole sample (hydrostatic) which means that only the volume of the sample changed during pressurization but not its shape. This hydrostatic system is also applied during the high pressure processing of food and is therefore of special interest.

2.3.1 The solubility of gases in polymers under pressure

In general the solubility *S*, also called sorption coefficient, describes the amount (e.g. concentration *c*) of a substance (gas) in a matrix (polymer) under equilibrium conditions at an applied partial pressure *p* (Barrer 1951). An explanation for variable results in the literature may be the different methods of determining and expressing solubility (Battino and Clever 1966). In this review the solubility is described as the weight of gas relative to the weight of the polymer $\left[\frac{g\ (gas)}{g\ (polymer)}\right]$, as is usual in the literature. Partial pressures above the solvent differing from the standard pressure of 1.013 bar may be corrected by Henry's law (Equation 2-1), a simple relationship that applies when there is proportionality between the molar fraction x_g [mol/mol] of gas diluted in the liquid (described by the Henry volatility constant K [bar]) and its partial pressure p_g in gas phase (Prausnitz et al. 1999, Sander 2015). There are also different ways of defining Henry's constant, as described in the work of Sander (2015).

Equation 2-1

$$p_g = K * x_g$$

Under low pressure conditions and at low gas concentrations Henry's law is independent of the pressure and concentration. However, there are some restrictions to the application of Henry's law at high concentrations of the solutions (the concentration of the substance or gas should not exceed a molar fraction of 3%) and at high pressures (the partial pressure should not exceed 5 to 10 bars), and when there are reactions of the solvent with the gas (Prausnitz et al. 1999). For real gases at high pressure, the partial pressure in Equation 2-1 must be replaced by the partial molal fugacity fi of the dissolved gas at the solvent total pressure (Wedler 1997). The fugacity f_i describes the deviant behaviour of a real gas to the ideal gas as a function of temperature and pressure and is defined by the dimensionless fugacity coefficient ϕ and the partial pressure pi (of an ideal gas) as shown in Equation 2-2.

Equation 2-2

$$f_i = \varphi * p_i$$

At high pressure the fugacity coefficient differs from one. Table 2-1 shows values of the fugacity coefficient of N_2, O_2 and CO_2 in water (Atkins and Paula 2006, Wedler 1997, Enns et al. 1965, Ludwig and Macdonald 2005, Spycher et al. 2003) and of CO_2 and CH_4 in PE (Sarrasin et al. 2015) at pressures up to 5,000 bars. The low fugacity values of CO_2 in PE were explained by the polarity of the molecules. This affects the attractive interactions, due to the fact that CO_2 is considered as a quadrupole. The CH_4 fugacity in PE decreases only slightly up to 300 bars and increases to ~2.9 at 2,000 bars. The coefficients of CH_4 and CO_2 in PE and of CO_2 in water presented in Table 2-1 were estimated based on a graph displayed in the work of Sarrasin et al. (2015) and Spycher et al. (2003).

Table 2-1 Fugacity coefficients of N_2, O_2 and CO_2 in water and of CO_2 and CH_4 in PE

P [bar]	**φ [-] N_2 in H_2O at 273 K**	**φ [-] O_2 in H_2O at 277 K**	**φ [-] CO_2 in H_2O at 300 K**	**φ [-] CO_2 in PE at 333 K**	**φ [-] CH_4 in PE at 333 K**
	Atkins and Paula 2006; Sarrasin et al. 2015; Wedler 1997	Enns et al. 1965; Ludwig and Macdonald 2005	Spycher et al. 2003	Sarrasin et al. 2015;	Sarrasin et al. 2015;
1	0.99955			~1	~1
10	0.9956			~0.97	
100	0.9703		~0.49	~0.7	
300		1.52	~0.24		~0.79
600			~0.21		
880					~1
1,000	1.839	4.0		~0.4	~1.14
1,330		6.34			
2,000		16.0			~2.9
5,000		1,041			

Different models exist for explaining diffusion and sorption processes of gases in polymers. Two models will be discussed here: The free volume theory and the dual sorption model. The free volume model is based on the assumption that the diffusing molecules are located in micro voids (free volumes) of the polymer matrix and movement of the molecules only takes place via statistical fluctuations of these voids by chain motion. For semi-crystalline polymers the theory predicts that it is largely the amorphous phase of the polymer or voids that are penetrable by the gas (Baudet et al. 2009, Michaels and Bixler 1961, Scheichl et al. 2005). Boyer et al. (2006) assumed that at higher pressures sorption may also take place in interstitial sites deeper in the polymer, such as in the crystal phase. The free volume model has been extensively described and reviewed elsewhere (Budd et al. 2005, Duncan et al. 2005, Fujita 1961, Mercea 2008, Vrentas et al. 1993, Vrentas and Duda 1977). Grolier and Boyer (2007) split the pressure dependence of CO_2 sorption into three parts. At low pressures, the sorption of gas on the surface and in the amorphous phase is an exothermic process. Secondly, at higher pressures, CO_2 also penetrates voids and interstitial regions in an endothermic process. At pressures above 300 bars the polymer acts as a pseudo-homogeneous phase saturated with supercritical CO_2. In scientific work concerning the influence of high hydrostatic pressure on the diffusion process it has become clear that the free volume is compressed by the pressure and therefore gas transport is reduced during this process (Fleckenstein et al. 2014, Richter et al. 2010, Richter 2011, Sterr et al. 2015b). However, plasticization effects may have an opposite effect on the transport properties of gases.

The dual sorption model assumes two types of sorption and solving molecules (Hilic et al. 2001, Muth et al. 2001, Vieth et al. 1976, Vieth 1991). Firstly, at the Langmuir type absorption sites in micro voids, molecules are completely immobilized, and secondly, in accordance with Henry’s law, small molecules with weak interactions are dissolved in the polymer matrix. Diffusion only occurs for the molecules dissolved in Henry’s mode (Tsujita 2003). The experiments of Hilic et al. (2001) show good agreement of the solubility of N_2 in PS up to 600 bars with the dual sorption model, whereas Chang et al. (1998) found the model to be inadequate for pressures exceeding 100 bars for CO_2 sorption in glassy polymers such as PC (35 to 50°C, 300 bars). Both were working with static gas pressures.

Several parameters that influence the sorption of gases in polymers have been identified including the temperature, pressure filler particles in the polymer, stiffness and the crosslinking density of the polymer chains (see sections below). Bonavoglia et al. (2006) also included the glass transition temperature and degree of crystallinity as parameters. Illustrative values for gas solubility in polymers at high pressure are listed in Table 2-2. More data on the solubility of gases in polymers under high static and dynamic pressures can be found in the work of Boyer et al. (2007), Briscoe and Mahgerefteh (1984), Lundberg et al. (1969) and Naito et al. (1991). For data on the transport properties at atmospheric pressure the reader is referred to the permeation and diffusion data of other authors (including Brandrup et al. 1999, Lewis et al. 2003).

2.3.1.1 *Influence of pressure on solubility*

It is generally observed that the solubility of gases in polymers increases with pressure (Areerat et al. 2002, Fairclough and Conti 2009, Kulkarni and Stern 1983, Lei et al. 2007, Ru-Ting and Xing-Yuan 2015, Sato et al. 1999, Tang et al. 2004b, Tang et al. 2007).

However, a few authors have observed a saturation behaviour of gases in polymers at elevated gas pressures (Boyer et al. 2011). For example, Muth et al. (2001) observed a flattening behaviour for CO_2 sorption in poly(vinyl chloride) (PVC) at 400 bars, but did not consider it as saturation behaviour. Briscoe and Zakaria (1991) found that the curve of mass uptake of CO_2 in a silicone elastomer at 42°C flattened from 110 bars up to 300 bars. Similar behaviour was observed by Spyriouni et al. (2009) for CO_2-PS systems (35 <T <132°C; 1< P< 300 bars). The levelling-off seemed to be more pronounced at the lower temperatures. Reasons for a solubility limit might reflect a decrease of the free volume, in addition to decreased chain motion. Sarrasin et al. (2015) observed an increasing but limited uptake of CO_2 in the amorphous PE phase (T = 60°C; 200 < Pgas < 1,000 bars). On the other hand, a decreasing solubility coefficient was observed for the same system under the same conditions when high hydrostatic pressures were applied (i.e. constant gas concentration).

Fairclough and Conti (2009) calculated the relative increase in solubility of N_2 in PP for gas pressures up to 7,000 bars at different temperatures on the basis of the ratio of the solubility at a given pressure to the solubility of the gas at liquid densities. They found that the solubility increases 50 fold at 20°C and 7,000 bars. However, no comparison with empirically collected data was undertaken. No other experimental data on the solubility of gases in polymers under isostatic pressures have been reported. A thermodynamic calculation developed by Klotz (1963) predicts that the solubility of O_2 in sea water is almost independent of the depth up to 1,000 m below the surface (~100 bars), whereas the N_2 solubility decreases 5 to 6% at 1,000 m depth. Wiebe and Gaddy found that the solubility of CO_2 in water increases by a factor of 4 (at 50°C) to 7 (at 100°C) when increasing the pressure from 25 to 700 bars (Wiebe and Gaddy 1939, 1940). No other investigations of the influence of isostatic pressures up to 6,000 bars or higher on the solubility of gases in polymers could be found in the literature.

2.3.1.2 *Influence of temperature on solubility*

At low pressures and temperatures up to 100°C the solubility of gases in common solvents decreases with increasing temperature. At higher temperatures, the solubility can increase with temperature (Prausnitz et al. 1999). At high pressures, two different effects of temperature on the solubility of gases in polymers are described in the literature. At constant pressure, increasing temperature decreases the solubility of gases in polymers

(Battino and Clever 1966, Boyer et al. 2011, Hilic et al. 2001, Sato et al. 1999, Sato et al. 2000, Tromans 1998). Areerat et al. (2002) measured a negative slope for CO_2 solubility in PP and PE-LD/TiO_2 systems with increasing temperature from 150 to 200°C and at constant pressures up to170 bars. Similar results were obtained by Lei et al. in a CO_2–PP system with increasing temperature (40< T< 120°C and 160 < T< 210°C) and at constant gas pressures up to 250 bars. When compared to the rubbery state, these authors observed a higher gas solubility in polymers in the molten state (>160°C). A larger fraction of available amorphous regions was assumed to explain this observation. Thus, gas solubility increases in the 120 to 160°C transition region (Lei et al. 2007). Hilic et al. (2001) presumed that a negative slope of the temperature dependence of the gas solubility should be commonly observed in binary systems comprising an amorphous polymer and light gases such as N_2, O_2 and Ar at temperatures below the glass transition temperature T_g. “Reverse solubility”, i.e., when the gas solubility increases with temperature, is observed for gases with low critical temperatures (e.g. N_2 and H_2; Sato et al. 1999) but only at high temperature. However, this effect has been found for N_2 and He in polytetrafluorethylene (PTFE) even at low temperatures (T< 80°C) and 380 bars (Briscoe and Mahgerefteh 1984). Flaconnèche et al. (2001a) measured a divergent solubility dependence on temperature. In PE they did not find a measurable influence of temperature on the solubility of CO_2, N_2 or He. CH_4 solubility in PE showed reverse solubility in the 80°C to 40°C range, whereas CO_2 solubility in polyamide (PA11) and poly(vinylidene fluoride) (PVDF) increased with decreasing temperature while it decreased for N_2 and He. The solubility of CH_4 in PA11 and PVDF seemed to be unaffected by temperature. A possible explanation for some of these conflicting results could be the different measurement methods used at high pressures and the inclusion of swelling effects (Lei et al. 2007). Additionally, adiabatic heating was not taken into account in any of the relevant publications. In the case of HPP applications, heat transfer to the pressurizing medium should also be considered.

2.3.1.3 *Influence of the nature of the gas on solubility*

Gas solubility is strongly dependent on the gas-polymer system properties. Experiments with silicone elastomers showed that the mass uptake of N_2 into the material is 6 to 7 times less than the CO_2 uptake observed at 42°C and pressures up to 220 bars (Briscoe and Zakaria 1990b). Flaconnèche et al. (2001a) measured the solubility of CO_2, CH_4, Ar and N_2 in PE, PA11 and PVDF ($40< T< 80°C$ and $P< 120$ bars). They observed the highest solubility values for CO_2, followed by CH_4, Ar and N_2. In other studies ($40 <T < 160°C$ and $100 < P < 220$ bars) it was confirmed that CO_2 has 4 to 16 times higher solubility than N_2 in PE-HD, PP, PS and also a silicone elastomer (Briscoe and Zakaria 1990b, Sato et al. 1999, Sato et al. 1996). These results at high gas pressures are similar to the solubility behaviour of gases under atmospheric conditions (Michaels and Bixler 1961).

The presence of additional gases may alter the transport behaviour of gas. This might be of importance for the high pressure processing of food, if modified atmosphere packaging is used. This phenomenon is also observed at atmospheric pressure and it has been shown that the solubility of N_2 and O_2 in PE is affected by the presence of CO_2, whereas the mechanisms of solubility and diffusion of CO_2 seemed to be unaffected by other gases (Pino et al. 2005). Comparable results were found by Lewis et al. (2003) concerning the modified transport properties of N_2 in PET in the presence of CO_2 or O_2. A decreasing solubility of CO_2 in a silicone rubber (poly(dimethyl) siloxane) at pressures up to 60 bars due to the presence of N_2 was measured by Jordan and Koros (1990). Sarrasin et al. (2015) found that the solubility coefficients of H_2S and CH_4 in PE were not altered by the presence of the other gas for total gas pressures of 2,000 bars.

2.3.1.4 Influence of polymer structure, filler particles, plasticizers and composites on solubility

The maximal amount of gas taken up by a polymer under elevated gas pressures is also influenced by the structural properties of the polymeric material such as the degree of crystallinity, density and molecular weight (Sato et al. 1999). Other studies have shown that higher stiffness and an accompanying lower amorphous content reduces the amount of dissolved gas (CO_2, N_2, Ar, etc.) in polymers such as PE and elastomers at high static gas pressures (Briscoe and Kelly 1996, Briscoe and Zakaria 1990b, Flaconnèche et al. 2001a). Under atmospheric conditions, a linear correlation between the solubility of thirteen different gases in PE and the amorphous content was found by Michaels and Bixler (1961).

In the studies of Briscoe and Zakaria (1992) it was shown that elastomers with filler particles could take up more gas at high pressures than the pure polymer, due to the weak internal matrix-filler bonds, except when a gas such as CO_2 is able to rupture the internal interfaces. In general, the affinity of the diffusing molecules to the filler particles and hence the solubility of the gas in the filler particles is of importance for reasoning this behaviour (Duncan et al. 2005). Briscoe et al. (1994) presents a good overview of the effect of filler particles on gas solubility. Areerat et al. (2002) pointed out the different ways for examining gas solubility in polymers with filler particles. The "apparent" solubility, which is defined as the weight of dissolved gas per unit weight of the composite, was compared to the "true" solubility, which is defined by the weight of dissolved gas per unit weight of polymer. Studies on the solubility of CO_2 in a blend of PE and titanium dioxide (TiO_2) at high pressures ($150 < T < 200$°C and P= 150 bars) showed that the apparent solubility decreases with increasing TiO_2 content, whereas the true solubility stays constant, even when the TiO_2 content changes. No information was given about the solubility of CO_2 in TiO_2. Yamabe and Nishimura (2010) tested the influence of carbon black and silica filler particles in rubbery polymers on decompression failure (T = 30°C, P = 100 bars) and observed that composites without particles and with silicon particles take up less H_2 than with carbon black particles. This is explained by the ability of carbon black to absorb H_2, whereas silica does not absorb H_2. Flaconnèche et al. (2001a) observed that the incorporation of different weight fractions of plasticizer (n-butyl-benzene-sulphonamide) had only a minor influence on the solubility of CH_4 in PA11 (T = 120°C and P = 40 bars). The solubility of CO_2 in PA11 under the same conditions was slightly increased by incorporation of 29.5% plasticiser.

Table 2-2 Effect of temperature (T) and pressure (P) on the solubility of gases in various polymers

Gas	**Polymer**	**T [°C]**	**P [bar]**	**Solubility / Sorption [$g_{(gas)}/g_{(polymer)}$]**	**Reference**
Experimental temperatures below the glass transition temperature T_g of the polymers					
N_2	PS	40	161 (1)	0.008	(Sato et al. 1999)
		60	165 (1)	0.006	
		80	175 (1)	0.006	
N_2	PS	40	700 (1)	0.026	(Hilic et al. 2001)
		60	500 (1)	0.021	
		80	620 (1)	0.018	
CO_2	PVC	50	400 (1)	0.12	(Muth et al. 2001)
CO_2	PVC	25	62 (1)	~0.08	(Berens et al. 1992)
	PC			~0.12	
	PMMA			~0.25	
CO_2	PSU	40	400 (1)	0.12	(Tang et al. 2004a,
	PC			~0.14	Tang et al. 2004b)
Process temperatures ranging between T_g and T_m of the polymer					

O_2	PE-LD	25	50 (2)	0.003	(Naito et al. 1991)
	PP			0.003	
CO_2	PE-LD	25	50 (2)	0.023	(Naito et al. 1991)
	PP			0.029	
CH_4	PE	60	2,000 – 5,500 (3)	~0.03 – 0.04	(Sarrasin et al. 2015)
CO_2	PE	60	500 (3)	~0.05	(Sarrasin et al. 2015)
CO_2	PE	20	23(1)	0.012	(Kulkarni and Stern 1983)
CO_2	PE-MD	40	40(1)	0.047	(Flaconnèche et al. 2001a)
	PE-LD			0.07	
N_2	PE-LD	70	100(1)	0.004	(Flaconnèche et al. 2001a)
	PA11			0.003	
CO_2	PE-MD	60	350(1)	~0.08	(Boyer et al. 2007)
CO_2	PP	40	100(1)	0.0201 – 0.0542	(Lei et al. 2007)
CO_2	PP	100	120(1)	~0.13	(Ru-Ting and Xing-Yuan 2015)
CO_2	PET	80	300(1)	~0.030	(Schnitzler and Eggers 1999)
		120		~0.033	

(1) Gas pressure

(2) Dynamic pressure. Pressure difference between upstream and downstream gas flow $\Delta P_{(dyn)}$

(3) Theoretical approach, computational simulations and/or calculations

2.3.2 Swelling and volume changes of polymers due to gas sorption

The determination of the solubility of gases in polymers is often measured by the relative volume change or the swelling of the polymer caused by the uptake of gases (Boyer and Grolier 2005b, Kazarian 2000). Concerning the measurement of solubility via the volume change of a polymer, the opposite effect of hydrostatic compression has to be taken into account under high pressure conditions. Ultimately the measured volume is a result of several factors such as the solubility of the gas (increasing solubility and amount of dissolved gas leads to increasing volume), the maximum applied pressure, the temperature and/or thermal expansion and whether the polymer has a rubbery, glassy or semi-crystalline structure (Bonavoglia et al. 2006, Briscoe and Zakaria 1991, Hilic et al. 2001, Jordan and Koros 1990). Increases in the polymer volume due to swelling range between 1% for N_2 in PS to 130% for CO_2 in a rubbery polymer (Table 2-3). The negative (relative) volume change of the PE amorphous phase is about 6% in the absence of gas, namely neglecting swelling, for pressures up to 2,000 bars (Sarrasin et al. 2015). The methods of measuring the gas solubility and the associated swelling have been reviewed by Grolier and Boyer (2007).

Table 2-3 Effect of temperature (T) and pressure (P) on the relative volume change (RVC) of gases in various polymers

Polymer	Gas	T [°C]	Gas P [bar]	RVC [%]	Reference
PET	CO_2	60	300	+2.4	(Schnitzler and Eggers 1999)
PET	CO_2	40	300	+2.5	
PC	CO_2	40	300	+9.5	
PS	CO_2	35	100	+11	
PMMA	CO_2	35	100	+17	
Rubbery polymer	CO_2	35	300	+130	(Chang et al. 1998)
PE	CO_2	80	1,000	+12	(Sarrasin et al. 2015)
PS	N_2	40	266	+1.1	(Hilic et al. 2001)
		40	695	+2.2	
		80	625	+0.7	
PS	CO_2	45	102	+9.4	
		90	246	+13.3	

2.3.2.1 *Influence of temperature on the swelling behaviour of polymers*

Schnitzler and Eggers (1999) found that the swelling of PET decreased with increasing temperature under low temperature conditions (40< T< 60°C), namely at temperatures less than Tg, due to the lower CO_2 density which resulted in a decreased amount of dissolved CO_2. On the other hand, the swelling increased with increasing temperature at higher temperatures (70 < T< 120°C), namely temperatures below melting temperature Tm, due to the higher chain mobility. These results were confirmed by Lei et al. (2007) for a CO_2-PP system up to 100 bars and by Spyriouni et al. (2009) for a CO_2-PS system, in particular for pressures below 100 bars. Also, Hilic et al. (2001) reported that the relative volume change in PS due to dissolution of N_2 and CO_2 decreased with temperature at temperatures below Tg. It was also presumed that the relative volume change is more important below Tg, because of the plasticisation effect of the solute, and thus solubility and volume changes are less pronounced above Tg. Schnitzler and Eggers (1999) assumed that the amount of swelling increases significantly on exceeding the glass transition temperature of the polymer. When the temperature approaches the melting temperature Tm, the amount of swelling increases with temperature. The authors assumed that the compression of the polymer by pressure is negligible. No published data were found concerning the temperature dependent swelling behaviour under high hydrostatic pressure with consideration of compression effects.

2.3.2.2 *Influence of pressure on the swelling behaviour of polymers*

Sarrasin et al. (2015) found that the swelling of the amorphous phase in PE by CO_2 reaches a maximum of about 8% (relative volume change) at 60°C and about 12% at 80°C for pressures up to 1,000 bars. The limited swelling ability was explained by the antagonistic effect of gas uptake and a compression effect that reduces the free volume and hence the sorption process. Likewise in the studies of Hilic et al. (2001) (N_2-PS system at $40< T< 80°C$, $P = 700$ bars and CO_2-PS system at $65< T< 130°C$, $P = 450$ bars), in the work of Spyriouni et al. (2009) (CO_2-PS system at $35< T< 130°C$, $P = 300$ bars) and in the experiments of Schrittesser et al. (2016) (CO_2-elastomer system up to 150 bars), the relative volume changes seemed to flatten with increasing gas pressures. However, no maximum was detected. The levelling off appears to be more pronounced at lower temperatures (32 and 50°C). On the contrary, Lei et al. (2007) noted that swelling of PP due to CO_2 sorption ($40< T< 210°C$) increases with pressure at higher pressures up to 250 bars.

2.3.2.3 *Correction of solubility calculation due to swelling behaviour*

Lei et al. (2007) and Sato et al. (2001) included the polymer swelling in their gas solubility estimations. The corrected solubility values are higher by a factor of 7 to 20% compared to the values obtained when neglecting swelling (e.g. using gravimetric measurements) and the factor increases with temperature (Sato et al. 2001). In contrast, the swelling-corrected values of Lei et al. (2007) were up to 160% higher and increased with pressure. Bonavoglia et al. (2006) corrected the values of swelling as a function of dissolved CO_2 concentration and noted that the curve in general can be divided into three regions. In the first region, gas sorption occurs without swelling of the polymer. In the second region swelling and gas sorption go hand in hand and in the third region swelling can be neglected again. Nilsson et al. (2013) noted that the calculation of solubility is independent of the swelling behaviour, because the solubility is linearly related to the density.

2.3.3 Plasticisation and changes in the glass transition temperature

Swelling does not merely change the volume of a polymer, it also increases the free volume and chain mobility (Chiou et al. 1985b, Kazarian 2000, Tang et al. 2004b). This phenomenon, called plasticisation, has an influence on the solubility and the rate of diffusion (See section *Diffusion*), which may then become a function of concentration and time and show non-Fickian behaviour (Klopffer and Flaconnèche 2001). The antagonistic effects of compression and swelling (or plasticisation) on the molecular chain motion also have to be considered here (Briscoe and Zakaria 1991). The plasticisation is linked to changes in the glass transition temperature T_g. Gases with higher critical temperatures such as CO_2 and CH_4 are more condensable and thus have a strong plasticising effect with an accompany effect on the T_g of the polymer (Bonavoglia et al. 2006, Berens et al. 1992, Chiou et al. 1985a, Jordan and Koros 1990). Plasticisation by these gases may dominate the compression effect, whereas for gases with low sorption behaviour such as N_2 and He the compressing effect may dominate. Another explanation was proposed by Bos et al. (1999) who predicted that polarisable CO_2 may interact with polar groups of the polymer and therefore show higher plasticisation tendency.

The influence of the applied pressure and the additional sorption of gas on Tg have been analysed by several authors (Berens et al. 1992, Bonavoglia et al. 2006, Boyer and Grolier 2005a, Grolier and Boyer 2007, Schnitzler and Eggers 1999, Tang et al. 2007, Wang et al. 1982, Wessling et al. 1994, Zhang and Handa 1998). All concurred that increasing gas pressure reduces Tg via the increased gas sorption and the resulting plasticising effects. Examples of values calculated using a model developed by Chow (1980) for predicting the pressure induced changes in Tg show that N_2 is able to reduce the Tg of PS by 47°C (at 40°C and pressures up to 700 bars), whereas CO_2 can depress the Tg of PS by 80 to 100°C at 250 bars and a temperature of 65°C (Boyer and Grolier 2005a). Similar results were obtained by Bonavoglia et al. (2006), Berens et al. (1992) and Chiou et al. (1985a) for common glassy polymers such as PMMA, PC, PVA, PVDF, PET and PVC.

Only a few reports support the idea that the Tg may also increase with pressure, in situations when the polymer matrix compression effect due to pressure dominates the plasticisation effect of the gas (Briscoe et al. 1994, Campion and Morgan 1992, Wang et al. 1982). Additionally, it is assumed that this is more common in elastomers than in glassy polymers. In experiments working at hydrostatic pressures up to 10,000 bars (water or petroleum ether as pressure transmitting fluid), Paterson (1964) found that the Tg of several rubbers increased by ~16°C per 1,000 bars, but only at pressures above 1,000 to 5,000 bars and when the Young's Modulus increased 1,000 fold. At lower pressures, the Young's Modulus only increased by a factor of 2-3. A good but older overview of pressure induced changes on the mechanical properties and of the pressure-induced increase in Tg of polymers can be found in the report by Jones Parry and Tabor (1973). Readers can find additional information on sorption-induced plasticisation and crystallisation in the work of Fleckenstein et al. (2014) and Kazarian (2000). For detailed data on the glass transition temperatures of polymers, readers are referred to the publication of Brandrup et al. (1999).

2.3.4 The diffusion coefficients of gases in polymers under pressure

The diffusion coefficient *D* describes the mobility of molecules passing through a matrix by random molecular motion and is defined by the root mean square displacement of the molecules per time [m²/s] (Crank 1975). The diffusion coefficient is highly dependent on the gas concentration and at high pressure, *D* increases with gas concentration (Briscoe et al. 1994, Flaconnèche et al. 2001a, Kulkarni and Stern 1983, Naito et al. 1991). This correlation is enhanced by the swelling of the polymer and increased chain motion due to the plasticisation effect at high gas concentrations and high pressures. It is reduced by compression of the matrix when applying very high pressures. Table 2-4 shows values for the diffusion coefficient, sorption diffusivity and desorption diffusivity of gases in polymers at high pressures.

2.3.4.1 Differentiation between sorption diffusivity (Ds) and desorption diffusivity (Dd)

Studies on the mechanisms of bubble formation require knowledge of how fast the gas enters the polymer during pressure build up and the pressure holding time and also how fast the gas can escape from the polymer during pressure release. In ideal systems, when *D* is constant, the sorption and desorption behaviour is symmetric. However, Duncan et al. (2005) postulated substantial asymmetry between gas uptake and release after pressure treatment and so additional differentiation between the sorption diffusivity D_s and desorption diffusivity D_d in polymers is necessary. In their work, they postulated a marked hysteresis if the "absorbed molecules are strongly bound in the polymer". Confirming results were reported by Lorge et al. (1999) for a CO_2-PVDF system at 80°C and gas pressures up to 300 bars. They reported that gas desorption was only detectable at pressure below 150 bars. Other studies have shown the hysteresis effect more often for polymers in the glassy compared to the rubbery state (Fleming and Koros 1986). The hysteresis effect may also reflect the swelling of the polymers which occurs during plasticisation, or even crystallization effects and possible damage such as XDF during sudden pressure release after high pressure processing.

Only a few studies have differentiated between Ds and Dd and found that desorption after pressure treatment is slower than the sorption diffusivity, namely Ds > Dd (Muth et al. 2001, Tang et al. 2007). Tang et al. (2004b) reported contrary results showing higher Dd than Ds values for CO_2 in PSU and PC (T = 40°C, P = 400 bars). The results were attributed to the plasticising effect of CO_2 during the desorption process and the stronger interaction between CO_2 and the carbonyl group of PC during sorption (Tang et al. 2004b). Flook (2000) noted that the “gas washout” of saturated tissue takes longer than the gas uptake to full saturation. The author was studying the transport properties of Ar, N_2 and He in human tissue in hydrostatic pressure systems for diving. Additional information on desorption kinetics has been reported by Grandidier et al. (2015). Concerning the temperature dependence of Ds and Dd it was found that at a given gas pressure P the desorption diffusivity of CO_2 in PSU and PVC increases with temperature, whereas Dd decreases (Tang et al. 2007, Muth et al. 2001). Other authors calculated the time to release a certain amount of gas from the polymer (Nilsson et al. 2013, Grandidier et al. 2015, Fleming and Koros 1986, Tang et al. 2004b).

2.3.4.2 *Influence of pressure and temperature on the diffusion coefficient*

Experiments on the diffusion coefficient of O_2 in seawater (35‰ salinity) show that D increases with temperature. Below a temperature-dependent maximum pressure, the diffusion coefficient increases with pressure. At 20°C, D reaches a maximum at 240 to 330 bars, whereas at 0°C data extrapolation suggest a maximum at 1,200 bars. Beyond these pressures the diffusion coefficient decreases when the pressure is increased (Ramsing and Gundersen 2000). Similar results were reported by Nilsson et al. (2013) using a model predicting the diffusivity of gases in polymers at gas pressures up to 700 bars. The maximum D value is centred at around 50 to 200 bars. The reason for diffusivities increasing with pressure at low pressures is assumed to reflect an increase in the free volume due to gas sorption and swelling. The opposite effect at higher pressures is assumed due to the dominating polymer compression effect relative to the swelling effect. This correlation was taken into account by Naito et al. (1991) when including in Equation 2-4 a compression effect due to the hydrostatic pressure given by the negative parameter β_h and a volume increase of the material given by the positive swelling factor α. Both parameters are assumed to be dependent on the size of the diffusing molecules. The diffusion coefficient D at higher pressures can be calculated from the diffusion constant D_0 under atmospheric conditions and the partial pressure of the gas p_g (Equation 2-3) (Naito et al. 1991). Flaconnèche et al. (2001a) could not detect any pressure or temperature dependence on the diffusion coefficient of CH_4 or CO_2 in PE in the 40 to 100 bars and the 40 to 80°C range. No relevant literature data was found concerning the diffusion coefficients of gases in polymers at isostatic pressures.

Equation 2-3

$$D = D_0 * e^{\beta p_g}$$

Equation 2-4

$$\beta = \beta_h + \alpha \frac{S}{2}$$

Table 2-4 Effect of temperature (T) and pressure (P) on the gas desorption and sorption diffusion coefficient (D) in various polymers

Gas	Polymer	T [°C]	P [bar]	D [m^2/s]	Reference
Desorption diffusivity D_d					
CO_2	PVC	50	400 (1)	$0.24*10^{-11}$	(Muth et al. 2001)
CO_2	PSU	40	400 (1)	$2.37*10^{-11}$	(Tang et al. 2004b)
CO_2	PMMA	40	60 (1)	$1.20*10^{-11}$	(Tang et al. 2007)
CO_2	PS >>>PVC >PMMA	25	65 (1)	10^{-10} to 10^{-11}	(Berens et al. 1992)
Sorption diffusivity D_s					
CO_2	PVC	50	400 (1)	$1.36*10^{-11}$	(Muth et al. 2001)
CO_2	PSU	40	400 (1)	$0.54*10^{-11}$	(Tang et al. 2004b)
CO_2	PMMA	40	60 (1)	$6.57*10^{-11}$	(Tang et al. 2007)
CO_2	PS	80	245 (1)	$2.4*10^{-10}$	(Arora et al. 1998)
Diffusion coefficient D					
CO_2	PET	80 120	300 (1)	$1.7*10^{-11}$ $5.0*10^{-11}$	(Schnitzler and Eggers 1999)
CO_2	PS	100	83 (1)	$1.67*10^{-10}$	(Sato et al. 2001)
CO_2	PBS	120	120 (1)	$1.23*10^{-9}$	(Sato et al. 2000)
CO_2	PE-MD	60	40 (1)	$1.04*10^{-10}$	(Flaconnèche et al. 2001a)
CO_2	PE	20	23 (1)	$5{,}24*10^{-11}$	(Kulkarni and Stern 1983)
O_2	Rubbery polymer	25	110 (2)	$7.5*10^{-11}$	(Naito et al. 1996)
	PA11	70 – 100	40 – 100 (1)	$D(He)>>>D(CO_2)\approx D(Ar)>D(CH_4)\approx D(N_2)$	(Flaconnèche et al. 2001a)
	PE	40 – 80	40 – 100 (1)	$D(He)>>>D(CO_2)\approx D(Ar)\approx D(CH_4)\approx D(N_2)$	(Flaconnèche et al. 2001a)

(1) Gas pressure

(2) Dynamic pressure. Pressure difference between upstream and downstream gas flow $\Delta P_{(dyn)}$

2.3.5 Permeation of gases through polymers at high pressures

The permeation is a product of the solubility and diffusion coefficient and therefore involves complex interaction between several parameters. Measurement difficulties may explain why few authors have reported data on the permeation of gases through polymers at pressures exceeding 100 bars (Campion and Morgan 1992). Campion and Morgan (1992) and Flaconnèche et al. (2001b) have described units for measuring the upstream and downstream pressure difference of the gas to determine the permeability coefficient P of pure and mixed gases (CH4, CO_2, H2S) in polymers at temperatures up to 200°C and dynamic gas pressures up to 1,000 bars. More recently Sterr et al. (2015b) presented a new setup for fluorescence-based measurement of O_2 permeation in an aqueous environment through polymers at isostatic pressures (T< 50°C, P< 2,000 bars) and independently controlled O_2 partial pressures of around 0.21 bar. These studies showed that the transport mechanisms at high pressures follow Arrhenius' behaviour. A measurable but complex influence of crystallinity on the permeability coefficient, due to a plasticisation effect was observed by Flaconnèche et al. (2001b). Flaconnèche et al. 2001a reported that increasing the plasticiser content in PA11 increased the CH_4 and CO_2 gas permeation rate (T = 120°C, Pgas = 40 bars). Similar conclusions on the influence of crystallinity were made by Sterr et al. (2015b) when reviewing previously reported data (Richter et al. 2010, Richter 2011).

The studies of Sterr et al. (2015b) showed a negative exponential pressure dependence of the permeability coefficient for pressures up to 2,000 bars at 23°C and a reduction of the coefficient by a factor of 35 to 70 in PE films. However, the permeability coefficient at around 100 bars is only reduced by a factor of 1.5 to 2. From the results of Naito et al. (1991) there is a similar factor for the reduced permeability coefficient of O_2 in PE at 100 bars (dynamic gas pressure, two-phase system). Campion and Morgan (1992) measured a two-fold reduction for H2 in different elastomers at gas pressures up to 400 bars (T = 50°C). For gases with a low critical temperature such as N_2 and He, Jordan and Koros (1990) observed that the permeability coefficients decreased by a factor of 1.5 to 1.6 in silicone rubbers for gas pressures increasing up to 62 bars at 35°C, whereas the permeation increased with increasing pressure for CO_2 (1.2 fold). These authors termed the former gases “compressors” and the latter gases “plasticisers”. These findings were confirmed by Naito et al. (1991) who reported that highly soluble gases with a large molecular diameter (e.g. CO_2, CH_4) show a positive dependence of the permeability coefficients with pressure, whereas less soluble gases (e.g. He, H_2, N_2, O_2 and Ar) present no reduction or only a low reduction in permeation with pressure in PP and PE-LD films at 25°C and at pressures up to 100 bars. N_2 molecules have a relatively large diameter, like the first group of gases, but only low solubility and therefore does not show similar permeation behaviour. It was also noted that the plasticising effect is higher in PP than in PE due to the different amounts of crystalline regions in the polymer. Other measurements of CO_2 permeation in 11 glassy polymers showed that at gas pressures of 10 to 40 bars the permeability coefficient decreases with pressure, while it rises at pressures above 50 bars. The pressure at which the minimum in permeation occurs was called the plasticisation pressure (Bos et al. 1999). It is questionable whether this effect is valid at pressures up to 6,000 bars, as applied in the high pressure processing of food. Probably the compression of the matrix at high hydrostatic pressure overcomes the plasticisation effect. Unfortunately no relevant data on gas permeation through polymers at such high hydrostatic pressures is available.

It is also important to examine the behaviour of gas mixtures, given that the permeation of a particular gas may be influenced by other gases (Scheichl et al. 2005). In the case of CO_2, its permeability coefficient in silicone rubber is decreased by N_2 (Jordan and Koros 1990). This may reflect the compressive nature of N_2. This effect also works the other way around, with increased permeation and an increased diffusion coefficient for N_2 in the presence of CO_2. In general, the effect depends on the mixing ratio of the gases. Additional permeability coefficient data and general observations on reported values are summarised in Table 2-5.

Table 2-5 Effect of maximum pressure (Pmax) and temperature (T) on the permeability coefficients (Q, P) at high pressure of gases in various polymers

Gas	Polymer	T [°C]	P_{max} [bar]	Permeability Q $\left[\frac{cm^3}{m^2*d*bar}\right]$ Permeability coefficient P $\left[\frac{cm^3*[100\mu m]}{m^2*d*bar}\right]$		Reference
Decreasing permeability coefficient with increasing pressure						
O_2	PE	23	1 2,000 (3)	P	1,5*10^3 - 2,1*10^3 29 to 44	(Sterr et al. 2015b)
N_2	Silicone rubber: Poly(dimethyl) siloxane	35	41 (2)	P	25*10^3	(Jordan and Koros 1990)
He					36*10^3	
CO_2					440*10^3	
CO_2	PVC	50	400 (1)	P	0.44*10^3 (Desorption) 2.49*10^3 (Sorption)	(Muth et al. 2001)
CO_2	PET	80	300 (1)	P	1.03*10^3	(Schnitzler and Eggers 1999)
		120			3.03*10^3	
CO_2	PE	20	23 (1)	P	11*10^3	(Kulkarni and Stern 1983)
CO_2	PE-LD	40	40 (2)	P	19*10^3	
N_2	PE-LD	70	100 (2)	P	4.4*10^3	
N_2	PA11	70	100 (2)	P	0.14*10^3	
He		40 – 130	40 to 120 (2)	P	PE > PA11 ≈ PVDF	(Flaconnèche et al. 2001a)
Ar	PE			P	He ≈ CO_2 >> Ar> CH_4 > N_2	
N_2	PA11	40 – 80		P	CO_2 > He > CH_4 > Ar > N_2	
CH_4	PVDF	40 – 130	40 to 100 (2)	P	He > CO_2 > Ar > CH_4 > N_2	
CO_2						

CO_2 He N_2	Silicone rubber: Poly(dimethyl) siloxane	35	62 (2)	P	$CO_2 >> He > N_2$	(Jordan and Koros 1990)
N_2 H_2 He	Synthetic rubber (VMQ and EPDM)	25	100 (2)	Q	$He = H_2 >> N_2$	(Koga et al. 2013)
No or only small reduction of the permeability coefficient with increasing pressure (sparingly soluble gases)						
	PP PE	25	100 (2)	P	$He \approx H_2 >> O_2 \approx Ar >> N_2$	(Naito et al. 1991)
	Polybutadiene	25	80 (2)	P	$He \approx H_2 >> O_2 \approx Ar >> N_2$	(Naito et al. 1996)
Increasing permeability coefficient with increasing pressure (highly soluble gases)						
	PP PE	25	100 (2)	P	$N_2O > CO_2 >> CH_4$	(Naito et al. 1991)
	Polybutadiene	25	80 (2)	P	$N_2O > CO_2 > C_2H_4$	(Naito et al. 1996)
CO_2	Silicone rubber	35	41 (2)	P	$440*10^3$	(Jordan and Koros 1990)

(1) Static gas pressure

(2) Dynamic pressure. Pressure difference between upstream and downstream gas flow $\Delta P_{(dyn)}$

(3) Hydrostatic pressure

2.4 Theory of the formation and nucleation of bubbles

2.4.1 Definition and formation of bubbles

Several definitions of bubbles and mechanisms for their initial formation have been reported. Lubetkin (1994) stated that bubbles are “gas surrounded by a bilayer of surfactant in a second gas phase, and gas surrounded entirely by a liquid with or without surfactant”. The latter form plays a significant role in HPP. It is generally accepted that bubbles have their origin in stable gas micronuclei or form spontaneously when the pressure drop is high enough. In theory, nanobubbles form spontaneously after decompression on hydrophobic surfaces from gas dissolved in the liquid (Arieli and Marmur 2011, 2013). Gas micronuclei arise from nanobubbles and visible bubbles grow from them. Lubetkin (1994) assumed six different sources for the formation of bubbles including homogeneous and heterogeneous nucleation, cavitation, electrolysis, Harvey nuclei and pre-existing, stable colloidal free bubbles. Harvey nuclei are pre-existing nuclei with a radius greater than the critical radius of curvature (Jones et al. 1999). Electrolysis is not relevant for bubble formation in HPP. Although homogeneous nucleation normally occurs only in single-component systems without surfaces or particles acting as inhomogeneities, it has been postulated that it may be relevant for systems with supersaturation ratios (*SSR*) in excess of about 1,000 and thus relevant to HPP applications (Campbell 1968, Lubetkin 1994, Wilt 1986). The dimensionless *SSR* of a system is defined as the ratio of the equilibrium pressure of the gas to the pressure in the system (Wilt 1986). According to Wilt (1986), a supersaturation ratio of more than 20 ($SRR > 20$) is required for heterogeneous nucleation to arise. Heterogeneous nucleation takes place due to fluctuations of density on particles or surfaces, especially on rough hydrophobic surfaces (Fischer 2001). For *de novo* formation of bubbles or for very small nucleation sites supersaturation pressures exceeding 100 bars ($P_{SS} > 100$ bars) and very high *SRR* must be achieved to overcome the surface tension of pre-existing gas nuclei (Papadopoulou et al. 2013, Jones et al. 1999). The supersaturation pressure, also called the “critical pressure” or “initial pressure”, is the maximum applicable pressure P_{max} before bubble formation is observed after decompression. The surface tension γ in relation to the radius of curvature r of the bubble and the difference in the (partial) pressure inside and outside the bubble Δp is the critical factor for a bubble to be stable, grow or dissolve

(Harvey et al. 1944). This correlation is described by the Young-Laplace-Equation (Equation 2-5). The minimum radius necessary for a bubble to be stable is called the critical radius r_{crit}.

Equation 2-5

$$r_{crit} = \frac{2\gamma}{\Delta p}$$

The growth and also the dissolution of a bubble in a polymer is thus dependent on Δp, on the solubility and diffusion coefficient of the gas in the matrix and on the diffusion of the gas across the surface surrounding the bubble. (Flook 2000, Harvey et al. 1944, Lubetkin 1994). At very high applied pressures (e.g. 1,000 bars) the pressure overcomes the surface tension and micronuclei redissolve in the matrix (Harvey et al. 1944). This could imply that in the high pressure processing of food at pressures up to 6,000 bars most of the gas nuclei would be dissolved and bubble formation would mainly originate from spontaneous formation. In addition, additives in polymers and crystallites may serve as nucleation points.

Cavitation occurs in gas-saturated fluids after a sudden pressure drop, as observed in a narrow pipe when fluid velocities are high enough (Harvey 1945). At higher pressures, cavitation effects, namely degassing cavitation, may emerge by desorption of the dissolved gas (Papadopoulou et al. 2013). In polymers, cavitation generally arises in the free amorphous phase (Baudet et al. 2009). A cavitation effect of H2 and CO_2 in PVDF after decompression was reported by Boyer et al. (2013).

The phenomenon of tribonucleation arises when two solid surfaces immersed in a liquid are separated rapidly (Hayward 1967, Ikels 1970). It may be of relevance for HPP when delamination of two films in a multilayer packaging film occurs due to the difference in their mechanical properties and compressibility. Reports on the delamination of HPP packaging can be found in the studies of Bull et al. (2010), Fairclough and Conti (2009), Fleckenstein et al. (2014), Fraldi et al. (2014), Galotto et al. (2008) and Richter et al. (2010).

Mathematical models for bubble formation in elastomers, rubbers and other polymers have been put forward by Baudet et al. (2011) and Kane-Diallo et al. (2016). A good overview of bubble formation during hyperbaric decompression was published by Papadopoulou et al. (2013).

2.4.2 Factors affecting the formation of bubbles in polymers

Several factors have been reported to be of importance for the phenomenon of explosive decompression failure (XDF) including material properties (e.g. rigidity and tensile strength), experimental conditions (e.g. temperature and decompression rate), nature of the gas and solution properties (Dewimille et al. 1993, Koga et al. 2011, Van Liew and Burkard 1993). In order to explain XDF, the number of the arising bubbles/blisters per volume of the matrix (also called the bubble density *BD*), the maximum size of the bubbles (*BS*) and the growth rate (*GR*) are important. A correlation between *BS* and *BD* was found by Ramesh et al. (1991). Gent and Tompkins (1969) found a positive correlation between the *BD* and the *GR*, whereas Handa and Zhang (2000) observed a negative correlation.

2.4.2.1 Influence of the nature of the gas and the transport properties on bubble formation

The solubility of a gas in a polymer influences bubble formation after decompression. According to Flook (2000) and Ikels (1970), a higher gas solubility leads to a higher bubble size. This findings are confirmed by Gent and Tompkins (1969), who found smaller bubbles formed from Ar due to its low solubility in the matrix. Ramesh et al. (1991) observed that *GR* is faster with N_2 than with CO_2. Harvey (1945) had predicted that bubbles of CO_2 would be bigger than those of N_2. Sheridan et al. (2000) showed that CO_2 has a greater ability to form bubbles in poly L-lactic acide (PLLA), polyglycolide (PGA) and their copolymers PLG compared to N_2 and He (~23°C, 60 bars). Dipolar interactions between CO_2 and the polar carbonyl groups in the polymer were proposed as possible explanations by Kazarian et al. (1996) and Bos et al. (1999). Experiments on cavitation in polymers demonstrated that the damage in PVDF is much more severe with CO_2 than with H_2 (Boyer et al. 2013).

Higher diffusion coefficients have been reported to reduce decompression failure in rubber (Koga et al. 2011, Koga et al. 2013) because the gas is able to escape from the polymer faster than gases that have a low diffusion coefficient ($0< T< 100°C$ and $P< 900$ bars). For example, blistering is less pronounced with He because of its higher diffusion rate (2 to 10 times) when compared to H_2 or N_2 (Koga et al. 2013). In contrast, Chen et al. (2006) reported a model showing that high diffusion coefficients may strongly increase the *GR* in a PS-CO_2 system, as the gas is able to enter the bubble more rapidly. These findings were confirmed by experimental data on the increased blistering effect of CO_2 in different thermoplastic polymers when compared to CH_4. The effect was explained by the higher diffusion coefficient of CO_2 (Dewimille et al. 1993). The competing effects of rapid gas entry into bubbles and rapid gas escape from the polymer (high diffusion coefficient) could not be evaluated using the current literature data.

2.4.2.2 Influence of the material properties on bubble formation

Koga et al. (2011) found that the diffusion coefficient has a higher impact on bubble formation than the tensile strength of the material. However, both a higher diffusion coefficient and a higher tensile strength may reduce the formation of bubbles. That is why Koga et al. (2011) concluded that increasing temperatures (0 to 100°C) have a negative influence on the blistering behaviour due to the accompanying decrease in tensile strength. Barth et al. (2013) collected data on the tensile properties of semi-crystalline thermoplastics under hydrostatic pressure and observed that the tensile strength of polymers increases with the applied pressure, particularly at high pressures up to 8,000 bars. Considering the prediction by Koga et al. (2011), this would mean that higher pressures would reduce bubble formation due to an increased tensile strength, a fact that conflicts with other findings (see Table 2-6). Gent and Tompkins (1969) predicted an influence of the shear modulus on the crack resistance. They found that higher shear moduli enable higher supersaturation pressures P_{SS} before blisters arise after decompression. Barth et al. (2003) reported a linear increase of shear moduli with pressure. It was reported by Goldman (2009, 2010) that in elastic materials small bubbles are more likely to form than large bubbles.

In a study on several polymers (PP, PVDF, fluorinated copolymer, PA11, PE-HD) tested at 40 to 140°C and 100 to 1,000 bars, it was concluded that thermoplastic materials suffer significantly less from blistering than elastomers (Dewimille et al. 1993 and Jarrin et al. 1994). Also, studies by Sheridan et al. (2000) demonstrated that crystalline polymers (e.g. PLLA, PGA) withstand the formation of blisters better then amorphous polymers (e.g. PLG). For plasticised polymers it was reported that pressure and temperature must be decreased to avoid bubble formation. These results are consistent with the fact that the solubility of gases and the accompanying swelling are higher in elastomers and amorphous polymers than in thermoplastics and crystalline materials. A fluorinated copolymer was shown to have the best resistance to bubble formation by CH_4 (T< 140°C and P< 1,000 bars). Fluorinated polymers such as PVDF seem to be unaffected at temperatures ranging from 70 to 115°C and at pressures up to1,000 bars, while PP had deformation stability only up to 40°C and 1,000 bars (Dewimille et al. 1993). The results of Jarrin et al. (1994) showed that PP is only able to withstand blistering below 200 bars at temperatures up to 100°C. In general, the resistance of PA and fluoride polymers to XDF was better than polyolefin polymers. Even the type of polyolefin was an important factor in bubble formation. These results agree with the findings of Grolier and Boyer (2007) who found a higher solubility for CO_2 in PE-MD than in PVDF. Arieli and Marmur (2011, 2013) found out that *BD* increased with increasing hydrophobicity of the material. Similar results had already been observed by Harvey (1945) who recommended avoiding hydrophobic materials. Harvey reported that bubbles can form spontaneously, even on hydrophilic surfaces, if the supersaturation pressure P_{SS} and the pressure drop ΔP are high enough.

Heterogeneous polymers and materials with fillers or other additives have an influence on the solubility of gases under pressure and therefore may also influence the formation of bubbles (see section 2.3.1.4). In the work of Harris et al. (1998) sodium chloride particles were used to alter the *BS* in PLG. The addition of high concentrations of surfactants by Gaskins et al. (2001) to a gelatine-water matrix was able to reduce the formation of bubbles. The work of Yamabe and Nishimura (2010) reveals that Carbon Black particles added to rubbers enables those materials to be exposed to higher critical pressures than pure rubbers before bubbles arise.

Ramesh et al. (1991) found that higher molecular weight decreased *BS* with concurrent higher *BD* in a PS polymer (115< T< 125°C and $P_{SS\,(N2)}$ = 100 bars). On the contrary, higher molecular weight resulted in a lower *BD* in PE with CH_4 (T = 70°C; P_{max}= 100 bars) in the work of Jarrin et al. (1994). Sheridan et al. (2000) observed that increasing the PLG molecular weight decreases the overall porosity in the matrix for a foaming process with CO_2 (T = 23°C; P = 59 bars). The porosity was calculated from the measured volume and weight of the matrix compared to the initial density. The authors postulated that the longer polymer chains of high molecular weight polymers may help to withstand the expansion.

2.4.2.3 Influence of pressurising conditions

The time-pressure profile influences the formation of blisters (Arieli and Marmur 2013, Dewimille et al. 1993, Van Liew and Burkard 1993). The process involved can be split into a compression, a pressure holding phase and a decompression phase. In addition, the maximum applied pressure P_{max} and the process temperature are of importance. In some scientific work the maximum pressure drop ΔP is reported to indicate the maximum pressure difference that can be applied before bubbles are formed during decompression. Flook (2000) reported that He tends to require the highest pressure drop for bubbles to form in human tissue, compared to N_2 and Ar. In general, the lower the gas concentration in the liquid or in the polymer, the higher the required pressure drop for bubbles to form (Ikels 1970).

Many authors have reported that damage is more severe when a higher P_{max} is applied (Arieli and Marmur 2013, Dewimille et al. 1993, Flook 2000, Jaravel et al. 2011, Yamabe and Nishimura 2010). This statement was refined by Ramesh et al. (1991), who assumed that *BD* increases in PS, whereas *BS* decreases with increasing applied gas pressure ($T = 115°C$ and $100< P_{(N2)}< 140$ bars). Dewimille et al. (1993) found that with increasing maximum pressure ($P_{max}< 1,000$ bars) the temperature has to be simultaneously reduced to avoid decompression failure with CH_4 in different polymers. Other authors have also found that lower temperatures result in lower *BD* (Koga et al. 2011, Van Liew and Burkard 1993, Gent and Tompkins 1969, Handa and Zhang 2000). At temperatures above 110°C the mean N_2 bubble radius in PS was found to increase with temperature (Ramesh et al. 1991).

The rate of compression was presumed to be of no importance for XDF in the studies of Jaravel et al. (2011). However, Briscoe et al. (1994) reported that a fast compression rate is able to reduce decompression failure. Our unpublished work has confirmed that fast compression rates reduce the amount of XDF. A reason for this may be found in Equation 2-5 which indicates that the critical bubble radius decreases when the difference in the partial gas pressure inside and outside a bubble is increased. Therefore fast compression rates lead to a collapse of the pre-existing gas cavities, whereas slow compression enables the diffusion of gas to the inside of the bubble and concomitant compensation of the pressure difference.

One of the most important ways to reduce XDF is to slow down the decompression rate (Arieli et al. 2007, Arieli and Marmur 2013, Fairclough and Conti 2009, Flook 2000, Goldman 2010, Jones et al. 1999, Jaravel et al. 2011, Richter 2014, Van Liew and Burkard 1993). A higher pressure drop and decompression velocity increase the thermodynamic imbalance in the gas-polymer system. The resulting triaxial tension may induce cavitation or tribonucleation via the mechanical separation of polymer films (e.g. delamination). The model of Baudet et al. (2011) for the prediction of blistering in semi-crystalline polymers indicates that higher decompression rates increases the amount of voids. The size of the damage is higher in the centre of the polymer due to a concentration gradient of the gas, especially at enhanced decompression rates. It has to be taken into account in any case that if the decompression rate is faster than the gas is able to escape from the polymer then bubbles will form spontaneously or the gas will diffuse into pre-existing micronuclei to overcome the supersaturation state.

Table 2-6 summarises the results of the literature review on XDF, listing the nature and transport properties of the gases, the material properties and process conditions. The systems studied in the scientific work are summarised in Table 2-7.

Table 2-6 Parameters influencing bubble formation (BF), bubble growth rate (GR), bubble size (BS) and the number of bubbles expressed as bubble density (BD).

Parameter	Observations	Reference
Nature of the gas and transport properties of the gas in the matrix		
Solubility ↑	↑ BF	(Flook 2000; Jarrin et al. 1994)
Solubility ↑	↑ GR	(Harvey et al. 1944)
Solubility ↑	↑ BS	(Ramesh et al. 1991)
Solubility ↑	↓ BS ↑ BD	(Handa and Zhang 2000)
Solubility ↑	$BS(CO_2) > BS(N_2) > BS(Ar)$	(Gent and Tompkins 1969)
Solubility	$BF(Ar) > BF(N_2) > BF(He)$	(Flook 2000)
Solubility	$BF(CO_2) >> BF(N_2) \approx BF(He)$	(Sheridan et al. 2000)
Gas nature	$GR(CO_2) > GR(N_2)$	(Ramesh et al. 1991)
Gas nature	$BS(CO_2) > BS(N_2)$	(Harvey 1945)
Gas nature	$BF(CO_2) > BF(O_2)$	(Götz and Weisser 2002)
Gas nature	$BF(CO_2) > BF(H_2S) > BF(CH_4)$	(Dewimille et al. 1993)
Diffusion coefficient ↑	$BF(N_2) > BF(H_2) > BF(He)$ ↓ BS	(Koga et al. 2013)

Desorption diffusion ↑	↓ BF		(Koga et al. 2011, Koga et al. 2013)
Diffusion coefficient ↑	↓ BF		(Jarrin et al. 1994, Koga et al. 2011)
Diffusion coefficient ↑	↑ BS	↑ BD	(Chen et al. 2006)
Material properties			
Molecular weight ↑	↓ GR and BS	↑ BD	(Ramesh et al. 1991)
Molecular weight ↑		↓ BD	(Jarrin et al. 1994)
Molecular weight ↑	↓ BF		(Sheridan et al. 2000)
Shear modulus ↑	Maximum pressure drop increases before bubbles arise		(Gent and Tompkins 1969)
Mechanical or tensile strength of the material ↑	↓ BF		(Yamabe and Nishimura 2010, Koga et al. 2011, Jarrin et al. 1994)
Viscosity of the liquid ↑	ΔP hast to be decreased to avoid BF		(Ikels 1970)
Elasticity ↑ (e.g. Elastomers ↔ Thermoplastics	↑ $BF_{(\text{Thermoplastics})} < BF_{(\text{Elastomers})}$		(Dewimille et al. 1993, Jarrin et al. 1994)
Elasticity ↑	↓ BS		(Goldman 2009, 2010)
Plasticisation of polymer by gas ↑	↓ GR		(Chen et al. 2006)
Crystallinity	$BF_{(\text{crystalline polymer})} < BF_{(\text{amorphous polymer})}$		(Sheridan et al. 2000, Jarrin et al. 1994)
Rigidity ↑	↓ BF		(Richter et al. 2010)
Hydrophobicity ↑	↑ BF		(Arieli and Marmur 2011, 2013, Harvey 1945)
Surface tension ↑	↓ BS		(Goldman 2009)
Surface tension ↑	↑ BF		(Gaskins et al. 2001)
Surface tension ↑		↑ BD	(Van Liew and Burkard 1993)
Homogeneity of the material ↑	↓ BF		(Koga et al. 2013, Jarrin et al. 1994)
Nature of polymer	BF (PVDF) < BF (Teflon) < BF(PP) BF (PVDF) < BF (PA11) < BF (PE-HD) < BF (PP) (at T< 80°C)		(Dewimille et al. 1993, Jarrin et al. 1994)
Experimental conditions			
Pressure-time profile			
Compression rate ↑		↓ BD	(Briscoe et al. 1994)
Decompression rate ↑	↑ BS	↑ BD	(Baudet et al. 2011)
Decompression rate ↑	↑ BS	↓ BD	(Arora et al. 1998)

Decompression rate ↑		↑ BD	(Arieli et al. 2007)
Decompression rate ↑	↑ BF		(Jaravel et al. 2011, Koga et al. 2011, Van Liew and Burkard 1993, Jones et al. 1999, Richter 2011)
Maximum applied pressure P_{max}; ↑ Maximum pressure drop ΔP ↑	↑ BF		(Yamabe and Nishimura 2010, Koga et al. 2011, Dewimille et al. 1993, Arieli and Marmur 2013)
Maximum pressure drop ΔP ↑	↑ GR	↑ BD	(Van Liew and Burkard 1993)
Max. applied pressure ↑	↓ BS	↑ BD	(Gent and Tompkins 1969, Ramesh et al. 1991, Arieli et al. 2007, Arora et al. 1998)
Pressure holding time ↑	↑ BF		(Masuda et al. 1992, Koga et al. 2011, Koga et al. 2013)
Pressure holding time	No effect		(Fradin et al. 1998)
Temperature			
Temperature ↑ (0 – 140°C)	↑ BF		(Dewimille et al. 1993, Koga et al. 2011, Van Liew and Burkard 1993, Richter et al. 2010)
Temperature ↑ (40 – 120°C)	↑ GR and BS	↓ BD	(Arora et al. 1998)
Temperature ↑ (110 – 135°C)	↑ GR and BS		(Ramesh et al. 1991)
Temperature ↑ (10 – 65°C)	↓ BS	↑ BD	(Handa and Zhang 2000)
Temperature ↑ (10 – 65°C)		↑ BD	(Gent and Tompkins 1969)
Temperature ↑ (75 – 90°C)		↓ BD	(Handa and Zhang 2000)
Combined effect of *T* ↑ and *P* ↑	↑ BF		(Dewimille et al. 1993)

Table 2-7 Overview of systems studied in the literature and the experimental conditions

Gas	Polymer / Matrix	Applied temperature [°C]	Applied pressure [bar]	Reference
Static gas pressure (two-phase system)				
CO_2	PS	40 – 120	70 – 480	(Arora et al. 1998)
CH_4,	Fluorinated polymer,	40 – 140	100 –	(Dewimille et al.

CO_2, H_2S	fluorinated copolymer, PP		1,000	1993)
CO_2	PMMA	10 – 95	34	(Handa and Zhang 2000)
Ar, N_2, CO_2	Butadiene-styrene copolymer, natural rubber (pale crepe)	10 – 65	~50	(Gent and Tompkins 1969)
CO_2, CH_4, H_2S	PVDF, PA11, PE-HD, PP	150	1,000	(Jarrin et al. 1994)
CO_2, He, N_2	PLG, PGA, PLLA	25	59	(Sheridan et al. 2000)
N_2, CO_2	PS	105 - 135	55 - 140	(Ramesh et al. 1991)
Dynamic gas pressure; Pressure difference between upstream and downstream (two-phase system)				
H_2	EPDM, VMQ, HNBR	0 - 100	950	(Koga et al. 2011)
H_2, He, N_2	EPDM, VMQ	25	100	(Koga et al. 2013)
CO_2	PS	model		(Chen et al. 2006)
H_2	EDPM, NBR containing carbon black or silica fillers	30	100	(Yamabe and Nishimura 2010)
CO_2	PVDF	Theoretical considerations + experiments	250	(Baudet et al. 2011)
	Elastomers	Literature research		(Briscoe et al. 1994)
H_2	Vinyltrimetoxy-silane	~20	270	(Jaravel et al. 2011)
Isostatic pressure (three-phase system)				
Ar, N_2, He	Human tissue	unknown	2 – 6	(Flook 2000)
O_2	PE film in water	20 – 30	2,000 bar	(Sterr et al. 2015b)
N_2, CO_2	MAP made from PE, PET, PA, EVOH	5, 23, 40	6,000 bar	(Sterr et al. 2015a)
Air in water	Silicon wafer	25	10	(Arieli and Marmur 2011)
Air, O_2	Prawn	25	2-8	(Arieli et al. 2007)
Air in water	Silicon wafer	25	1.5 – 4	(Arieli and Marmur 2013)
Air, O_2	Animal tissue			(Harvey 1945)
CO_2, O_2	PA/PE bag	~23	5,000	(Götz and Weisser 2002)
He, Ar, N_2	Metal ball in glass tube filled with	25	Pressure drop	(Ikels 1970)

	liquid (olive oil, glycerol-water)		$\Delta P < 10$ bars	
Air	Agar gel	unknown	unknown	(Gaskins et al. 2001)
N_2, CO_2, O_2	Packaging made from PE, PET, PA, EVOH	10 – 70	6,000	(Richter 2011)
-	Packaging made from PE, PET, EVOH, PP, PA etc.	20 – 40	6,000	(Masuda et al. 1992)
Air	Packaging made from PE, PA, PET etc. filled with water	25	2,000	(Fradin et al. 1998)
Air	Packaging made from PP	70	6,950	(Fairclough and Conti 2009)
Theoretical considerations				
	Bubble growth in soft elastic materials	Theoretical considerations		(Goldman 2009)
N_2	Stability of bubbles in soft elastic materials	Theoretical considerations		(Goldman 2010)
Gases	Liquid	Literature research		(Jones et al. 1999)
Gases	Animal tissue, liquids	Theoretical considerations, literature research		(Harvey et al. 1944)
Air, N_2	Blood, human tissue	Mathematical simulations	2	(Van Liew and Burkard 1993)

2.4.3 Bubble formation in packaging used for HPP

Insufficient data is available on the formation of bubbles in multilayer films as part as modified atmosphere packaging used for foods processed at high pressure (4,000 to 6,000 bars) and moderate temperatures. However, some results and considerations were gleaned from the literature. Increasing the headspace volume and/or high internal gas pressure p_i ($p_i > p_{atm}$) in packaging used for HPP lead to increased blistering (Fairclough and Conti 2009, Sterr et al. 2015a). A reason might be that the enhanced internal gas pressure increases the amount of gas dissolved in the material even under atmospheric conditions. Also, the packaging geometry might play a role and this has been considered by a few authors (Fairclough and Conti 2009, Sterr et al. 2015a, Richter 2011). The edges and folds of tray packaging seem to be more vulnerable to blistering. Additionally, it has to be taken into account that gases do not merely dissolve in the polymeric part of the packaging but also in the food product and may therefore also form bubbles there (Al-Nehlawi et al. 2014). To our knowledge, no scientific work has dealt with the interaction and combined effect of polymer and packed food. Also, the adiabatic heating of the gas, food and polymers, and even the pressure transmitting fluid, may influence the amount of blistering. In general, the effect of the pressure transmitting medium is unknown (Barth et al. 2013). An interesting fact mentioned by Muth et al. (2001) was that visible blisters and foam like structures can be reduced by thermal treatment above the glass transition temperature of the material for a specific time. In their studies, opaque PVC samples became transparent again after treatment at 75°C for several hours.

2.5 Conclusion

Even though most of the studies about the solution, diffusion and permeation of gases in polymers under pressure were performed with significantly different measurement methods under differing temperature and pressure conditions, same common conclusions can be drawn. Most authors suggest that under the low temperature conditions used for HPP (below 50°C) gas solubility decreases with increasing temperature and that it increases with increasing pressure at medium pressures. However, a possible saturation behaviour was postulated at higher pressures by a few authors no exact predictions can be made for pressures up to 6,000 bars. The data suggest that CO_2 has a higher solubility in all the tested polymers than gases that have low critical temperatures such as O_2, N_2 and He. Although numerous studies have been performed on the sorption of CO_2 in common polymers, little information is available about the solubility of O_2 at high pressures and low temperatures. A lower density or a higher content of amorphous phase in polymers results in an increased solubility of gases and therefore swelling and plasticisation may change the amount of gas that is able to dissolve in the polymer. Only a few authors have taken swelling into account when determining gas solubility. It is generally assumed that the relative volume change increases with pressure and temperature at pressures below 100 bars in the low temperature range. However, the influence of the competing effect of plasticisation of the polymer chains and the compression of the free volume on the transport properties of gases in polymers is still difficult to predict, especially at very high pressures. The glass transition temperature is expected to decrease with applied pressure, but some authors have observed that T_g

increases at pressures above 1,000 bars. Filler particles have diverse effects on the transport properties, depending on the affinity of the particles to the diffusing gas molecules. The sorption and desorption behaviour shows strong hysteresis. Permeation increases with pressure for highly soluble gases such as CO_2 and decreases with increasing pressure for sparingly soluble gases such as N_2 and O_2. Permeability coefficients are reduced 2 fold at pressures up to 100 bars, but are highly reduced (70 fold) at pressures up to 2,000 bars.

Based on the available data it is not possible to make reliable predictions about the transport properties of gases under the pressure conditions used for the high pressure processing of food. No relevant data are available about the transport properties of supercritical fluids. Further research is necessary to measure the solubility, diffusion and permeation of relevant gases (O_2, N_2, CO_2) in packaging-related polymers (PE, PET, PA, PP) at isostatic pressures up to 6,000 bars and at low temperatures. The measurement of CO_2 permeation at high hydrostatic pressures could be possible by adapting the measurement setup described by Sterr et al. (2015b). The competing effects of swelling, plasticising and compression should be taken into account.

Concerning the influence of certain parameters on the formation of bubbles some conclusions can be drawn. . However, the literature contained conflicting data. Differences in the measurement methods and processing conditions may be the reason for the conflicting results. It should be pointed out that in some of the published work information on important parameters is missing. Opinion about which type of gas leads to the most severe decompression failure differs in the literature. However, most authors agree that a higher solubility enhances blistering. Bubble formation with He is comparably rare, whereas the use of CO_2 affects the materials more markedly. It is not clear yet how the diffusion coefficient influences packaging failure as a high diffusion coefficient allows both high access of the gas to the bubbles in the compression phase and high desorption of gas out of the polymer in the decompression phase. Material properties such as crystallinity, tensile strength, shear moduli, surface energy, viscosity, molecular weight and hydrophobicity affect the polymer behaviour during decompression. In general, thermoplastic polymers are more stable than elastomers and fluorinated polymers. Also, polyamides show better performance than polyolefin polymers. Considering these facts, a polymer with a higher crystalline content such as high density polyethylene may have improved packaging performance than low density polyethylene for use as the inner layer of packaging for HPP. In multilayer films used in the food industry, differing mechanical properties and solution effects of the single layers may lead to increased dissolution of gas at interstitial sites. Delamination may also arise. Inhomogeneities acting as nucleation points in polymers increase XDF. However, filler particles have the ability to control the uptake of gas and hence also the formation of bubbles. Apart from the solubility of the gas in the polymers, the decompression rate seems to be the most important factor. Most authors report that a slow decompression rate results in reduced blistering. Increasing the temperature seems to promote bubble formation. However, no adiabatic heating or heat transfer from the pressure transmitting fluid in more complex systems, such as those used in HPP, was taken into account in any of the relevant literature. Other parameters such as a faster compression rate and a lower maximum applied pressure and lower pressure drop also aid crack prevention. In summary, the occurrence and behaviour of explosive decompression failure is not easy to predict due to the many parameters involved and the fact no relevant scientific studies have been performed at pressures up to 6,000 bars on sealed packaging. Future studies on bubble formation in modified atmosphere packaging for high pressure processing should focus on the influence of the food products and their adiabatic heating and heat transfer properties. The transport, mechanical and structural properties of different types of polymers should be taken into account.

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3 The effect of high pressure processing on the integrity of polymeric packaging – Analysis and categorization of occurring defects

The fact that most of the food products are ready packed before high pressure treatment raises the question whether the packaging still fulfils all necessary requirements after processing. In this review manuscript investigations concerning the structural behaviour and the stability of packaging materials under high pressure processing were considered and it was getting clear that often damages and alterations of the polymeric structure occur. Common damage mechanisms of high pressure-treated packaging materials are defined and classified in this review. These effects are allocated to the physicochemical impact that created them. The effects were separated into direct effects induced by the action of the high pressure alone and indirect effects that are mediated via compressed contents of the package, i.e. filled product and gaseous headspace. The direct effects were split up in reversible and irreversible structural changes. Reversible structural changes could be only detected indirectly via in-situ measurements of transport processes under high pressure. Results concerning the permeation, diffusion and solubility of aroma compounds in different polymers are presented. Irreversible changes, like changes in gas permeation, alterations in crystallinity or density or macroscopic damages (e.g. delamination) were listed. The indirect effects are mainly generated by compressed headspace gases, the concomitant heat of compression and the consequences of increased amounts of gases dissolved in the polymers. Topics regarding strain induced crystallisation, local thermal effects, solution effects, extraction, localised decompression failures and sorption induced plasticization and crystallization are discussed. If applicable, current theoretical approaches have been allocated to the different categories of damage.

The effect of high pressure processing on the integrity of polymeric packaging – Analysis and categorization of occurring effects

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ABSTRACT

As high pressure processing is used increasingly for the treatment of packed products, different packaging has been investigated with respect to their structural behaviour and stability under high pressure processing. Often, failures and changes of the polymeric structure occur. Common damage symptoms of high pressure-treated packaging materials are defined and classified in this review. These damage symptoms are allocated to the physicochemical effects that created them. The effects may be separated into direct effects induced by the action of the high pressure alone and indirect effects that are mediated via compressed contents of the package, i.e. filled product and gaseous headspace. The direct effects split up again in reversible and irreversible structural changes. The indirect effects are generated by compressed headspace gases, other compressed substances and the consequences of increased amounts of gases dissolved in the polymers. If applicable, current theoretical approaches have been allocated to the different categories of damage.

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Content Publication II

3.1 Introduction

"The real value of packaging is that the package is an integral part of the product today" (AHMED ET AL. 2005). This is naturally in force for packaged and high pressure processed food. The visual and structural integrity of a packaging material after high pressure processing (HPP) is a very important criterion for its selection. First, the consumer demands an intact, visually undamaged appearance. Second, the structural integrity of packaging material is the basis of its protective effect. This is not easy to achieve in the case of flexible vacuum packages. For instance, high pressure treatment may affect gas or water vapour permeability and thus hamper packaging integrity (JULIANO ET AL. 2010). Instead of flexible vacuum packages, the packaging industry more often asks for tray packages, comprising a gaseous headspace filled with modified atmosphere for reasons of better handling, of a more attractive appearance and of the additional protective effect of gases such as CO_2.

Generally, the developments in different disciplines of HPP research for food preservation have been extensively reviewed (BALASUBRAMANIAM, FARKAS 2008; BARBOSA-CÁNOVAS, JULIANO 2008; BERMÚDEZ-AGUIRRE, BARBOSA-CÁNOVAS 2011; CANER ET AL. 2004a; GALIĆ ET AL. 2011; GUILLARD ET AL. 2010; GUPTA, BALASUBRAMANIAM 2011; JUNG ET AL. 2011; MIN, ZHANG 2007; MORRIS ET AL. 2007a; NORTON, SUN 2008; RASTOGI ET AL. 2007; SAN MARTÍN ET AL. 2002; TOEPFL ET AL. 2006; TORRES, VELAZQUEZ 2005). For plastic packaging for food in combination with HPP, an extensive review has recently been published by JULIANO ET AL. (2010). The paper mainly deals with the general requirements for pouches in HPP applications. The authors focus on industrial standards, q.v. (LAMBERT ET AL. 2000), on the Commission directive 90/128/EEC (The European Commission 2/23/1990) and on the overall packaging integrity on the basis of barrier and mechanical characteristics. High pressure-induced damages of the packaging materials were not treated in detail. So, the aim of the present paper is to give an overview of the different damages as induced by HPP and the related mechanisms in view of the different packaging materials.

In the following, the current state of knowledge of the effects of HPP on packaging materials is presented. The observed damages have been systematized with regard to their origin and the mechanisms of their generation (Figure 3-1). The main principle behind this scheme is to separate between direct high pressure-induced effects and indirect effects, which are mainly created by the compressed contents of the packages, i.e. products and gaseous headspace.

3.2 Direct effects

In this paper, we define direct effects as the immediate consequences of the HPP on the polymer. As the schematic representation shows (Figure 3-1), we differentiate these in microscopic structural changes in the nanometre to micrometre range and changes of layers and layer structures.

3.2.1 Microscopic structural changes in the nanometre to micrometre range

One group of immediate consequences of the HPP on polymers is represented by structural changes in the nanometre to micrometre range. The detectable effects of these consequences may be reversible or irreversible. The effects themselves may be detected directly by structural investigations or indirectly by studies of the permeation/diffusion properties of different substances in the polymers during HPP.

3.2.1.1 Reversible structural changes

Reversible structural changes cover alterations where the polymeric structure changes during the high pressure treatment and returns to its original state after the process. Such behaviour asks for measurement methods that may be carried out in situ, i.e. during the HPP. So far, for hydrostatic pressures >50MPa, this kind of effects has only been observed with the help of the permeation of flavour substances. The following studies show that the permeation and the absorption of specific liquid substances are significantly reduced even at moderate hydrostatic pressures. An overview on observed reversible structural changes is given in Table 3-1.

Recently, RICHTER ET AL. (2010) could show directly by in situ studies that during high pressure treatment, the permeation coefficients of benzoic acid through polyamide 6 (PA6) and of β-ionone through low-density polyethylene (PE-LD) decrease reversibly upon an increase of pressure during the treatment. After pressure release, the permeability returns to its initial value within the accuracy of the measurement. Similar findings were published by SCHMERDER ET AL. (2005) for the solution and diffusion of raspberry ketone through PA6.

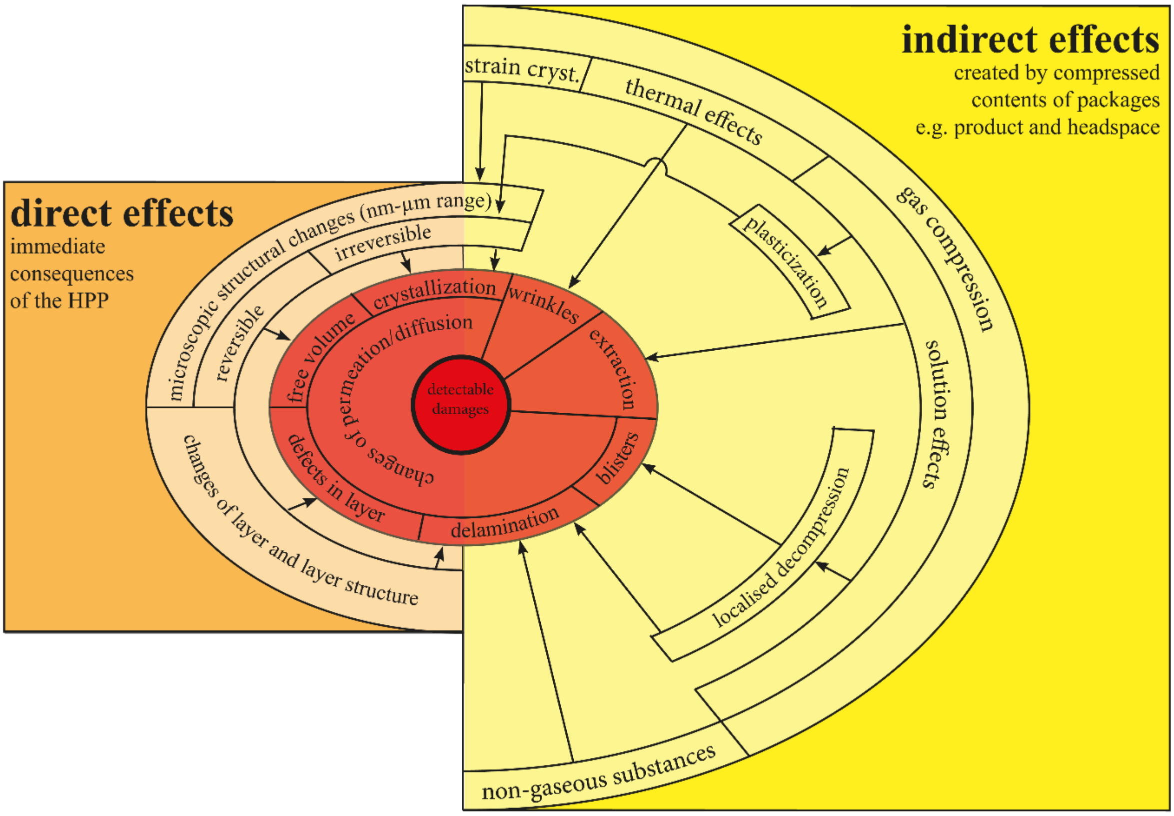

Figure 3-1 Schematic representation of the effects of high pressure on polymeric packaging materials

Other papers report on more indirect experiments like Götz, Weisser (2002) who compared the in situ measured concentration of *p*-cymene permeating into a solution outside a bag over time at 0.1 and 50 MPa. In this case, the amount of *p*-cymene outside the bag increased slower at 50 MPa than at 0.1 MPa, indicating a reduction of the permeation coefficient. Kübel et al. (1996) could show that “high hydrostatic pressure raised the diffusion barrier in the polymers” for PE-LD/high-density polyethylene (PE-HD)/PE-LD, PE-HD and polyethylene terephthalate (PET)/aluminium (Al)/PE-LD. The experimental set-up in their study was an inner bag, filled with *p*-cymene, which was packed in an outer bag, filled with an ethanol/water solution. Their findings on PE-LD/PE-HD/PE-LD films show that a lower amount of *p*-cymene permeates out of the inner bag in the case of pressurized samples and that the latter absorb only one third of *p*-cymene at 500 MPa in comparison with untreated samples. These findings are in concert with the results of Ludwig et al. (1994). They measured the change of *p*-cymene concentrations before and after HPP also via a bag-in-bag method.

Table 3-1 Reversible structural effects: decrease of diffusion or permeation coefficients of flavour substances

Polymer	Treatment	Thickness	Permeate	Method	Effect of high pressure		Reference
PA6	0.1-200 MPa; 23 or 60°C	20 µm	Benzoic acid; Carvacrol; Rasperry ketone	UV/Vis in situ	P * is reduced by a factor of up to 7 (Benzoic acid, 23°C)		(Richter et al. 2010)
PE-LD		50 µm	β-ionone		P is reduced by a factor of ~ 125		
PA6	0.1-400 MPa; 23 or 60°C	55 µm	Rasperry ketone	in situ	P is reduced by a factor of ~ 4 (40°C)		(Schmerder et al. 2005)
PE-LD/PE-HD/PE-LD	0.1 and 50 MPa; 23°C	12/12/12 µm	*p*-Cymene	UV/Vis; in situ bag in bag	Reduced permeation $P_{50MPa} \sim 2.7 * 10^{-13}$ mg*m/s*m^2*Pa $P_{0.1MPa}$= n/a		(Götz, Weisser 2002)
PET/Al/PE-LD	0.1-450 MPa; 25°C; 60 min	8/7/75 µm	*p*-Cymene; Acetophenone	UV/Vis; bag in bag	Less decrease in the inner bag (*p*-Cymene)	No diffusion of Acetophenone neither through nor into the film at 450 MPa	(Kübel et al. 1996)
PE-LD/PE-HD/PE-LD		12/12/12 µm			~ 2/3 less sorption (*p*-Cymene)		
PE-HD		14 µm			~ 40% less sorption (*p*-Cymene)		
PE-LD	500 MPa; 25°C; 24h	100 µm	*p*-Cymene	UV/Vis; bag in bag	~50% less decrease in the inner bag		(Ludwig et al. 1994)
PE-LD/PE-HD/PE-LD		12/12/12 µm			~35% less decrease in the inner bag		
PET/Al/PE-LD	500 MPa; 25°C; 60h	8/7/75 µm			Slight decrease of loss by sorption, no permeation		
PE-LD	800 MPa; 20-40°C; 5 min	50 µm	2-Hexanone; 2-Heptanol; Ethyl hexanoate; *D*-Limonene; *n*-pentane; Dichlormethane; Ethyl butanoate; Acetic acid	Filled with food simulating liquid; Extraction from film and solution Detection via gas chromatography	Slight increase of the total amount (~15%; out of water, 3% acetic acid); no change (out of 15% ethanol)		(Mauricio-Iglesias et al. 2011)
PLA		40 µm			Decrease of the total amount (~ 65%)		
PE-LD	800 MPa; 90°C-115°C; 5 min	50 µm			Strong rise of total amount of sorbed aroma compounds (up to 350% out of water)		
PLA		40 µm			Increase of total amount of sorbed aroma compounds (up to 120% out of 15%ethanol)		

UV/Vis, Ultraviolet-visible spectroscopy; n/a, not applicable.
* P = Permeation coefficient

Whereas the aforementioned authors measured the amount of substances permeating through polymers after a time of at least 25 min, MAURICIO-IGLESIAS ET AL. (2011) measured the uptake of several flavouring substances (Table 3-1) by polylactide (PLA) after a treatment of 7 min at 0.1 MPa and 5 min at 800 MPa to reproduce a realistic treatment time. They detected a reduced uptake of flavour out of a food-simulating liquid by PLA, if treated at temperatures below T_g. Furthermore, they showed that the uptake of flavour by PE-LD during the time of high pressure treatment depends on the food-simulating liquid.

MAURICIO-IGLESIAS ET AL. (2011) also tested the consequences of combined high pressure/high temperature on the solubility of substances in polymers. In this case, temperatures above T_g (90 to 115°C) increased the uptake of flavour substances by PE-LD and PLA.

For completeness, it is to be mentioned that in a study by CANER ET AL. (2004b), pouches made from single layer polypropylene (PP) (25 µm) and PE/PA6/ethylene-vinyl alcohol copolymer (EVOH)/PE (62.5 µm) did not show significant changes in the sorption behaviour during high pressure treatment. A study by CAMPION, MORGAN (1992) deals with the high pressure permeation of gases in polymers. Even if the test set-up implied a pressure gradient (42MPa to ‘low pressure’) and the decompression was not recorded, the occurring decrease of the permeation coefficient indicates that reversible effects may also occur at the permeation of gases.

Whereas these in situ studies of gas permeation at high pressures still need further attention, there are many papers that deal with the gas or vapour permeability through polymers after high pressure treatment. Most of them have been reviewed by JULIANO ET AL. (2010). Recent publications about this topic that were not reviewed in the paper of Juliano et al. are for example: (BULL ET AL. 2010; DHAWAN ET AL. 2011; GALOTTO ET AL. 2009; GALOTTO ET AL. 2010; LARGETEAU 2010; SANSONE ET AL. 2012).

3.2.1.2 Models to describe the high pressure effect on sorption, diffusion and permeation

The free-volume model

The observation of a temporary change of the permeation coefficient can be explained via the free-volume model for diffusion in polymers (RICHTER ET AL. 2010). The model is based on the assumption that within or throughout an ordered matrix, there are discrete cavities, which may be either fixed or mobile. Dissolved molecules may only move when there is a free space to jump in. The polymer chains, which form the cavities, are subject to the Brownian motion. In case that one of the formed cavities is large enough to contain the diffusing molecule and the molecule possesses enough energy to jump in, movements occur, cf. (BARRER 1951; VIETH 1991; VRENTAS, DUDA 1977; ZIELINSKI, DUDA 1992). A bibliographic review about common theories of transport properties of gases in polymers at moderate pressure was written inter alia by KLOPFFER, FLACONNÈCHE (2001). They show that the permeability of gases and organic vapours depends on the polymer structure, on the penetrant size and on the conditions of pressure and temperature.

However, SCHEICHL ET AL. (2005) pointed out that for gas–polymer systems “an increase of the hydrostatic pressure leads to a competition between two phenomena with opposite effect”:

- The free volume inside the polymer matrix may be reduced because the polymer density increases via polymer compression.
- The free volume inside the polymer matrix may be increased because the macromolecular chains in the polymer are plasticized by an increase of the gas concentration.

Even though many substances may act as plasticizers (see the Section ’Sorption-induced plasticization and crystallization’), according to the findings of the aforementioned authors, the first of these phenomena appears to predominate at least at *p*-cymene and acetophenone in combination with PE.

Gas and vapour diffusion at pressures over 100 MPa has not yet been studied in the literature. Studies at CO_2 pressures up to 100 MPa indicate that the permeability of a polymer depends on the gas–polymer interaction regarding plasticization, diffusivity, sorption and others: (CAMPION, MORGAN 1992; HOUDE ET AL. 1992; JORDAN ET AL. 1989;

SADA ET AL. 1988; SANDERS 1988). For a better understanding of diffusion processes at high pressure, it would be essential to measure the permeation of both gases and vapours at high pressure in situ.

'Dual sorption' model

It is well known that sorption is the first step of permeation. If Henry's law is no longer applicable, another approach to describe the solubility is the dual sorption model. In this model, Henry's-type sorption and Langmuir-type sorption occur simultaneously. As a function of the external pressure of the penetrant, the resulting overall concentration of the penetrator can be calculated (ANGELIS, SARTI 2011; VIETH 1991). In the literature, however, most papers deal with pressures below 70 MPa. In this pressure range, the solubility of molecules in polymers increases with rising partial pressure, e.g. (BOYER, GROLIER 2005b; CHANDRA, KOROS 2009; ESLAMI, MÜLLER-PLATHE 2007; PATERSON ET AL. 1999; SOLMS ET AL. 2005). It has to be said that at higher pressures, common headspace gases are in their supercritical state. This generally will lead to a higher solubility (cf. overview of critical temperature and pressure in Table 3-4 and Chapter 'Solution effects').

For liquid penetrants, only two groups report on solubility measurements at higher pressures, showing that the solubility decreases at a pressure range above several hundred MPa (KÜBEL ET AL. 1996; LUDWIG ET AL. 1994).

3.2.1.3 Irreversible structural changes: changes in crystallinity

The question whether high pressure treatment directly affects the crystallinity of polymers cannot be answered unambiguously. In the literature, different trends are to be found in the field of high pressure-induced irreversible changes in the crystallinity of polymers, depending on the nature of the polymer. There is still an inconsistency between different methods to determine the crystallinity, e.g. Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and small angle X-ray scattering, e.g. (GRUVER ET AL. 2000; RUNT, KANCHANASOPA 2004). LÓPEZ-RUBIO ET AL. (2003) mentioned the "complex issue of rigorous crystallinity determination for [...] polymers". Because of these facts, it is essential that additional reference tests should always be carried out with pure monolayer materials to gain a common background.

In the following, the related papers are dedicated to three subcategories: in findings that indicate differences due to the measurement method, in papers that report on multilayer with EVOH and in unspecific studies. An overview of reported effects is shown in Table 3-2.

Table 3-2 Irreversible structural changes: changes in crystallinity.

Polymer	Treatment	Method	Changes in crystallinity	References
PE-LD	200 to 800 MPa 5/10 min 25/75°C	XRD	crystallinity increased with increasing pressure from ~42% (control) to ~58% (800 MPa-5 min-75°C Time no effect	(Yoo et al. 2009)
		DSC	No significant changes	
PLA	650 MPa 15 min 22 to 26°C	DSC	Decrease from ~20% to ~12% (L-isomer)	(Ahmed et al. 2009)
		FT-IR	No change observed	
PET/EVOH32/PP	680 MPa 3/5 min 105/100°C	DSC XRD	No change of T_m and ΔH (DSC) Decrease in the overall crystallinity (XRD)	(Dhawan et al. 2011)
PET/PP/tie/ PA6/EVOH27/PA6/tie/PP			No change of T_m and ΔH (DSC) Slight increase of crystallinity (XRD)	
PP/EVOH26/PP	400/800 MPa 5/10 min 40/75°C	FT-IR	Increase of crystallinity	(López-Rubio et al. 2005)
		DSC		
		WAXS, SAXS	Certain improvement	
PP/EVOH48/PP		FT-IR	No change of crystallinity	
		DSC		
		WAXS, SAXS	Small changes	
PA6/EVOH/PE	690 MPa; 10 min; 95°C	DSC	No significant differences	(Schauwecker et al. 2002)
PA6/EVA	600 MPa 10 min 110°C	DSC	EVOH: significant decrease of ΔH	(Ayvaz et al. 2012)
PA6/EVOH/EVA			PA6, EVA: slight, but not statistically decrease ($p>0.05$) of ΔH	
PETmet/PE			PE: significant decrease of ΔH PET: no change of ΔH	
PET/AlOx	500 MPa 15 min 50°C	DSC	Increase from 28,5% to 36.3% (oil simulant) and 35.5% (aqueous simulant)	(Galotto et al. 2009)
PLA/SiOx-PLA			Decrease from 2.4% to 1.9% + redistribution (aqueous simulant) Decrease from 2.4% to 1.7% (oil simulant)	
PLA/PLA/PLA (multilayer)	700 MPa; 15 min; 40°C	DSC	Untreated crystallinity: 25.3-25.8% (in each case multilayer average) Crystallinity (tap water): 24.2-25.4% Crystallinity (solid carrots): 26.4-26.9% Crystallinity (carrot juice): 25.2-25.7%	(Sansone et al. 2012)

Polymer	Treatment	Method	Changes in crystallinity	References
	700 MPa; 15 min; 90°C		Untreated crystallinity: 25.3-25.8% (in each case multilayer average) Crystallinity (tap water): 29.2-29.6% Crystallinity (solid carrots): 29.3-29.7%	
PA6	50 to 600 MPa 23°C	DSC	No change	(Schmerder et al. 2005)
PET/PE-LD	600 MPa 30°C	Raman	Increase (not specified) Failure analysis - white spot	(Richter et al. 2010)
PP/PET	695 MPa 10 min 70 to 86°C release 2s	SAXS	Increase Strain-induced (see Section on ‘Indirect effects: strain induced crystallization’)	(Fairclough, Conti 2009)

Tested layer; WAXS, wide-angle X-ray scattering; SAXS, small-angle X-ray scattering.
ΔH= heat of fusion; numbers following EVOH give ethylene content in mol%.

Differences due to measurement method (changes in crystallinity)

As previously mentioned, discrepancies in the changes in crystallinity obtained by different measurement methods were reported by some authors. YOO ET AL. (2009) described the influence of DSC and XRD as methods to characterize crystallinity on the findings. In their study on PE-LD film material, they investigated the effect of different HPP conditions (200–800 MPa; 5/10 min; 25/75°C) on the degree of crystallinity. The results of the DSC analysis indicate that HPP does not affect the crystallinity of the specimens significantly, whereas the XRD results suggest an increase of crystallinity from 42% to 58%. In addition, the XRD data show that the crystallinity increased with increasing pressure from 200 to 600 MPa, whereas the processing time had no significant consequence on the crystallinity. Similar discrepancies between the findings obtained by DSC and XRD were found by DHAWAN ET AL. (2011) (see Section on 'Influence of ethylene content'). A similar difference between the results obtained by two methods was detected for PLA by AHMED ET AL. (2005): In this case, DSC indicates a decrease of the degree of crystallinity from 20% to 12% at a pressure rise of 650 MPa (for 15 min at 22–26°C), whereas the crystalline bands of the FT-IR show no changes.

YOO ET AL. (2009) interpreted the differences of the methods as a result of the dependencies on different physical effects. In XRD measurements, crystallinity is obtained from the volume fraction of different structures, whereas DSC measures crystallinity as a function of the heat of fusion. So, when the volume of a polymer is reduced by HPP, cf. (BERET, PRAUSNITZ 1974; KOVARSKII 1994; SCHAUWECKER ET AL. 2002), XRD will produce higher values. In the application of DSC, however, the heat of fusion obtained has to be compared with the heat of fusion of a perfect crystal (100% crystallinity). At this, it is difficult to construct the correct 'peak baseline' for the integration (SCHICK 2009).

Influence of ethylene content of EVOH on changes in crystallinity.

In some publications, the authors report on an influence of the ethylene content of EVOH on high pressure-induced changes of crystallinity. In the case of EVOH with 26% ethylene content in a multilayer structure (PP/EVOH26/PP), a slight increase in crystallinity could be detected, whereas for EVOH with an ethylene content of 48% in a multilayer structure (PP/EVOH48/PP), no increase in crystallinity was observed at equal process conditions (400/800 MPa; 5/10 min; 40/75°C). This was measured by FT-IR, DSC, wide angle X-ray scattering and small angle X-ray scattering (LÓPEZ-RUBIO ET AL. 2005).

In a recent paper, DHAWAN ET AL. (2011) have tested two films (PET/EVOH32/PP and PET/PP/tie/PA6/EVOH27/ PA6/tie/PP) with DSC and XRD after pressure-assisted thermal processing (600 MPa; 3/5 min; 105/100°C). The DSC results show no influence of the pressure-assisted thermal processing on the thermal characteristics (T_m and ΔH) of the EVOH layer. In contrast, the XRD measurements show a decrease in the overall crystallinity of the former film and a slight increase of crystallinity of the latter film. The increase in crystallinity at EVOH27 shows similarities with the findings of LÓPEZ-RUBIO ET AL. (2005).

Unfortunately, also papers without specifications for the content of ethylene in EVOH are to be found: SCHAUWECKER ET AL. (2002) analysed a multilayer film with an EVOH core (PA6/EVOH/PE). In their case, no changes in crystallinity fraction could be detected by DSC measurements (690 MPa; 10 min; 95°C). AYVAZ ET AL. analysed a PA6/EVOH/ethylene-vinyl acetate copolymer (EVA) multilayer after pressure-assisted thermal processing (600MPa; 10min; 110°C). Here, the DSC shows a significant decrease of the heat of fusion (ΔH) of EVOH.

Unspecific studies

A small decrease in crystallinity from 2.4% to 1.7% (oil simulant) respectively to 1.9% (aqueous simulant) was found by GALOTTO ET AL. (2009) when they analysed high pressure-treated PLA with DSC. But the analysed film (PLA/SiOx/PLA) had a very low initial crystallinity of 2.4% before HPP (500 MPa; 15 min; 50°C), and the changes are within the error of measurement. Furthermore, the results of the DSC point out that there was a redistribution in the crystallites size when PLA is in contact with a liquid of a great affinity to PLA (in this case an aqueous simulant). In this study, GALOTTO ET AL. also give an account of a large increase in the degree of crystallinity (from 28.5% to ~36%; DSC) in PET after HPP treatment (500 MPa; 15 min; 50°C).

By contrast, in a study on the suitability of PLA films for HPP, SANSONE ET AL. (2012) detected an increase of crystallinity by DSC (700 MPa; 15 min; 40–110°C). In this case, the magnitude of the increase depended on temperature and the packed food and was about 4% for a treatment at 110°C. No variation of crystallinity through HPP (50–600

MPa; 23°C) was found by DSC in PA6 (SCHMERDER ET AL. 2005). AYVAZ ET AL. (2012) analysed EVOH in combination with PA6, EVA, PET and PE thermally. The heats of fusion of PA6, EVA and PET show no significant decrease after high pressure treatment (600 MPa; 10 min; 110°C), whereas the heat of fusion of PE after the same process is significantly decreased.

In a failure analysis, RICHTER ET AL. (2010) detected an increase of crystallinity in a damaged area of a PE-LD layer of a PET/PE-LD multilayer at 600 MPa and 30°C by Raman spectroscopy.

3.2.2 Changes of layers and layer structure

Packaging films with an inorganic layer showed to be affected by HPP in two ways. On the one hand, the insufficient flexibility of the inorganic material in conjunction with a high pressure treatment can lead to cracks in the layer. On the other hand, delamination between a layer and an adjacent polymeric layer can occur because the materials respond differently to compression and temperature.

Defects generated in inorganic layers

GALOTTO ET AL. reported on defects in inorganic layers caused by HPP (GALOTTO ET AL. 2008; GALOTTO ET AL. 2009; GALOTTO ET AL. 2010). They investigated coated and laminated films with different coatings on the substrates, namely PET/AlOx, PLA/SiOx/PLA, PP/SiOx and PETmetallized (met)/PE.

PET/AlOx showed many pinholes and cracks after HPP (500 MPa; 15min; 50°C). It is noticeable that the damage caused by HPP treatment was less severe when using water as a food simulant compared with oil as a food simulant. In this case, the damages in the PET/AlOx film affected all physical properties of the film (modulus of elasticity, tensile strength and percent elongation). On the contrary, the PLA/SiOx/PLA film showed some pinholes after HPP treatment independent of the used food simulant. Additionally, bright areas appear in the film that was in contact with water (GALOTTO ET AL. 2009).

Scanning electron micrographs of PP/SiOx showed that the complete SiOx layer was destroyed after HPP treatment at 400 MPa and 60°C for 30min (GALOTTO ET AL. 2008). After the same treatment of PETmet/PE, only cracks could be detected in the layer by scanning electron microscopy (SEM) (GALOTTO ET AL. 2010). Table 3-3 shows a summary of all process parameters and occurring damages.

GALOTTO ET AL. (2008) and BULL ET AL. (2010) explained the destruction of the inorganic layer via the insufficient flexibility of the layer material. By nature, cracks will appear if tensile stresses are greater than the cohesive strength of the coating. Internal stresses will be generated in most multilayer systems because the materials show different thermo-mechanical properties (LETERRIER 2003). For example, first cracks appeared in a coating of 30 nm SiOx on 12 µm PET already at a nominal strain of around 2.5% in the uniaxial mode (LETERRIER ET AL. 1997).

Delamination of multilayers with inorganic layers or polymeric coatings

Another group of direct effects is the occurrence of delamination of different laminates. So, a polyester/PA6/aluminium/PP (142 µm) multilayer film shows delamination between PP/Al when pressurized at ≥200 MPa and ≥90°C for 10 min (SCHAUWECKER ET AL. 2002). Analogue to these findings, GALOTTO ET AL. (2008) detected delamination in metallized multilayer polymer. They studied PETmet/PE (75/19 µm) films by visual inspection and SEM. The parameters of the HPP were 400 MPa for 30 min and at 20±2°C or 60±2°C.

These findings confirm the results from the study of CANER ET AL. (2003): On scanning electron micrographs of high pressure-processed (600/800 MPa; 45°C; 5–20 min) PETmet/ EVA/linear PE-LD, they detected numerous folds and wrinkles on the food contact side of the film and a delamination between the adjacent PETmet and PE layers via C-mode scanning acoustic microscopy. In contrast, the multilayer systems of PET/AlOx/PE-LD and PET/SiOx/PE-LD (and PET/polyvinylidene chloride/EVA/linear PE-LD) also showed some surface deformation (by SEM) but no indications of a delamination after an HPP treatment at 800 MPa with 45°C for 20 min. Both SCHAUWECKER ET AL. (2002) and GALOTTO ET AL. (2008) saw the reason for the delamination in the different response of metal, polymer and adhesive layers to compression and temperature.

Table 3-3 Damages in inorganic layers.

Polymer	Treatment	Thickness	Description	Method	Remark	Reference
PP/SiOx	400 MPa 20 or 60°C 30 min	20 µm	significantly damaged	n/a	s. Galotto et al. 2008	(GALOTTO ET AL. 2010)
PET/AlOx	500 MPa 50°C 15 min	11.6±0.5µm	pinholes, cracks	SEM	Depends on the food simulating liquid	(GALOTTO ET AL. 2009)
PLA/SiOx/PLA		35.8/21.5µm	pinholes			
PETmet/PE	400 MPa 20 or 60°C 30 min	75/19 µm	disruption of the coating, delamination wrinkles	vis., SEM	Not affecting mechanical properties	(GALOTTO ET AL. 2008; GALOTTO ET AL. 2010)
PP/SiOx		21±1 µm				

3.3 Indirect effects

Indirect effects arise from the compression of substances and cover a wide field of reported damages in HPP. The compression of headspace gases, which goes along with a changeover into the supercritical state of the gas, leads to numerous defects. So, a localized increase of temperature can cause an alteration of the packaging. A more complex topic is the influence of solution effects. First, the solubility of other substances in gas increases. This may induce an extraction of value-adding components out of the food on the one hand; on the other hand, the supercritical gas can extract constituents out of the polymers. Second, the concentration of the gases in polymers increases. This in turn has two effects. Initially, the absorbed gas acts as a plasticizer and can lead to changes in crystallinity. Furthermore, a too rapid decompression conducts to explosive decompression failures (blisters) because the specific volume increases too fast. Another source of damage is the enhanced solubility of liquid substances that can lead to delamination.

3.3.1 Gas compression

The category ‘gas compression’ contains the consequences of headspace gas compression caused by a high pressure treatment. It can be divided into three subcategories: Strain-induced crystallization, local thermal damages caused by the heat of compression and solution effects caused by the supercritical state of headspace gases during HPP. This implies both the increase of solved gas in a polymer and the increase of solubility of substances in the supercritical gas.

Strain-induced crystallization

In addition to the named irreversible structural change in the category direct effects, another kind of these irreversible structural changes is strain-induced crystallization. This phenomenon has been observed in the form of white lines after HPP (695 MPa; 10 min; 70–86°C) of PP/PET multilayer films (FAIRCLOUGH, CONTI 2009). These lines were allocated by the authors to both strain induced crystallization and decompression. The same phenomenon can be found in the papers of GORLIER ET AL. (2001) and FERNANDEZ, SWALLOWE (2000) and in publications about applications of rapid decompression (HANDA ET AL. 1999; ZENG ET AL. 2003). The latter will be treated more precisely in the succeeding section.

Local thermal effects

During high pressure treatment, the phenomenon of adiabatic heating occurs. Because the product, the headspace gases and also the pressure-transmitting fluids differ in the emerging heat of compression and the thermal conduction between sample, media and pressure vessel is different, the temperature distribution in the vessel can be inhomogeneous (DENYS ET AL. 2000; HARTMANN ET AL. 2003; TING, BALASUBRAMANIAM 2002). Whereas the heat of compression of pressure-transmitting fluids, polymeric packaging and liquid foods has been well studied, e.g. (BALASUBRAMANIAN, BALASUBRAMANIAM 2003; BARBOSA-CÁNOVAS, RODRIGUEZ 2005; BUZRUL ET AL. 2008; KNOERZER ET AL. 2010; PATAZCA ET AL. 2007; RASANAYAGAM ET AL. 2003; TING, BALASUBRAMANIAM 2002) there are no systematic investigations on the influence of compressed headspace gas on the packaging. As the compressive heating effect of gases is much higher than that of liquids, as TING, BALASUBRAMANIAM (2002) mentioned, a localized increase of temperature by compressed headspace gases, especially in the corners and angles of a packaging, will largely influence the damage symptoms . In this regard, RICHTER ET AL. (2010) related the observed increase in crystallinity in area of white spots to local thermal effects.

Solution effects

The solution effects base mainly upon the fact that the headspace gases are in their supercritical state during high pressure treatment (cf. overview of critical temperatures and pressures in Table 3-4). This leads to two different impacts. First, the solubility of substances in the supercritical fluid is enhanced. Second, larger quantities of supercritical fluid can be solved in polymers. For the HPP of packed food, two potential causes of defect arise from there: Both negatively impacts on the quality of food by extraction and localized decompression failures by the oversaturation of the polymers with supercritical headspace gas.

Table 3-4 Critical temperature and critical pressure of typical headspace gases (EMSLEY 1989; LAX ET AL. 1998).

Gas	Critical temperature (K)	Critical pressure (MPa)	Density [STP] (mol/dm³)	Supercritical density (by way of example)	Reference
CO_2	304.19	7.38	0.0450	33.9 mol/dm³ at 330 K and 800 MPa 24.2 mol/dm³ at 310 K and 75 MPa	(SPAN, WAGNER 1996)
N_2	126.25	3.39	0.0445	10.9 mol/dm³ at 300 K and 31.3 MPa	(DILLER 1983)
O_2	154.55	5.05	0.0447	19.6 mol/dm³ at 310 K and 65.3 MPa	(RODERT 1982)

Extraction

The enhanced solubility of certain substances in supercritical fluids is used for extraction in numerous industrial applications (BRUNNER 2010). This enhanced solubility may have an impact on two different negative effects in the area of HPP: First, as pressurized CO_2 is used, e.g. in supercritical fluid extraction of food components, high pressure treatment will probably affect the quality of food in some cases. Influencing factors in this connection are the nature of the extracting solvent, the pressure level, the dwell time and the solvent: material ratio (JUNG ET AL. 2011). Whereas HPP-induced changes of the aroma of vacuum-packed food were published recently (RIVAS-CAÑEDO ET AL. 2009; RIVAS-CAÑEDO ET AL. 2011), negative effects caused by extraction by supercritical headspace gases are not reported in the literature.

Second, supercritical CO_2 can extract additives out of polymers (cf. polymer analysis, (COTTON ET AL. 1991; VENEMA ET AL. 1993). For example, COTTON ET AL. reported on the extraction of phenol, 2-(5-chloro-2H-benzotriazole-2-yl)6-(1,1-di-methylethyl)4-methyl (Tinuvin 326) out of PP with supercritical CO_2. This effect may thus lead to a higher migration out of packaging materials. So far, to our knowledge, tests of global and specific migration of packaging components into food simulants during HPP were only performed without headspace gases (CANER, HARTE 2005; DOBIÁS ET AL. 2004; LAMBERT ET AL. 2000; MAURICIO-IGLESIAS ET AL. 2010; MERTENS 1993; OCHIAI, NAKAGAWA 1992). Even though the additional extraction effect may be small and its contribution to the migration of packaging components low, it should be investigated with regard to the plastics implementation measure (PIM 10/2011) (Commission Regulation (EU) No 10/2011).

Localized decompression failure

The damages that can be traced back to increased gas solution in polymers are usually due to a rapid decompression of the solved fluid. The increased solubility of supercritical fluids in polymers can be seen exemplary in a comparison of the solubility of CO_2 in polysulfone (PSU) at 313 K in Figure 3-2. The chart shows the solubility of CO_2 (in weight%) versus pressure on a double logarithmic scale. The red-dotted vertical line represents the critical pressure of CO_2 (Table 3-4). At an increase of pressure to values above the critical value, the solubility is increased by a factor of ~100.

TANG ET AL. (2007) looked at the sorption isotherms of CO_2 in the transition region of gaseous to supercritical state (up to 15 MPa) in poly(methyl methacrylate) (PMMA) at different temperatures. Thereby, every sorption isotherm shows a turning point for the sorption saturation, i.e. below the turning point the sorption saturation increases slightly with pressure, whereas the increase of the sorption saturation is steeper with pressures above the turning point. Interestingly, the turning point can also be below the critical pressure of CO_2, depending on the temperature.

To our knowledge, there is no experimental data of the solubility of gases in polymers at very high pressure (PATERSON ET AL. 1999). FAIRCLOUGH, CONTI (2009) conducted a rough calculation of the solubility of N_2 in PP at pressures up to 700 MPa. According to their calculation, the solubility of nitrogen in PP increases by a factor of 36.3 upon a pressure rise from 0.1 to 700 MPa.

At the decompression during high pressure treatment, the solved supercritical gas will expand to avoid an oversaturation and balance the thermodynamical equilibrium. If the decompression is too rapid, the expansion can induce visible consequences such as cracks (Figure 3-3), blisters, voids and microstructures such as foams and thus may affect the integrity of composite films particularly with an inorganic layer (Figure 3-4 and Figure 3-5) (BOYER, GROLIER 2005b; DEWIMILLE ET AL. 1993; RICHTER 2011). The occurring phenomena can be summarized in the term 'explosive decompression failure' (XDF) (BOYER, GROLIER 2005b; BRISCOE ET AL. 1994; BRISCOE ET AL. 1998). This phenomenon is known from other technical areas (e.g. petroleum industry, BRISCOE, ZAKARIA (1992)) and is, e.g. intentionally used to produce polymeric foams (ARORA ET AL. 1998), whereas it is unwanted in HPP, cf. (RICHTER 2010).

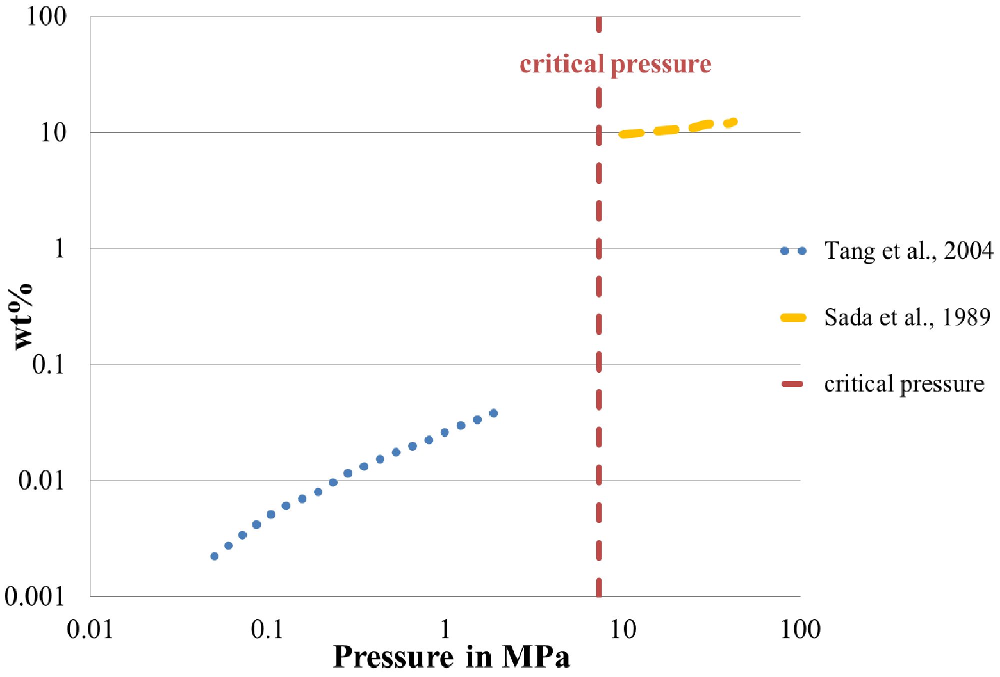

Figure 3-2 Plot of the equilibrium sorption amount of CO2 in PSU against pressure at 313K. Data taken from TANG ET AL. (2004b) and SADA ET AL. (1989). The wt% from SADA ET AL. was calculated with rPSU=1.24g/cm³.

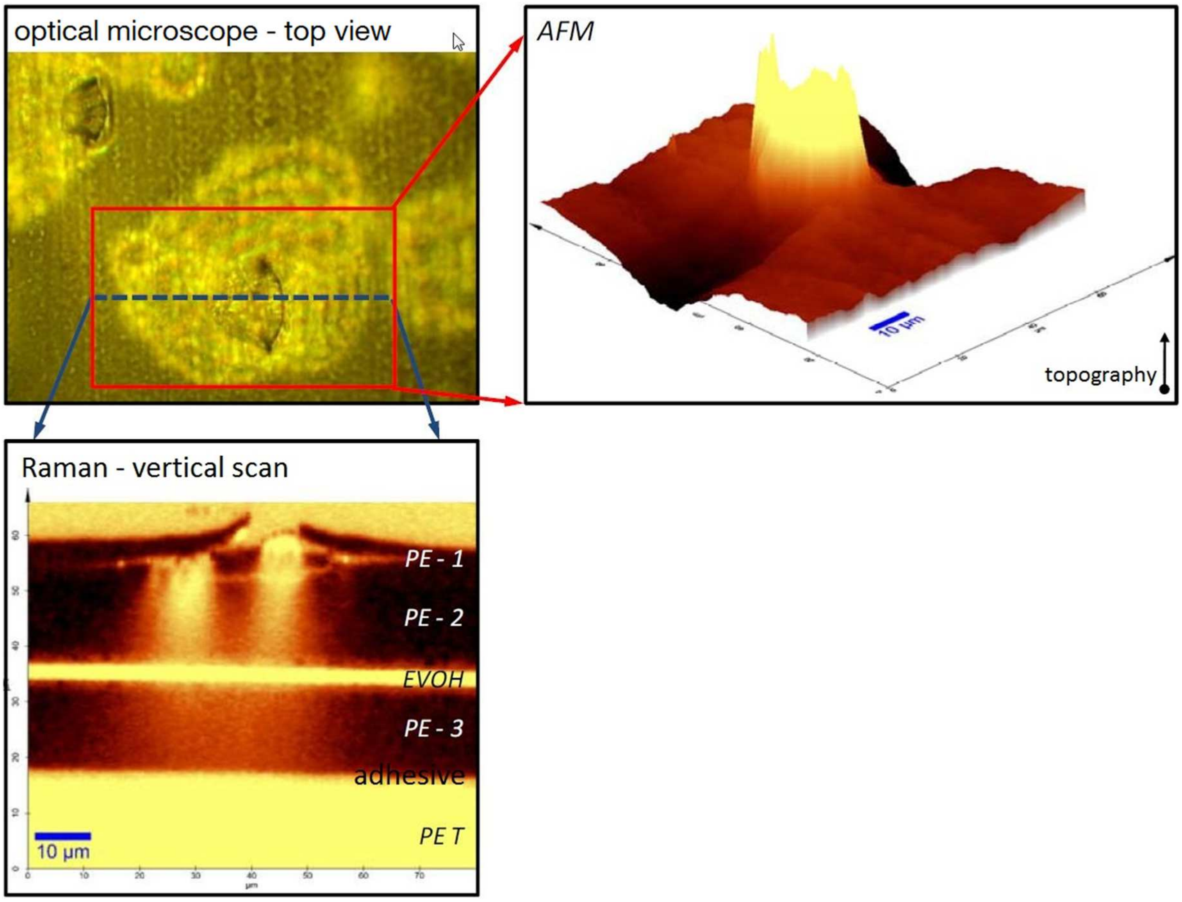

Figure 3-3 Analysis of a local decompression failure by optical microscope, Raman microscopy and atomic force microscopy (AFM) (Richter 2011).

These occurring effects were detected by several authors: Fairclough et al. reported on small pits and sub-surface bubbles after HPP treatment (695 MPa; 86°C; 10min; release 2s) of PP bags with an air headspace. Recently, Richter published Raman and atomic force microscopy images of an aluminium foil delamination (Figure 3-4) and a damaged SiOx coating (Figure 3-5). He traces both of these damages back on an explosive decompression failure (500 MPa; 40°C; N_2 and CO_2 headspace) (Richter 2011).

Another group that reports on damages within polymeric packaging material that can be allocated to explosive decompression failure is Götz, Weisser (2002). After high pressure treatment (500 MPa) of PA/PE bags that were filled with CO_2, bubbles arose within the film, whereas O_2 filled bags remained unaffected. This discrepancy may be explained by the fact that in PE, the solubility of CO_2 is higher than the solubility of O_2 and a smaller amount of O_2 will be dissolved in the polymer (van Krevelen, Nijenhuis 2009).

Also BULL ET AL. (2010) postulated that the delamination of some multilayer systems is caused by explosive depressurization. In one case (600 MPa; 115°C; 5–10 min), the expansion of the dissolved gas is reported to "push the laminated layers apart, leaving behind a delaminated area". The extent of delamination is correlated with the solubility of the corresponding gases in the film layers. Multilayer systems with aluminium foil showed less delamination than those without aluminium foil.

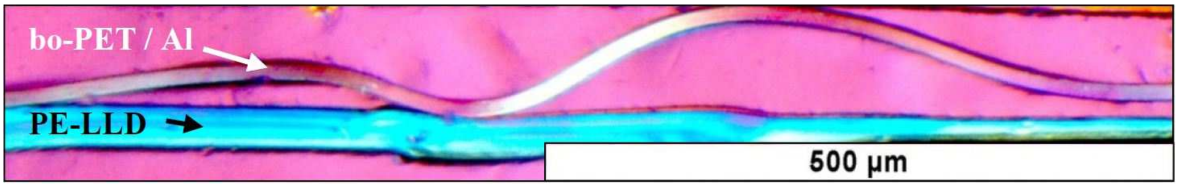

Figure 3-4 Microtome cut of a delamination (RICHTER 2011).

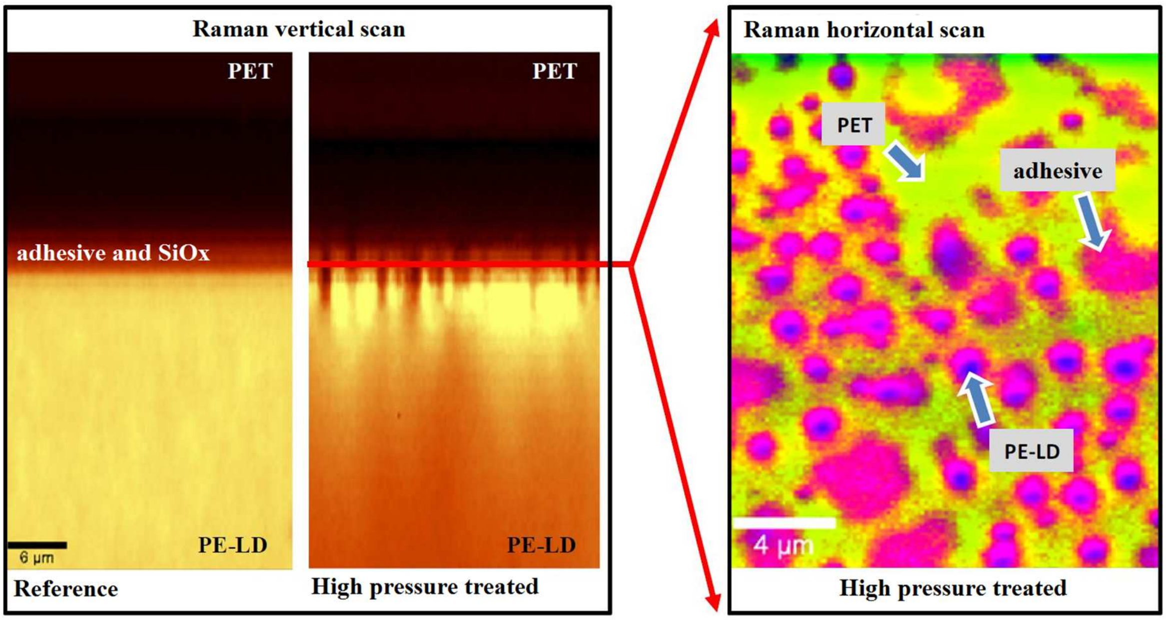

Figure 3-5 Damaged SiOx layer; Colour assignment in the right image: green, PET; blue, PE-LD; magenta, adhesive SiOx (RICHTER 2011).

The findings in the paper by FRADIN ET AL. (1998) from the earlier years of HPP research also suggest an explosive decompression failure. They compared vacuum-sealed pouches with pouches with a headspace of about 10%. In this paper, all multilayer specimens with a gaseous headspace showed delamination and small bubbles, whereas a monolayer (PE-LD) just showed a reduced transparency after high pressure treatment (200 MPa; 25°C; 15–45 min). The observed damages were independent of the duration of treatment.

Already at pressures under 50 MPa, explosive decompression failures can occur. So, TANG ET AL. (2004b) found defects on PSU via a field emission scanning electron microscope at their studies about sorption of supercritical carbon dioxide at pressures up to 40MPa. There are some papers from the field of the petroleum industry dealing with explosive decompression failures at lower pressures as well (BOYER ET AL. 2006; BOYER ET AL. 2007; BOYER, GROLIER 2005b; HILIC ET AL. 2001).

Also, the circumscriptions occurrence of 'voids' (MASUDA ET AL. 1992) and 'sporadic blisters' (KOUTCHMA ET AL. 2009) indicate explosive decompression failures, but there is not enough information in these papers to allocate failures definitely. Different process parameters and the damages caused by gas solubility in polymers after high pressure treatment are summarized in Table 3-5.

Sorption-induced plasticization and crystallization. Next to explosive decompression failures compressed gases lead to other effects that affect the integrity of polymeric packaging. Some of these interactions of compressed gases with polymers have been widely studied. First of all, CO_2 is reported to acts as a plasticizer, especially in its supercritical state (COOPER 2000). The most frequently used way to quantify plasticization is the decrease of the glass transition temperature T_g of the polymers under study. This was done in many studies (cf. Table 3-6) (CHIOU ET AL. 1985a; FRIED ET AL. 1989; HANDA ET AL. 1997; HOUDE ET AL. 1992, 1994; SANDERS 1988; WANG ET AL. 1982; WISSINGER, PAULAITIS 1991; WONDERS, PAUL 1979). For a more detailed overview about penetrant induced plasticization ISMAIL, LORNA (2002) see, e.g. the review of .

BOS ET AL. (1999) defined plasticization of glassy polymers as the increase in CO_2 permeability as a function of fed pressure. In this paper, BOS ET AL. hypothesized "that all polymers need a similar CO_2 concentration to plasticize but require different pressures to reach it." This critical plasticization concentration was 71±14mg CO_2/cm^3 polymer for the studied 11 polymers (inter alia PSU, polyethersulfone and polycarbonate).

The influence of pressure on T_g, however, is not always unidirectional. For polystyrene, WANG ET AL. (1982) observed a minimum of T_g at a CO_2 pressure of 20 MPa and a slight increase of T_g at higher CO_2 pressures (tested up to 105 MPa). Also the influence of supercritical CO_2 on the temperatures of crystallization T_c and melting T_m was tested. KISHIMOTO, ISHII (2000) reported that compressed CO_2 gas up to 9.4 MPa reduces T_m and T_c of isotactic PP. These findings were confirmed by VARMA-NAIR ET AL. (2003).

Table 3-5 Solubility of headspace gases: damages.

Polymer	Treatment	Thickness	Headspace	Description	Method	Remark	Reference
PA/PE	500 MPa 5 min	30/60 µm	CO_2	Bubbles, delamination	SEM		(Götz, Weisser 2002)
			O_2	No delamination			
PP/PET	695 MPa 70 to 86°C 10 min		air	Small pits, bubbles	SEM CLSM	Release 2s	(Fairclough, Conti 2009)
PET/oPA6/PP*/**	600 MPa 115°C 5 to 10 min	12/25/80 µm	Less than 10 % of the packaging volume (air)	Large delamination	Visual detection	Independent of time and temperature	(Bull et al. 2010)
PET-AlOx/oPA6/PP		12/15/80 µm					
PET/oPA6/R-PP		12/15/80 µm		Delamination			
PET/PVDC-MA/PP		12/50/70 µm					
PET/PA6/Al/R-PP		12/15/7/70 µm					
PET/PET-SiOx/PP		23/12/75 µm					
PET-SiOx/oPA/PP		12/15/75 µm					
PET-AlOx/oPA6/PP		12/15/70 µm					
PET-AlOx/oPA6/whitePP		12/15/100 µm					
PET/Al/PP		12/7/70 µm		Less delamination			
PET/Al/PP		12/12/70 µm					
PSU	20 to 40 MPa 40 to 60°C 24 h	0.8-1.2 mm	CO_2	Defects on surface	FESEM		(Tang et al. 2004b)
PE-LD	200 MPa 25°C 15 to 45 min	200 µm	Less than 10 % of the packaging volume (air)	Reduced transparency	Visual	Independent of duration No damages at a vacuum of 25mbar	(Fradin et al. 1998)
BB4L (PA6/PE)				Delamination Small bubbles			
PA/PE		100 µm					
PA/SY		180 µm					
PET/PVDC/PE		65 µm					
PET/BOA/PE		62 µm					

n/a, not applicable; CLSM, confocal laser scanning microscopy; FESEM, field emission scanning microscope; SY, surlyn (copolymer of ethylene and methacrylic acid); PVDC, polyvinylidene chloride; BOA, benzyl-octyl-adipate.
* o = oriented; ** PA6 = nylon

Table 3-6 Reduction of the glass transition temperature by solved CO$_2$.

Polymer	T_g (°C)		ΔT_g (°C)	CO$_2$ pressure (MPa)	Remark	Reference
	untreated	treated				
PVC	75	57	18	2.0		(CHIOU ET AL. 1985a)
PS	100	78	22			
PC	148	97	51			
PET	74	52	22			
PMMA	105	67	38			
Syndiotactic PS	97	65	32	3.5	*	(HANDA ET AL. 1997)
PMMA	105	32.7-58.8	46.2-72.3	4.0	Dependent on the solved amount of CO$_2$	(WISSINGER, PAULAITIS 1991)
PS	100	35	65	6.0		
PES	235	135	100	3.5		(SANDERS 1988)
PC	158	147	11	3.0		(FRIED ET AL. 1989)
PSU	197	179	18			
PEI	219	213	6			
PS	100	~41	59	20.0	at 45 °C Amount of plasticization is higher at lower ambient temperature*	(WANG ET AL. 1982)
	100	46	54	92.0		
PSU	286-291	260	26-31	2.0	PSU phenolphthaleine based	(HOUDE ET AL. 1992, 1994)
PC	142	133-134	8-9	0.8	*	(WONDERS, PAUL 1979)

* Original data were represented graphically

The effect of plasticization, however, is not always a simple decrease in T_g. Because of the increase in the mobility of the polymer chain segments (BRISCOE ET AL. 1998; SCHULTZE ET AL. 1991), recrystallization may be induced, leading to an increase in crystallinity and morphological damages (MA ET AL. 2004). The sorption-induced increase in crystallinity was investigated in the first instance for CO$_2$. Also there is only information in the range of moderate pressures (cf. Table 3-7) (BECKMAN, PORTER 1987; BRISCOE ET AL. 1998; CHIOU ET AL. 1985a; LAMBERT, PAULAITIS 1991; MIZOGUCHI ET AL. 1987).

Even though these studies were conducted at moderate pressures (up to 50 MPa) in comparison with HPP (~800 MPa) and longer treatment times (several hours to days vs. several minutes at HPP), they show that HPP of packaging with modified atmosphere can affect the morphology of the polymeric material.

Table 3-7 Sorption-induced increase in crystallinity

Polymer	Crystallinity (%)		ΔCrystal-linity (%)	CO_2 pressure (MPa)	Temp. (°C)	Remark	Reference
	Un-treated	treated					
PET	4.4	29.2	24.8	5.1	85	-	(Mizoguchi et al. 1987)
PET	8.0	29.0	21.0	4.1-6.1	35	Max. value independent of pressure Faster crystallization at higher pressures	(Lambert, Paulaitis 1991)
PC	19.3	43.1	23.8	2.0	35	-	(Chiou et al. 1985b)
	19.3	48.7	29.4	3.5			
PC	A.	17.5	17.5	50.7	75	Bisphenol A polycarbonate *	(Beckman, Porter 1987)
	A.	22.0	22.0		88		
PVDF	63.0	62.0	-1.0	30.0	42 and 80	Rods made from an extruded cylinder	(Briscoe et al. 1998)
	53.0	53.0	0.0			Parallelpiped made from injected sheet	

* Original data were represented graphically
A., Amorphous polymer; PVDF, polyvinylidene fluoride

3.3.2 Influence of non-gaseous substances

Delamination in multilayer systems without inorganic layer

In multilayer systems without inorganic layer, the reasons for the delamination are interactions between the product and the tie layer or the pressure sensitivity of the tie layer. For example, the former occurs in a PE/EVOH44/PE multilayer that is in contact with oil and pressurized at 400 MPa for 30min at 20±2 or 60±2°C. In a parallel experiment, the same multilayer shows no delamination in contact with water. A possible explanation for this is an additional migration of low molecular compounds from the adhesive into the oil (Galotto et al. 2010).

The latter was suggested by Lambert et al. (2000). In their study, six multilayer films were analysed, which could be considered as identical except for the used adhesives. Only one specimen (PA/adhesive/PE) showed delamination after treatment with 200–500 MPa at 20°C for 30 min. Because all specifications and filling material except for the adhesive were identical, LAMBERT ET AL. assumed that the adhesive is responsible for delamination. However, the affected multilayer has an extraordinary thick adhesive layer (20 µm) between PA and PE, and the specimen was sealed at a pressure of 80% below atmospheric pressure. That means that a residual headspace gas exists, which can lead to interactions (see Section on ‘Indirect effects’).

3.4 Conclusion

High pressure-induced damages in polymeric packaging materials can be assigned to different mechanisms: effects that are directly caused by the high pressure treatment (direct effects) and effects that are generated by the compression of other substances in the package (indirect effects). To achieve a maximum of functionality in high pressure-treated packaging, those mechanisms have to be identified.

Direct effects

During high pressure treatment, the permeation coefficient for some polymer/substance combinations shows to decrease reversibly, mainly because of a decrease in the diffusion coefficient. In the common free-volume model of permeation, this can be directly assigned to a pressure-induced reduction of the free volume. Although a qualitative correlation between polymer morphology and permeation has so far not been established, the temporal and reversible decrease in permeability seems to be a general phenomenon, which, besides, does not negatively affect the functionality of the packaging.

Another direct effects of high pressure treatment on polymers are changes in crystallinity. Because of several different measurement methods and the application of different blends and parameters, the various published papers do not show homogeneous findings. Permanent effects of HPP are directly reflected by changes in the morphology in the bulk of polymers or at the interface of polymeric and inorganic layers. First, changes in crystallinity have been observed by different authors, but the findings do not show a clear trend. Second, delamination or other damages have been found by many authors for multilayer systems. These effects have a clearly negative effect on the functionality of the whole package.

In the case of multilayer systems that include inorganic layers, both direct damages of the inorganic layers and delamination at the interface between inorganic and polymeric layers are frequently observed. Both mechanisms can be assigned to the discontinuity of the mechanical properties across the interface, which a priori cannot be totally avoided. It is certainly a good strategy to improve the adhesion between the layers, but, as a general rule, polymeric multilayer systems without inorganic layers will be superior.

Indirect effects

Indirect effects represent all influences of compressed substances inside the package. Primarily, these effects are caused by compressed gases. They will first generate thermal effects, ranging from, e.g. localized increase of crystallinity up to catastrophic failures such as melting of the sealing layer.

Another potential effect can be summarized as solution effects. There, the higher concentration of gases in the polymeric matrix at high pressure can lead to a plasticization of polymers, followed by structural changes or an extraction of constituents from the polymer enabled by the supercritical state. In addition, (explosive) decompression failures may occur because of decompression, which leads to an oversaturation of the gas in the polymer. These failures arise in the form of cracks, blistering or other microstructures and turn up to concentrate in weak zones of the materials and, again, in interfacial zones.

As a final conclusion, it can be stated that the impacts of HPP on barrier properties and visual appearance as the most important properties of plastic packaging are treated phenomenologically at best. Many questions concerning physicochemical processes in the polymeric materials still remain unanswered: How does the morphology change upon the action of high pressure, especially in combination with supercritical gases? Does high pressure affect gas sorption and permeation in the same way as already reported for aroma substances? As the answers to these questions are crucial for a wider application of HPP, many work still has to be done in this area.

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4 In-situ measurement of oxygen concentration under high pressure and the application to oxygen permeation through polymer films

Up until now, gas permeation through polymers under high pressure has not been able to be measured continuously. The combination of a special high pressure cell and a commercially available fluorescence-based oxygen measurement system allows in-situ monitoring of oxygen permeation through a polymer sample under pressure in an aqueous environment. The principle of the oxygen sensor is based on dynamic fluorescence quenching and measurement of the fluorescence decay time. It was observed that the decay time increases non-linearly with the applied pressure and hence the displayed oxygen concentration has to be corrected. This deviation between the measured and the real concentration depends not only on the pressure but also on the absolute oxygen concentration in the water. To obtain a calibration curve, tests were performed in the pressure range between 1 and 2,000 bars and initial oxygen concentrations in the range between 40 and 280 µmol/L. The polynomial calibration curve was of the fourth order, describing the raw data with a coefficient of determination $R^2>0.99$. The effective oxygen permeation through polymeric samples can be calculated with this function. A pressure hysteresis test was undertaken but no hysteresis was found. No temperature dependence of the oxygen sensor signal was observed in the range of between 20°C and 30°C. This study presents for the first time data showing the oxygen permeation rates through a low density polyethylene film under pressures up to 2,000 bars. It could be shown that the oxygen permeation coefficient is reduced by a factor of between 35 and 70 at 2,000 bars applied pressure compared to the value at atmospheric pressure at 23°C. These results are in good accordance with the findings for the permeation of aromatic compounds at similar pressure conditions. The lowered permeability was attributed to the reduction of free volume and the decreased chain mobility in polymers. The effect is expected to be more severe for polymers with initial higher free volume compared to polymers with higher density.

In-situ measurement of oxygen concentration under high pressure and the application to oxygen permeation through polymer films

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Abstract

Up until now, gas permeation through polymers under high pressure has not been able to be measured continuously. The combination of a special high pressure cell and a commercially available fluorescence-based oxygen measurement system allows in-situ monitoring of oxygen permeation through a polymer sample under pressure in an aqueous environment. The principle of the oxygen sensor is based on dynamic fluorescence quenching and measurement of the fluorescence decay time. It was observed that the decay time increases non-linearly with the applied pressure and hence the displayed oxygen concentration has to be corrected. This deviation between the measured and the real concentration depends not only on the pressure but also on the absolute oxygen concentration in the water. To obtain a calibration curve, tests were performed in the pressure range between 1-2,000 bars and initial oxygen concentrations in the range between 40-280 µmol/L. The polynomial calibration curve was of the fourth order, describing the raw data with a coefficient of determination $R^2>0.99$. The effective oxygen permeation through polymeric samples can be calculated with this function. A pressure hysteresis test was undertaken but no hysteresis was found. No temperature dependence of the oxygen sensor signal was observed in the range between 20°C and 30°C. This study presents for the first time data showing the oxygen permeation rates through a polyethylene film in the pressure range between 1 to 2,000 bars at 23°C.

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Content Publication III

4.1 Introduction

High pressure processing is an innovative and already well-established technique for prolonging the shelf life of temperature-sensitive foods such as fresh juices, guacamole and seafood. Pressures up to 8,000 bars are used. Furthermore, an increasing number of foods such as ham and cold meat are being packed into packaging having a modified atmosphere. In order to understand the complex processes that occur in food at high pressure, it is very important to monitor the chemical, physical, biological and other processes in-situ. Several attempts have been made to carry out in-situ optical measurements to monitor changes to food systems, enzymes and microorganisms under high pressure processing. TORRES, VELAZQUEZ (2005) described a prototype for in-situ optical polarisation measurements for study processing effects on foods. OGER ET AL. (2006) developed a diamond anvil cell for observing the growth and fate of microbes using confocal microscopy and STIPPL ET AL. 2004 described a method for the optical in-situ measurement of pH. A few other in-situ studies have been performed, but MARTÍNEZ-MONTEAGUDO, SALDAÑA (2014) mentioned in their review article on “Chemical Reactions in Food Systems at High Hydrostatic Pressure” that many mechanisms are not yet fully understood due to the lack of in-situ measurement of chemical reactions. In particular, the monitoring of in-situ oxygen reactions could help to better understand the processes that take place under pressure.

Up until now, the permeation of gases through polymer and multilayer films in modified atmosphere packaging has not been able to be measured. Knowledge of this is very important because increased amounts of gas dissolved in the polymer can lead to damage to the polymer packaging after a sharp pressure drop. BOYER ET AL. (2007) described this phenomenon in their work as “explosive decompression failure” (XDF). The estimation of gas sorption and diffusion under pressure can help better understand this phenomenon and make predictions about its occurrence. Some papers have dealt with the sorption of (supercritical) gases in polymers under pressure using gravimetric methods (LIN ET AL. 2010) or have analysed the amount of gas entering a polymer under controlled temperature and pressure conditions using a vibrating-wire detector and a pVT technique (BOYER ET AL. 2009). However, no in-situ oxygen permeation or oxygen reaction measurements have been performed. In previous studies the permeation of flavour compounds through polymers was investigated by RICHTER ET AL. 2010. By applying pressure up to 2,000 bars a reduction in the permeation coefficient of ß-ionone through a low density polyethylene (PE-LD) film was observed by a factor of 55. A reduction by a factor of six to seven was found in the permeation coefficient of various aroma compounds (benzoic acid, raspberry ketone and carvacrol) through a polyamide 6 (PA6) film.

In order to study oxygen permeation through a polymer film, a commercially available sensor system, a so called optode, based on the principle of dynamic fluorescence quenching was used for our work. The application of fluorescence lifetime based optodes in aquatic systems is already used in marine biology and chemistry (TENGBERG ET AL. 2003). Although the measurement of dissolved oxygen is a well-known and often used technique, the systems are however only designed to operate for low pressure processes.

Inside the sensor spot which is used for dynamic fluorescence measurements, a fluorophore is embedded in a matrix. This is excited to the electronic singlet state on illumination with sinusoidally modulated blue light (HUBER 2011; JORGE ET AL. 2004; MCEVOY ET AL. 1996). Upon fluorescence, the fluorophore returns to the energetic ground state. In the presence of oxygen, a well-known quencher, collision-induced energy transfer takes place. The oxygen is excited to its singlet state and the amount of fluorescence radiation is reduced. This quenching process is described by the Stern-Volmer Equation 4-1 (STERN, VOLMER 1919):

Equation 4-1

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} pO_2$$

The equation indicates that the ratio of the fluorescence light intensity in the absence (I_0) and in the presence (I) of a quencher is proportional to the oxygen partial pressure p_{O2} and the Stern-Volmer quenching constant K_{SV}. The constant K_{SV} is, according to WELLER 1959 (Equation 4-2), proportional not only to the sum of the molecular radii a and the number of molecules per millimole N', but also to the sum D of the diffusion coefficients of oxygen and fluorophore. As diffusion coefficients are pressure sensitive, this might explain the observed influence of increasing pressure on the concurrently measured reduction in fluorescence intensity.

Equation 4-2

$$K_{SV} = 4\pi a D N' \tau_0$$

The equipment used in this study determines the luminescence lifetime τ of a fluorophore, the time for which it is in the excited state. The typical lifetime τ_0 of a fluorophore in the absence of a quencher is in the range of 10 ns to 10 µs (LAKOWICZ 2006; MORRIS ET AL. 2007b). The advantage of measuring the lifetime instead of the intensity is that it is independent of photobleaching or other external factors such as changes in the light source intensity or turbidity of the media (HUBER 2011). Additionally, the measuring method is not oxygen-consuming and shows no sensitivity to stirring (HOLST ET AL. 1995; TENGBERG ET AL. 2003). Upon excitation of the optode with sinusoidally modulated light the fluorescence lifetime can be related to a phase delay ϕ in the luminescent emission relative to the extinction with the modulation frequency f_{mod} (Equation 4-3) (JORGE ET AL. 2004):

Equation 4-3

$$\tan[\phi] = 2\pi f_{mod}\tau$$

During our experiments it was observed that under identical oxygen concentrations the fluorescence signal from the sensor spot was strongly dependent on the pressure. Higher pressure values lead to increasing phase angle ϕ and therefore to decreasing displayed oxygen concentration c_{dO2}, while the “true” oxygen concentration does not change. The absence of outgassing phenomena observed through the sapphire window also proves the constancy of the oxygen concentration. TENGBERG ET AL. (2006) tested a lifetime-based optode (like the optode used in our studies) at high pressures up to 400 bars. They found a linear reduction of the sensor response of about 4% per 100 bars. This result could not be confirmed in our studies, where a non-linear decrease was observed. A reason for the discrepancy may be, that over a smaller pressure range (3 - 400 bars) the reduction is approximately linear, but is non-linear over a larger pressure range. Tests were therefore performed to determine the correlation of the pressure dependent change of the phase angle ϕ. A test was also undertaken to see whether there was an additional temperature effect on the signal in the temperature range from 23°C to 29°C. Furthermore a hysteresis test and reproducibility test were carried out. The results were fitted to a polynomial function transcribing the raw data to real oxygen concentration values. This study presents for the first time results for the oxygen permeability of a polyethylene film up to a pressure of 2,000 bars. Other time-resolved experiments involving oxygen-consuming or oxygen-forming reactions under pressure (such as microbiological respiration or enzymatic reactions) could be undertaken using this measurement method.

4.2 Materials and Methods

A high pressure vessel from SITEC (Sieber Engineering AG, Maur, Switzerland) was used for the experiments. This was originally built for studying aroma compound migration and permeation (RICHTER, LANGOWSKI 2005). Inside the pressure vessel a polymer sample (ø = 0.7 cm) can be fixed with a retainer (Figure 4-1), so separating the pressure cell into two chambers. The upper chamber has a volume of 5.4 cm³, the bottom chamber a volume of 6.7 cm³. Both chambers can be filled and drained separately with different fluids (e.g. oxygen saturated water and water with reduced oxygen concentration). The temperature inside the vessel was measured with a thermocouple (Fe-CuNi Type J) and could be regulated from 20°C to 50°C with the help of a heating jacket mounted around the vessel. Both chambers were pressurised simultaneously by a common manual spindle pump. The maximum pressure was 2,500 bars and the pressure build-up and pressure release rates were around 2,000 bar/min. A pressure sensor made by EBM Brosa Messgeräte (Tettnang, Germany) was integrated into tubing next to the vessel. The pressure transmitting fluid was the sample water itself. In the bottom chamber a sensor spot was fixed on the inside of a sapphire window (thickness 1 cm) for optical measurement of the fluorescence quenching by the oxygen present in the cell. The sensor spot PSt3 is commercially available from PreSens - Precision Sensing GmbH (Regensburg, Germany). It operates within a specific measurement range (0 to 1,400 µmol/L dissolved oxygen) and has a resolution of 6%. The sensor spot is illuminated from the outside with blue light by an optical fibre connected to the Fibox 3 LCD Trace measurement system (PreSens - Precision Sensing GmbH Regensburg, Germany).

The oxygen measurement system was calibrated before starting the experiments and after every 100,000 data points. A two-point calibration was carried out at atmospheric pressure by first adding sodium sulphite (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) to the water to create an oxygen-free environment. The second calibration point was taken with 100% air-saturated water. At 23°C and 1,013 mbar pressure, air-saturated water contains 280 µmol oxygen per litre water (calculated using Equation 4-7, SANDER 2015).

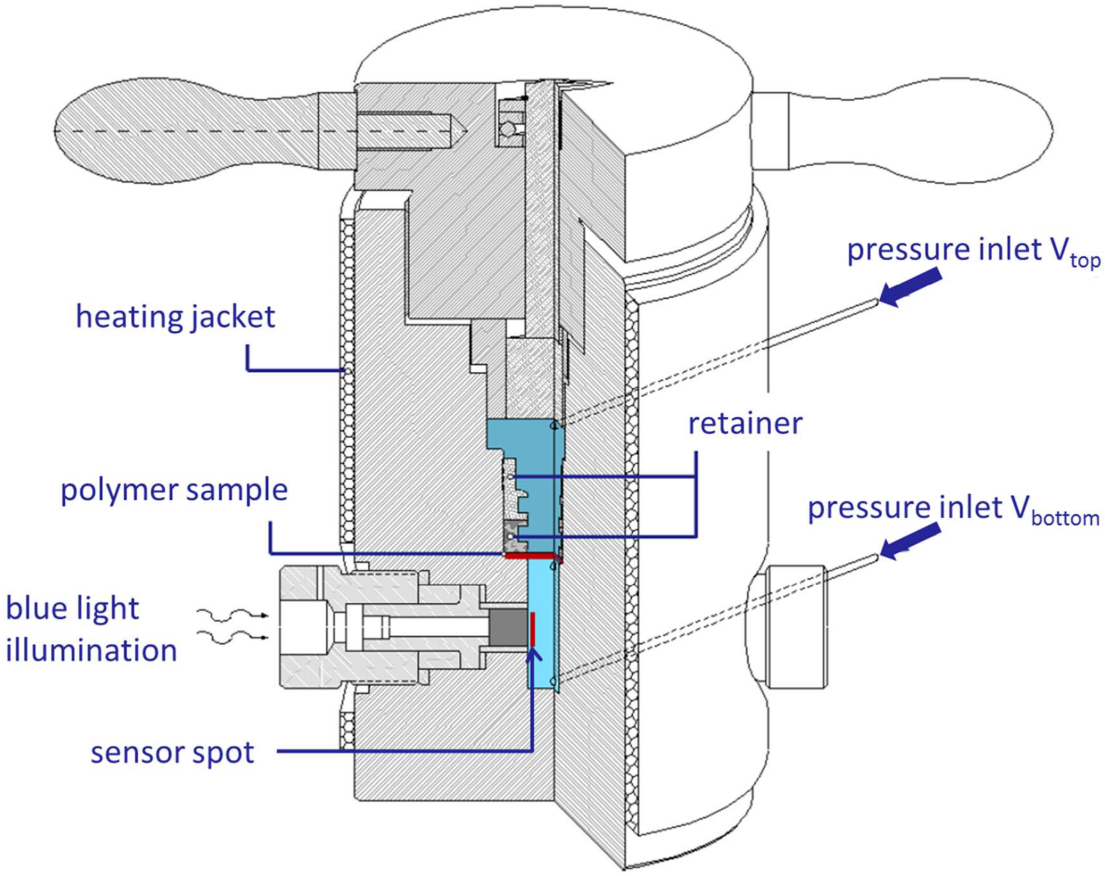

Figure 4-1 Schematic presentation of the pressure cell [according to RICHTER, LANGOWSKI (2005); Copyright Tobias Richter. Reproduced with permission of Der Weihenstephaner 44, 85 (2005).]

For the experiments, water with reduced oxygen concentration was prepared by boiling and subsequent cooling water to 23°C in hermetically sealed glass containers. This enabled oxygen concentrations of down to 40 µmol/L to be reached (approx. 20% of the oxygen saturation of water under atmospheric conditions). To produce water with different concentrations of dissolved oxygen, the cooled water was stirred under atmospheric conditions for varying periods of time. For the preparation of air-saturated water, the water was stirred for at least 30 minutes. The oxygen concentrations were validated before every experiment by take measurements with the sensor in the pressure vessel. All the experiments were performed with demineralised and boiled water to prevent microbiological contamination. Additionally, the system was cleaned between every experiment with RIMASAN®-AQ N-34524 (Tensid Chemie GmbH, Muggensturm, Germany) to avoid microbiological growth and hence oxygen attrition.

4.2.1 Hysteresis, reproducibility and temperature dependence

Preliminary experiments were carried out to check the reproducibility and reliability of the sensor reaction. As the vessel has two sapphire windows it was possible to fix two sensor spots inside the vessel, one spot on each window. With two independently working measuring devices the reduction of the two phase angles with the applied pressure could be monitored independently. Data for testing for hysteresis and temperature dependence were collected at the same time as the determination of the oxygen response signal correction.

4.2.2 Method for determining the dependence of the oxygen response signal on the applied pressure

For these experiments, water with varying initial oxygen concentrations (40 µmol/L < c_{iO2} < 260 µmol/L) was prepared and filled into the vessel. To check whether air bubbles remained in the system, the pressure was first increased to 20 bars and held for a few minutes (Figure 4-2 and Figure 4-3). At this low pressure the sensor works within standard parameters and additional dissolved oxygen immediately increases the displayed oxygen concentration. In such an eventuality, the experiment was interrupted and restarted. Otherwise the pressure was increased gradually up to a maximum pressure of 2,000 bars in steps of 200 bars (Figure 4-2). After every step the pressure was held for a few minutes until the response signal was stable. The pressure release was also performed in steps to check for possible pressure hysteresis. The temperature was kept constant in each experiment at respectively 23°C, 25°C, 27°C and 29°C. In order to obtain a correlation curve describing the raw data as real values, a mean oxygen concentration at every pressure step as a function of the initial oxygen concentration c_{iO2} was calculated. Curve fitting was performed with the Curve Fitting Toolbox of MATLAB R2013b. A polynomial function was chosen as the regression model and the order of the polynomial function was selected, considering the sum of squared errors due to error (SSE) and the coefficient of determination.

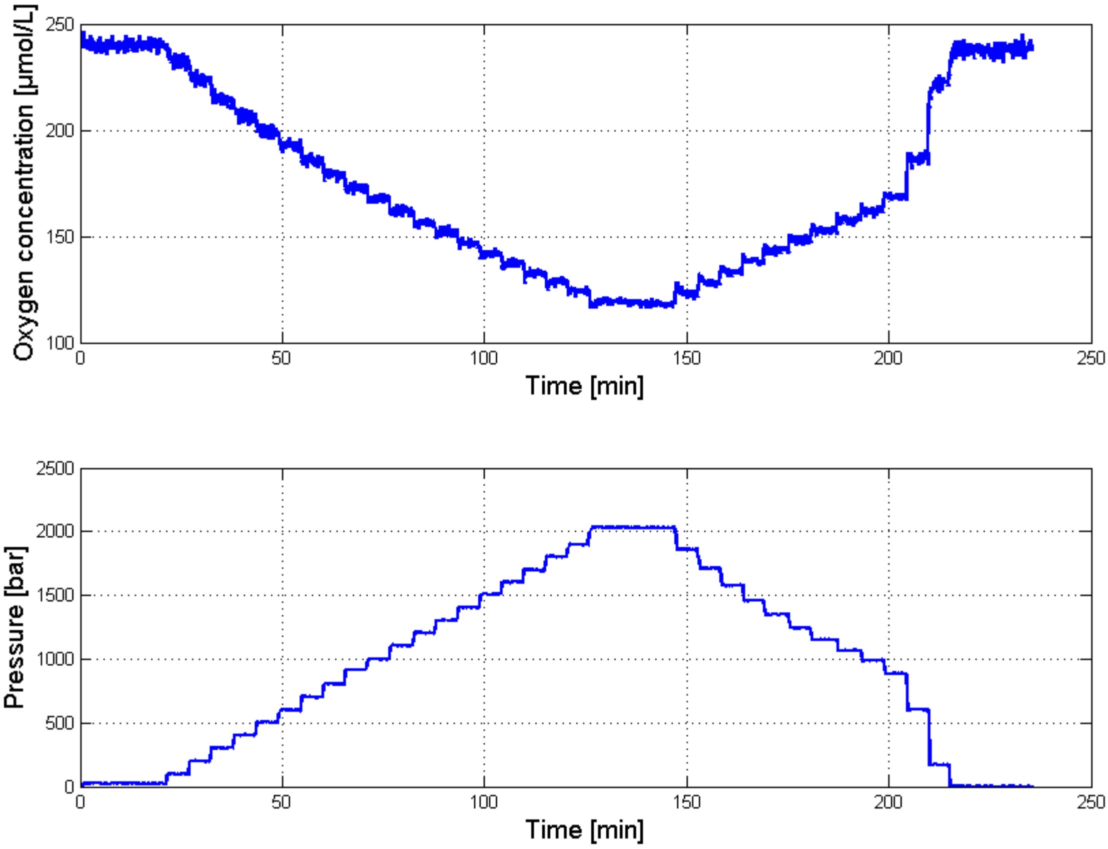

Figure 4-2 Stepwise increase in pressure leads to a simultaneous decrease in the displayed oxygen concentration c_{dO2}.

4.2.3 Oxygen permeation experiments

For the permeation measurements, the bottom chamber was filled with water having a reduced concentration of oxygen. After mounting the polymer sample, the upper chamber was filled with air-saturated water. To overcome the low diffusion coefficient of oxygen in water, two magnetic stirrers (one in each chamber) ensured the homogeneous distribution of oxygen in the water during the permeation experiments. All the permeation experiments were carried out with low density polyethylene (PE-LD) film samples of 50 µm and 100 µm thickness made from additive free granulate (Lupolen 3020 K by LyondellBasell, Wesseling, Germany) on a Collin lab extrusion line at the Fraunhofer Institute for Process Engineering and Packaging IVV in Freising, Germany.

4.4 Results and Discussion

4.4.1 Hysteresis, reproducibility and temperature dependence

The results in Figure 4-3 demonstrate that the sensor response to the oxygen concentration is reproducible, namely the two independently operating sensors show identical signals at the same time within the working range of the sensor (the maximum deviation of the measured oxygen concentration was about 6%).

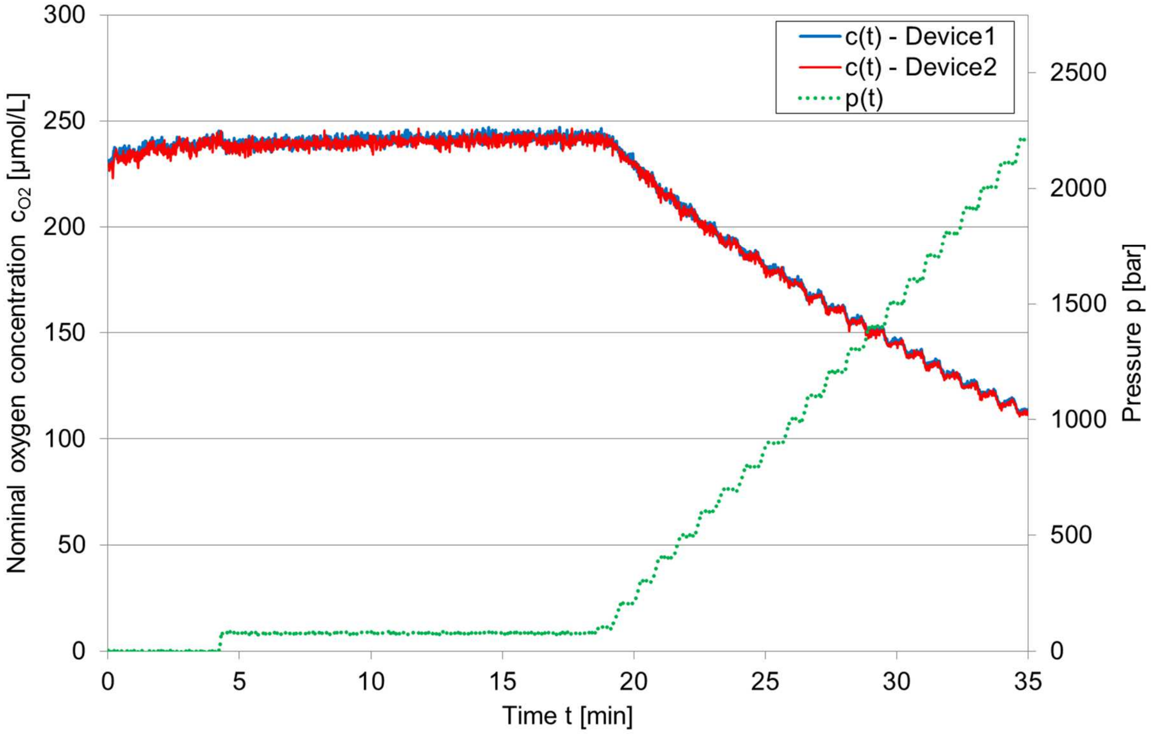

Figure 4-3 Comparison of two independently operating sensors. Nominal oxygen concentration and applied pressure, at an absolute O_2 concentration of 237 µmol/L.

Neither a hysteresis effect nor a temperature dependence could be detected. Figure 4-4 shows the oxygen concentration as a function of the pressure p for three representative trials with varying absolute oxygen concentrations c_{aO2} (pink, blue and black). The different symbols represent pressure build-up and pressure release. It can be clearly seen that the oxygen signal decreases non-linearly with increasing pressure and vice versa and that the values follow the same curve for pressure build-up and release. Additionally, it should be mentioned that the initial and final values at atmospheric pressure lie in the same range. Thus, it can be concluded that there is no hysteresis effect.

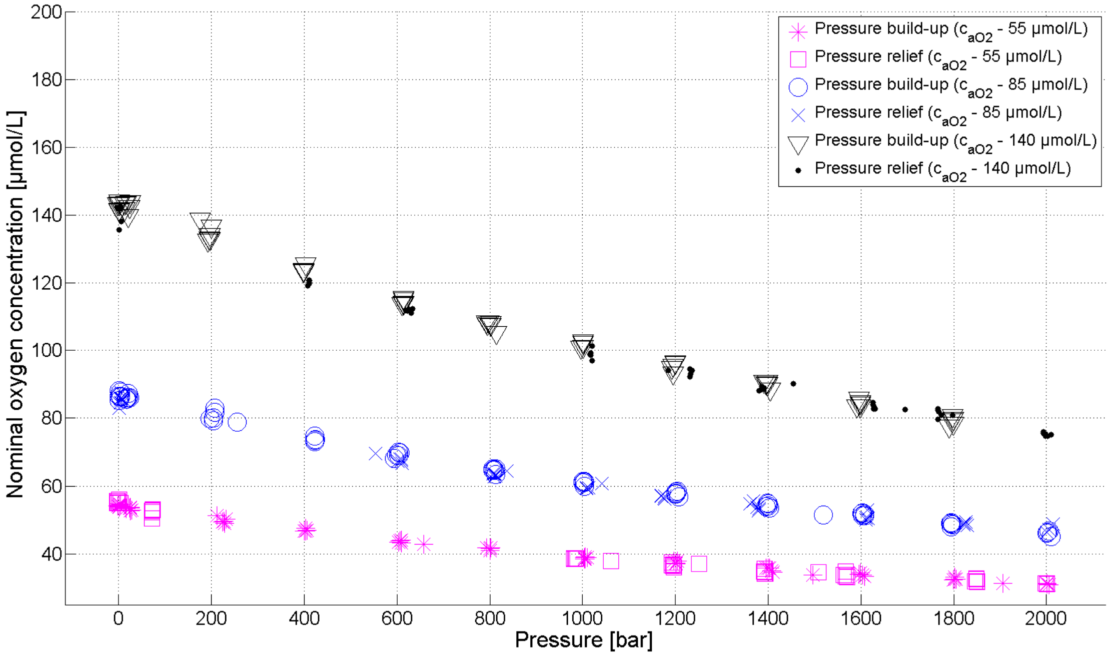

Figure 4-4 Hysteresis test. Nominal oxygen concentration as a function of pressure at different absolute oxygen concentrations c_{aO2}.

To examine the temperature dependency, the relative deviation $\Delta c_d(T)$ of the data from the experiments at 23°C and 29°C were plotted as a function of the pressure p and absolute oxygen concentrations c_{aO2} (Figure 4-5). A maximum deviation of 6% was found for the lowest absolute oxygen concentration (50 µmol/L) at atmospheric pressure and this is comparable with the measurement error of the sensor. Based on these findings, there was assumed to be no additional temperature dependence in the 20 to 30°C range at high pressures. A temperature influence was therefore not taken into account for further measurements. No predictions can be made, however, for temperatures above or below this range. The maximum adiabatic heating was found to be less than 1°C at the maximum pressure build-up rate (1,000 bar/min) and therefore can also be neglected.

4.4.2 Response correction

The correlation of the displayed and real oxygen concentration as a function of the pressure p and absolute oxygen concentration c_{aO2} was described by a polynomial function of the fourth order (Equation 4-4) with a coefficient of determination $R^2>0.99$ within the data range.

Equation 4-4

$$
\begin{aligned}
f(p, c_{O2}) = c_{cO2} \\
&= a00 + a10 * p_n + a01 * c_{nO2} + a20 * p_n^2 + a11 * p_n * c_{nO2} + a02 \\
&* c_{nO2}^2 + a30 * p_n^3 + a21 * p_n^2 * c_{nO2} + a12 * p_n * c_{nO2}^2 + a03 * c_{nO2}^3 \\
&+ a40 * p_n^4 + a31 * p_n^3 * c_{nO2} + a22 * p_n^2 * c_{nO2}^2 + a13 * p_n * c_{nO2}^3 \\
&+ a04 * c_{nO2}^4
\end{aligned}
$$

The terms p_n and c_{nO2} in the function stand for the normalised raw data values for the pressure p and displayed oxygen concentration c_{dO2} (Equation 4-5 and Equation 4-6). For fitting with a high-order polynomial, the data should be normalised by centring it at zero mean and scaling it to unit standard deviation.

The values of the coefficients used for Equation 4-4 can be found in Table 4-1.

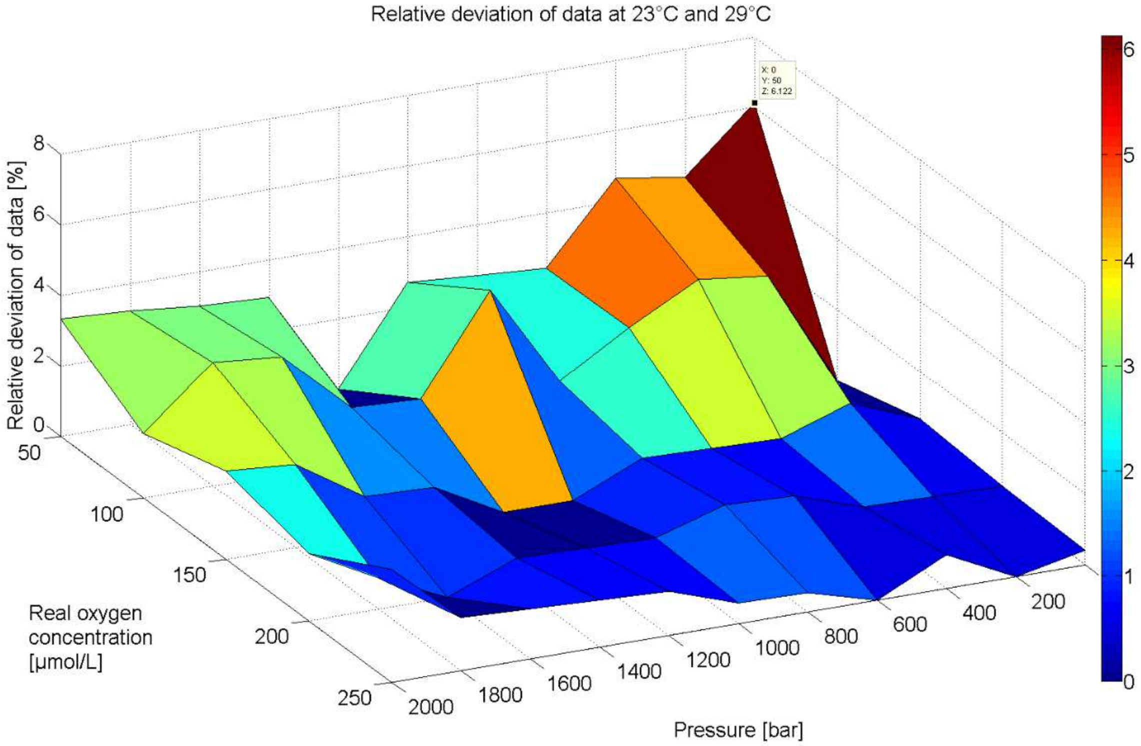

Figure 4-5 Test for temperature dependence. Relative deviation of data at 23°C and 29°C as a function of pressure p and absolute oxygen concentration c_{aO2}.

Equation 4-5

$$p_n = \frac{(p - 1000\ hPa)}{638.3\ hPa}$$

Equation 4-6

$$c_{nO2} = \frac{(c_{dO2} - 110.3\ \mu mol/L)}{55.47 \mu mol/L}$$

Table 4-1 Coefficients for Equation 4-4 with 95% confidence interval.

Coefficient	Value	95% confidence interval	95% confidence interval
a00	152.3	151.5	153.1
a10	29.03	27.98	30.09
a01	76.61	75.3	77.92
a20	2.679	1.299	4.129
a11	19.42	17.64	21.2
a02	2.162	0.6126	3.711
a30	1.1	0.5822	1.617
a21	5.932	4.827	7.036
a12	8.968	7.441	15.5
a03	5.219	4.226	6.212
a40	0.03086	-0.5146	0.5763
a31	0.9104	0.2155	1.605
a22	3.385	2.056	4.717
a13	4.804	3.11	6.498
a04	1.799	0.9609	2.637

An example of the verification of the function is shown in Figure 4-6, whereby the data of Figure 4-4 were recalculated with Equation 4-4, Equation 4-5 and Equation 4-6. The fact that the values do not change with pressure demonstrates the accuracy of the function.

4.4.3 Oxygen permeation experiments

For calculation of the permeability values, the initial slope of the oxygen concentration at the beginning of the permeation process was used, representing the permeation rate at maximum concentration difference. The polymer was already saturated with oxygen at atmospheric pressure and a possible time lag was too short to be observed. Figure 4-7 shows, for example purposes, the oxygen concentration at the bottom chamber of the pressure vessel for permeation measurement through a polyethylene film (50 µm) at 500 bars and 23°C. The gradient of the oxygen concentration between the two chambers was 212 µmol/L. The increase in the oxygen concentration in the first three hours approximately represents the steady state of permeation.

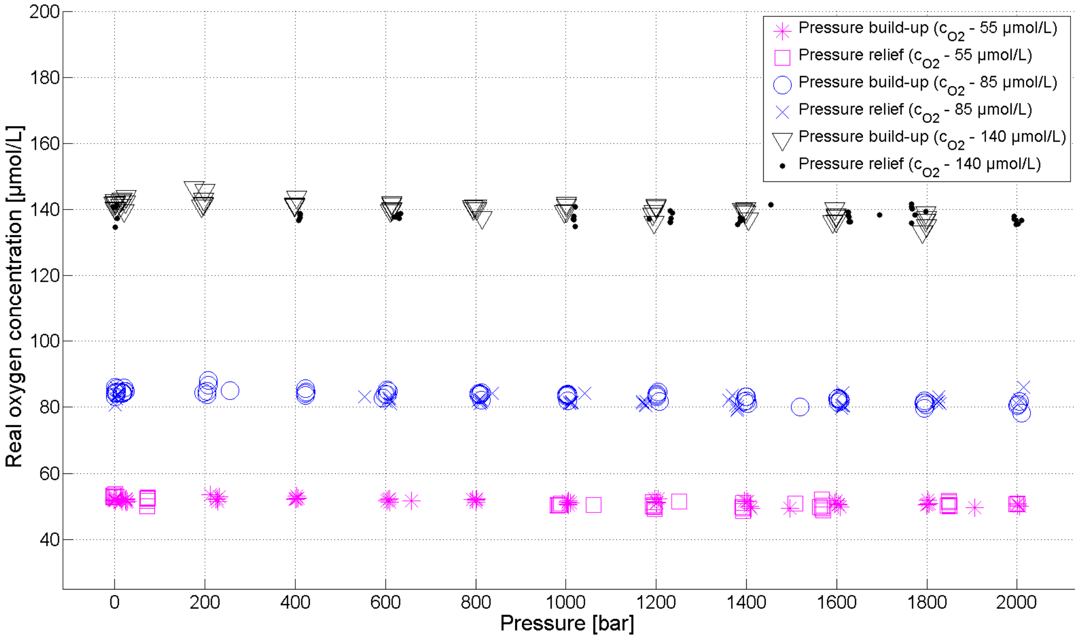

Figure 4-6 Recalculated raw data giving real values for the hysteresis test shown in Figure 4-4.

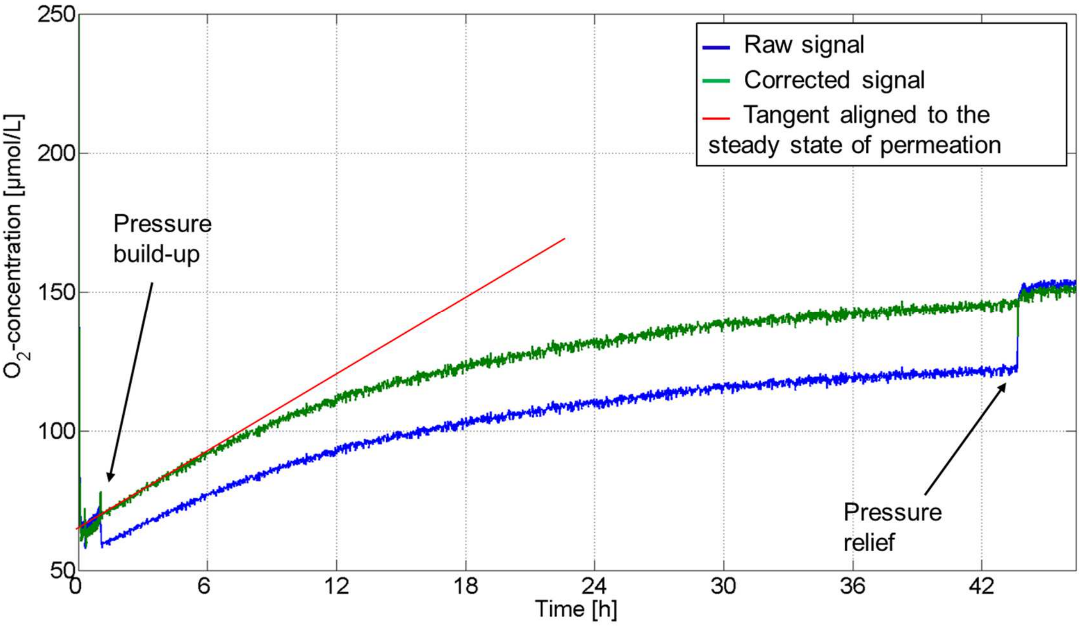

Figure 4-7 Permeation measurement through a polyethylene film of 50 µm thickness at 23°C and 500 bars pressure. The oxygen concentration was measured at the bottom chamber of the pressure vessel.

The oxygen concentration values were converted to absolute amounts of oxygen using the volume of the bottom chamber (6.7 cm³) and the molar volume of oxygen (22.4 L/mol). For gas permeation measurements, it is traditional to use a volume unit (cm³) at standard temperature and pressure STP (273K and 1,013.25 mbar). The oxygen concentration was converted into a partial pressure of oxygen (mbar) using Henry's law ($c = k * p$). Values of Henry's constant $k_{H,cp}$ can be found in SANDER (2015), giving a value for oxygen in pure water of:

Equation 4-7

$$k_{H,cp} = 1.3 * 10^{-3} \frac{mol_{gas}}{L * 1013.25\, mbar} * exp\left(1700\, K * \left(\frac{1}{T} - \frac{1}{298K}\right)\right)$$

The measured values for the oxygen permeation rate through polyethylene films are then displayed in cm³ [STP] /(m²*d). With further normalisation to a film thickness of 100 µm and to a partial pressure oxygen gradient of 1 bar, namely the driving force for the permeation, the permeation coefficient *P* is obtained in cm³ [STP] 100 µm / (m²*d*bar). The normalised results for two polyethylene films of different thickness (50 and 100 µm) are shown in Figure 4-8 and Table 4-2. The error bars indicate the 95% confidence interval. The fact that the decrease in the permeation coefficient on pressure increase is very similar for both films demonstrates clearly that the pressure effect is independent of the film thickness. Apparently, there is an exponential correlation between the oxygen permeation coefficient and the applied pressure. Comparison of the oxygen permeation coefficient at atmospheric pressure with data from literature shows good agreement. Typical permeation coefficients for oxygen in low density polyethylene in a gaseous environment range from 1,800 to 2,000 *(cm³(STP) 100 µm) / (m² d bar)* (LANGOWSKI 2008).

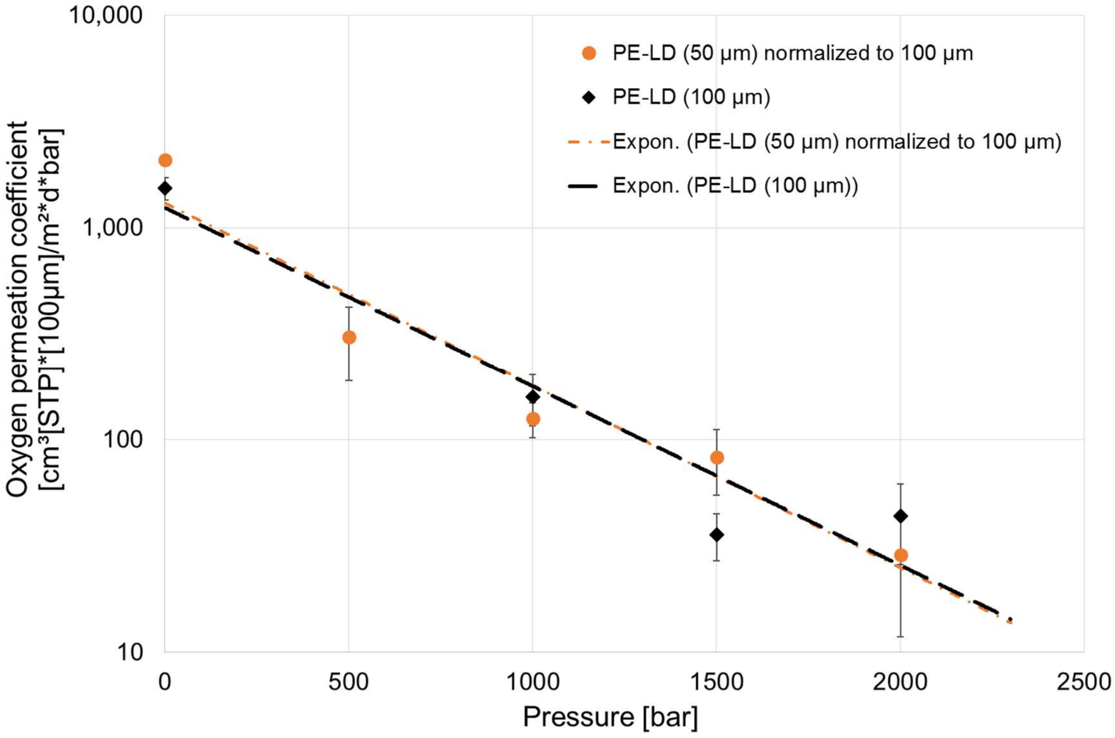

Figure 4-8 Oxygen permeation coefficient of polyethylene films (50 and 100 µm thickness) at 23°C for pressures up to 2,000 bars

Table 4-2 Pressure dependence of the oxygen permeation coefficient in PE-LD at 23°C

Film thickness [µm]	Pressure [bar]	Oxygen permeation coefficient $\left[\frac{cm^3[STP]}{m^2 * d * bar}[100\mu m]\right]$	95% confidence interval
100 µm	1	1,540	165
	500	-	-
	1,000	160	44
	1,500	36	6
	2,000	44	13
50 µm	1	2,090	75
	500	307	146
	1,000	126	24
	1,500	83	20
	2,000	29	17

In relation to the values at atmospheric pressure, the permeation coefficients of the polymer films are reduced by factors between 35 and 70 at pressures up to 2,000 bars. These findings are in very good agreement with the results of RICHTER ET AL. (2010) and RICHTER (2011), where a lowering of the permeation coefficient of β-ionone through a low density polyethylene film by a factor of 55 was observed. These results confirm that the lower permeability at high pressure can be attributed to the reduction in the free volume and the decreased chain mobility in polymers. This is in agreement with the findings for the permeation of model substances (ß-ionone, benzoic acid, carvacrol and raspberry ketone) through polyamide 6 which indicated a lowering of the permeation coefficient by only a factor of 7 (RICHTER 2011; RICHTER ET AL. 2010). Apparently, an increase in pressure has more influence on the reduction of the permeation for polymers having a high free volume and high chain mobility, such as low density polyethylene.

Finally, it should be mentioned that the process conditions easily exceed the critical point of oxygen (154K, 50 bars). Therefore, further permeation measurements using this new method would be worthwhile in the pressure range around the critical point of oxygen and using different types of polymers.

4.5 Conclusions

The principle of fluorescence quenching was used for in-situ measurement of the concentration of oxygen dissolved in water under high pressure and was applied for permeation measurements. At constant real oxygen concentration, a non-linear correlation was observed between the fluorescence quenching, and hence the displayed oxygen concentration, and the applied pressure. The correlation can be formally described by a polynomial function of the fourth order. This function enables correction of the displayed oxygen concentrations and the calculation of oxygen permeation rates under high pressure conditions. The measurement method is reproducible and the data show no hysteresis effect and no temperature dependence in the range of 23°C to 29°C. Using this experimental setup it is possible to measure oxygen transport processes (such as permeation through polymers) at high pressure. It was shown that the oxygen permeation coefficient of a low density polyethylene film is reduced by a factor of between 35 and 70 at 2,000 bars applied pressure compared to the value at atmospheric pressure.

In general, the experimental system has potential for addressing a host of other scientific problems and issues, for example measurement of the oxygen uptake of microorganisms under pressure and monitoring oxygen in reactions involving antioxidants, free radicals and isomerization processes.

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5 The effect of high pressure processing on tray packages with modified atmosphere

From previous studies (Chapter 3) it was getting clear, that relevant scientific work is missing concerning the effect of HPP on tray packages with modified atmosphere. Up until now scientific information about the influence of gases at high pressure conditions on the morphology of polymers, the barrier properties and the overall integrity of polymeric packaging was lacking.

Hence for this study the changes in the morphology of different polymeric materials after high pressure treatment was determined. The density of polyethylene terephthalate as well as the crystalline and amorphous content of polyethylene were analysed quantitatively with Raman spectroscopy. This spectroscopic method allows non-destructive determinations of the samples with very good spatial resolution.

For the investigations headspace volume (15 to 50% of the total package), headspace gas composition (air, CO_2, N_2 and a mixture of 20% CO_2/ 80% N_2), multilayer structures, film thickness and flexibility of the lid were varied. Additionally the influence of headspace gases in HPP on the barrier properties of an organic and an inorganic material and on the specific as well as overall migration of additives into liquid food simulants has been studied.

The results show small but technically negligible changes in polymeric structure. An increased volume of headspace gas seemed to have an influence on the amorphous phase of polyethylene. The density of polyethylene terephthalate (PET) decreases only slightly after high pressure treatment. Considering the barrier properties of organic and inorganic barrier layers it was getting clear that ethylene-vinyl alcohol copolymer (EVOH) is suitable for the HPP process, whereas metalized layers showed bad performance due to insufficient mechanical properties. No additional risk by the supercritical CO_2 extraction of packaging components could be detected in the migration studies.

With respect to these outcomes it can be concluded that flexible polymeric packaging is suitable for the use as modified atmosphere packaging at high pressure treatment.

The effect of high pressure processing on tray packages with modified atmosphere

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ABSTRACT

High pressure processing (HPP) is a small, but growing and profitable technique to extend the shelf life of high quality food products. As tray packages with modified atmosphere (MAP) provide better product presentation and also improved product protection, it seems logical to combine HPP with MAP. Due to the fact that the used gases like oxygen, nitrogen and carbon dioxide are in a supercritical state during high pressure processing, it is important to give extra attention to these conditions. Several studies were performed dealing with the influence of high pressure on the mechanical and/or barrier properties of packages and polymers. However, little information is known about the combined effect of MAP gases and high pressure on packaging. This study hence evaluates the influence of headspace gases on the morphology and integrity of packages subjected to HPP. Pressure related changes of the morphology of polymers as commonly used for packaging will be shown. Density as well as crystalline and amorphous content were analyzed quantitatively with Raman spectroscopy by varying headspace volume (15 to 50% of the total package), headspace gas composition (air, CO_2, N_2 and a mixture of 20% CO_2/ 80% N_2), multilayer structures, film thickness and flexibility of the lid. Additionally the influence of headspace gases in HPP on the barrier properties of an organic and an inorganic material and on the migration of additives into liquid food simulants has been studied.

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Content Publication IV

5.1 Abbreviations

Adh.	Adhesive
Al	Aluminum
CCD	Charged coupled device
DSC	Differential scanning calorimetry
EVA	Ethylene-vinyl acetate copolymer
EVOH	Ethylene vinyl alcohol copolymer
FT-IR	Fourier transform infrared spectroscopy
HPP	High pressure processing
MAP	Modified atmosphere packaging
PA	Polyamide
PA6	Polyamide 6
PE-HD	High density polyethylene
PE-LD	Low density polyethylene
PE-LLD	Linear low density polyethylene
PE-MD	Medium density polyethylene
PET	Poly(ethylene terephthalate)
o PET	Poly(ethylene terephthalate), biaxially oriented
a PET	Amorphous Poly(ethylene terephthalate)
PP	Polypropylene
PTFE	Polytetrafluoroethylene
SiO_x	Silicon oxide
XRD	X-ray diffraction

5.2 Introduction

High pressure processing (HPP) of food serves the rising demands of the consumers for natural, low processed food with less additives. Compared to a thermal treatment fresh and safe products with prolonged shelf life can be created and allow to fulfil the consumers requests. In HP batch processes packed products are treated to avoid recontamination or contact with the pressure transmitting fluid. But the packaging has to withstand the pressurizing process and the producer has to ensure that the material still maintains its original properties and fulfils legal requirements. Several investigations have been made about changes generated by high pressure inside polymers and packages. Both FLECKENSTEIN ET AL. (2014) and JULIANO ET AL. (2010) give an overview about publications related to this topic. Most of the cited studies, however, just deal with films and/or pouches used for vacuum packages without headspace. However in industrial applications many products (e.g. meat products like ham or sausages) are packed in tray / lid combinations with a headspace of modified atmosphere. Nitrogen (N_2) and carbon dioxide (CO_2) are the gases most often used in MAP. But to our knowledge no paper tackled the effect of headspace gases on the morphology, permeability and migration properties of polymers used in the food industry. Additionally it has to be taken into account that common headspace gases undergo a transition to the supercritical state in HPP (critical points: oxygen 154 K/51 bar; nitrogen 126 K/33,8 bar; CO_2 303,2 K/73,81 bar) and, therefore, show changed properties like a better solubility in other media (LAX ET AL. 1998). Although the critical temperature of carbon dioxide is as high as 30°C, pressure build up in almost adiabatic conditions will always raise the temperature above the critical point of CO_2. Supercritical carbon dioxide is well known to be an efficient extraction solvent (e.g. for decaffeination). An increased extraction of polymer additives in high pressure treatment is a possible risk that should be considered. Also little information is available about the influence of supercritical fluids on the structure of polymers.

Another consequence of headspace gases in combined HPP and MAP are bubbles, blisters and so called White Spots inside the films as observed after HP treatment. BOYER ET AL. (2007) identified the phenomenon of "explosive decompression failure" in plant components of the petroleum industry and explained it by the immediate and rapid expansion of gas dissolved in polymeric parts upon pressure release. This unwanted effect may also delaminate films or destroy barrier layers (BULL ET AL. 2010; FAIRCLOUGH, CONTI 2009; RICHTER ET AL. 2010). So the aim of this study is to analyse the influence of headspace gases in packages for HPP on the morphology of polymers and the integrity of packages.

First the impact of HPP on the morphology on the polymeric material was investigated, because the structure strongly affects the properties of the films. Structural modifications would have a direct consequence on the polymer characteristics, like permeability, appearance or mechanical properties. Morphological analyses were performed using Raman spectroscopy with a high spatial resolution in a confocal laser scanning microscope, further called Raman microscopy. At a lateral and vertical spatial resolution down to 260 nm, physical information of the inside of a transparent material can be obtained non-destructively in three dimensions, e.g. for the identification of inclusions or for the identification and determination of the individual thickness of layers in a multi-layer system (HOLLRICHER, IBACH 2011).

To separate the influence of high pressure process parameters (pressure, time and temperature) from packaging design parameters (headspace volume, gas composition, thickness and layer sequence of films) on the polymer structure, the results obtained for the single-layer samples had to be compared with those from examinations with tray packages filled with a model food product under modified atmosphere. In addition, possible changes in the oxygen permeability and of the specific and overall migration were investigated.

5.3 Materials and Methods

5.3.1 Monolayer materials

For the analysis of pressure dependent changes in crystallinity and density with Raman microscopy, different single layered films were used as basic reference samples. The samples were treated at different hydrostatic pressures, temperatures and periods of exposure. Sheets of approximately 20x30 cm² were cut from samples PE-LD2, PET1 and PET2 and pressurized in a NC Hyperbaric apparatus. The samples PE-LD1 and PE-HD were treated 1-5 days in a high pressure measurement cell from Sitec (RICHTER, LANGOWSKI 2005). The experiments were part of another scientific study to measure the in-situ permeation of aroma compounds through polymers under pressure. The experimental setup is described in RICHTER ET AL. (2010) and also in the dissertation of RICHTER (2011). The duration of these experiments (1-5 days) depended on the permeation rate of the compounds through the polymer and of the applied pressure. The influence of the parameters (processing time and pressure) to the values of crystallinity were compared separately but no influence of time was found. Therefore all results with different time were pooled together. Due to the small inner volume of the cell, a negligible adiabatic heating could be achieved. During the pressurizing process all samples were in direct contact with the pressure transmitting fluid (PE-LD1 and PE-HD: solution of ethanol at a volume concentration of 5,2% in water; PE-LD2, PET1, PET2: water). For detailed information about the films and the applied conditions see Table 5-1.

5.3.2 Multilayer films in model packages

For the evaluation of the influence of headspace gases model packages were built. Basis was a tray from a multilayer film with the layer sequence PET/EVA/PE-MD/EVOH/PE-MD/PE-LLD (See Figure 5-1 and Table 5-1). The thickness of PET was varied (400 or 600 µm) to check the influence of the total thickness on the overall integrity of the packaging. Trays were made by vacuum thermoforming in a circular mold of 16 cm diameter and 3 cm depth. Two lids with different stability to deformation were used:

- An elastic multilayer lid (thickness 120 µm) consisting of PE-mLLD/Adh./EVOH/Adh./PE-mLLD (Table 5-1).
- A laminated lid made of oPET, vacuum coated with a thin SiO_x layer, laminated to PE-LD, with a low elasticity, i.e. a stretching limit of about 5% in elongation until loss of barrier properties (Table 5-1).

The trays were filled with an agar gel (Agar-Agar Kobe I, 15g/L, Carl Roth, Karlsruhe, Germany) to simulate a water based, compact food product. With the agar gel it was possible to vary the headspace volume reproducibly over a wide range (volume fraction of the headspace: 15, 30 and 50%). The atmosphere inside was either air, 100% CO_2, 100% N_2 or a mixture of 20% CO_2 with 80% N_2. Every combination (tray, lid, headspace volume and gas composition) was prepared in triplicate. The high pressure treatment was performed at 600 MPa for 5 min at room temperature (Table 5-1).

For the investigations with MAP, common industrial packages were also used, supplied by a company from the project consortium. The tray material consists of PET/PEcoex

(210 µm/34 µm). It was previously investigated in the study of RICHTER, LANGOWSKI (2005) with respect to its performance in HPP. Examinations of a microtome cut with a polarizing microscope and the compared investigations with Raman spectroscopy showed that the PE layer consists of three different types of PE (see also Figure 5-2). The trays (dimension of 21 cm x 18 cm x 0,5 cm) were filled with 100 g of sliced dried prosciutto at a headspace gas composition of 20% CO_2 an 80% N_2 and HP treated under industrial conditions (600 MPa, 2 min, 5°C). After HPP, all packages were stored at ambient conditions, i.e. room temperature. Detailed information to find in Table 5-1.

5.3.3 Layer thickness

To find out whether differences in the thickness of the material have a measurable impact on the polymer structure and therefore favor the formation of XDFs, the morphology of polyethylene in multilayer trays was investigated via Raman spectroscopy. The inner side of the model tray contains two (Figure 5-1 left side) and of the industrial tray three (Figure 5-2) different polyethylene types. With confocal Raman spectroscopy the thickness of the different PE layers could be estimated based on a depth scan of the film. The estimation of layer thickness via confocal Raman microscopy has a limited accuracy. Although an oil immersion objective was used in this study, the results should be considered more as a qualitative indication than as a precise measurement of the individual layer thickness.

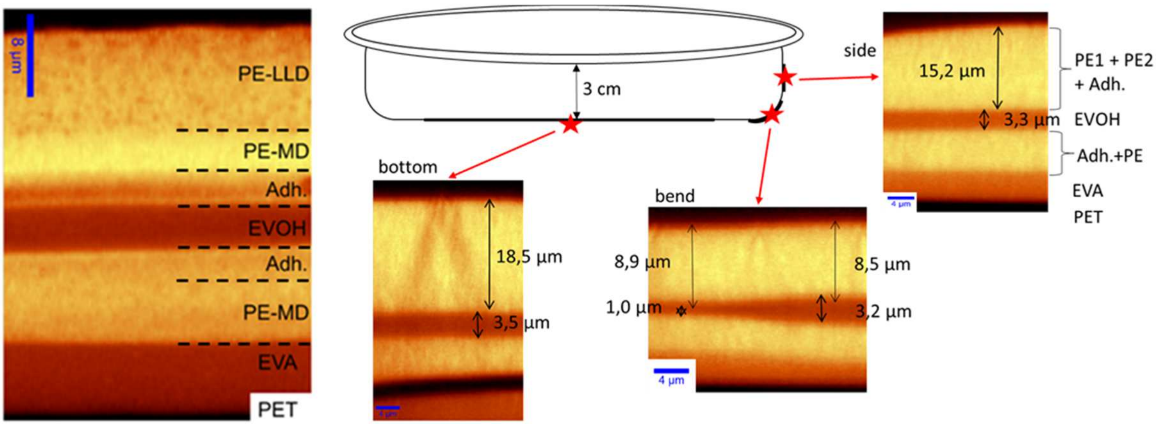

Figure 5-1. Model tray. Left: Raman depth scan of a model tray (PET/EVA/PE-MD/Adh./EVOH/Adh./PE-MD/PE-LLD) and differences in layer thickness due thermoforming (right side)

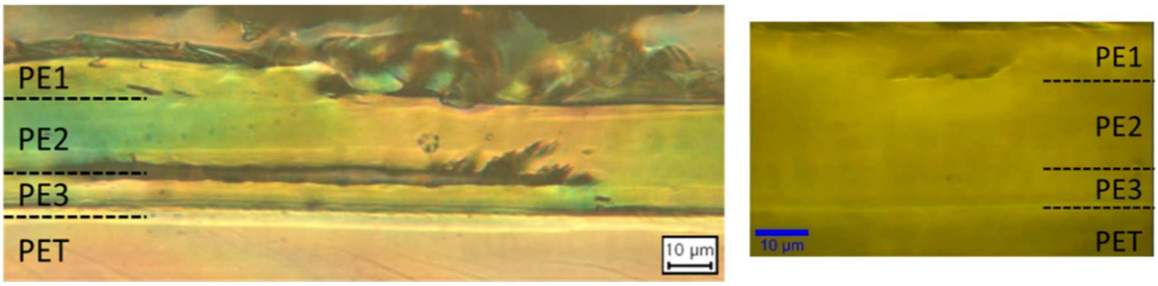

Figure 5-2. Industrial tray. Optical micrographs of two microtome cuts through white spots in the PE-LD layer in a PET/PEcoex laminate. (Sterr 11/2/2012)

5.3.4 Raman spectroscopic measurements

Raman spectra were recorded using a confocal laser scanning microscope with a green laser (532 nm) (WITEC Confocal Raman and Atomic Force Microscope Alpha 500). For the measurements a Nikon oil immersion objective (100x/1.25 Oil∞/0,17 WD 0.18) was used with oil modified for microscopy (following ISO 8036) from Merck (Darmstadt, Germany). The objective provides a calculated spatial resolution of less than 0,3 µm. The scattered light is collected by a spectrograph equipped with a CCD camera and allows a resolution of the spectral shift of about 2,5 cm^{-1} in the range from 0 to 3700 cm^{-1}. The pinhole diameter to the spectrograph is 50 µm.

Due to the confocal setup of the microscope the samples did not have to be cut or prepared for analysis. For the quantitative determination of crystallinity or density area scans were taken at the same depth (6 µm underneath the surface). For the analyses in coextruded polyethylene layers the scanning position of the second and third layer depended on the overall thickness. It should be noted that changes in the morphology of the polymers were only compared for samples of identical vertical scan position. Scans were always performed with a lateral size of 6 µm to 10 µm edge length. Per scan minimum 90 single spectra/ points per line and 90 lines per image were created. This results in a minimum number of 8100 spectra for each scan. The average of these spectra was used for further calculations. Peak fitting was performed with the mathematical program OriginPro8. For the deconvolution of the spectra of polyethylene the fingerprint region was divided into three parts. The first part contains four peaks and represents the C-C-stretching vibration. For this part, approximately from 950 – 1240 cm^{-1}, a Lorentzian function was used to model the peak shapes. The bands in the second spectral range (1200 – 1400 cm^{-1}), belonging to the CH_2-twisting vibration and the third range from 1390 cm^{-1} to 1500 cm^{-1}

(CH_2-bending vibration) were fitted with a Gaussian function (see Figure 5-3) (MAXFIELD ET AL. 1978). All fits had a minimum coefficient of determination of $R^2>0,99$.

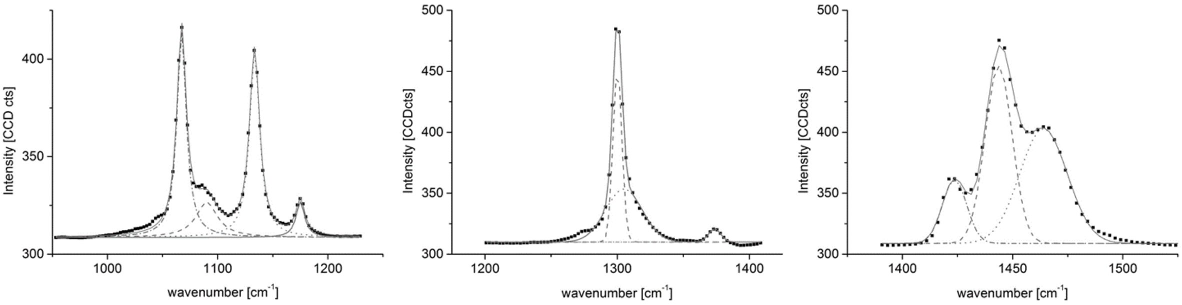

Figure 5-3 Peakfitting of three parts of the fingerprint region of PE. Squares represent raw data. Solid line show fitted data. Dotted lines show fitted bands. ($R^2>0,99$)

Table 5-1 Films, packages, HP-systems and conditions

High pressure systems				
Nr.	**Short name**	**Supplier**	**Pressure build up**	**Maximum adiabatic heating**
1	Sitec	SITEC-Sieber Engineering AG, Maur, Switzerland	300 MPa/min	negligible
2	NC Hyperbaric	NC Hyperbaric, Burgos, Spain	120 MPa/min	~30°C
3		System from project consortium	n/a	n/a
High pressure conditions				
HP system	**HP condition**	**Pressure applied**	**Initial temperature**	**Treatment time**
1	A	50 - 200 MPa	23°C	1-5 days
	B	50 - 200 MPa	40°C	1-5 days
2	C	300 MPa	23°C	5 min
	D	600 MPa	23°C	5 min
	E	600 MPa	23°C	60 min
3	F	600 MPa	5°C	2 min
Monolayer films (tested without headspace)				
Polymer	**Thickness**	**Type**	**Supplier**	**HP condition**
PE-HD	45 µm	-	defa-Folien, Lohmar, Germany	A
PE-LD 1	30 µm	-	defa-Folien, Lohmar, Germany	A/B

PE-LD 2	50 µm	Lupolen® 3020k	LyndellBasell, Ludwigshafen, Germany	D/E
PET 1	23 µm	Melinex® 377	Pütz, Taunusstein, Germany	C/D
APET 2	75 µm	Hostaphan® RNK	Mitsubishi, Wiesbaden, Germany	D/E

Multilayer (packages with headspace)

Package component	**Multilayer film spec.**	**Supplier**	**HP condition**
Model tray	PET (400 or 600µm)/ EVA (10µm)/ PE-MD (10µm)/Adh./EVOH (7µm)/ Adh./ PE-MD (10µm)/ PE-LLD (13µm)	Mondi Technologies (Gronau, Germany)	D
Elastic lid	PE-mLLD (48µm)/ Adh. (9µm)/EVOH (7µm)/Adh. /PE-mLLD (48µm)		
Inelastic lid	oPET (12 µm) SiOx/Adh./PE-LD(80 µm)		
Pouch	PE-LD (40µm)/Adh./PA (5µm)/EVOH (2,7µm)/PA (5µm)/Adh./PE-LD (40µm)		
Industrial tray	PET (210 µm)/PEcoex (34µm)	Packer from project consortium	F

Based on relevant literature (see specific references below) on Raman spectroscopy of polyethylene, the crystalline and amorphous content was determined. The fingerprint region of the spectrum contains ten peaks, each allocated to different vibrations in the polymer. A good overview about the assignment of the Raman bands is given by Pigeon (1991). For the calculation of the crystallinity in polyethylene Strobl, Hagedorn (1978) found a proportional correlation between the integrated intensity $I_{1416\,cm^{-1}}$ of the band at 1416 cm^{-1} (CH$_2$ bending), due to factor group splitting in an orthorhombic crystal (Equation 5-1). The isotropic amorphous phase is proportional to the intensity $I_{1080\,cm^{-1}}$ at 1080 cm^{-1}, according to the C-C stretching vibration (Equation 5-2). An internal standard I$_{St}$ to which the intensity of the peaks could be referred to, was found at around 1300 cm^{-1} and belongs to the C-H twisting vibration. Polyethylene contains not only crystalline and amorphous phases, but also a “disordered phase of anisotropic nature, where chains are stretched but have lost their lateral order” (Strobl, Hagedorn 1978), the so-called interphase.

Equation 5-1

$$a_c = \frac{I_{1416cm^{-1}}}{I_{St} * 0{,}46}$$

Equation 5-2

$$a_a = \frac{I_{1080cm^{-1}}}{I_{St} * 0{,}79}$$

For the determination of the density in poly(ethylene terephthalate) (PET) MELVEGER (1972) found a good linear correlation of the bandwidth of the C=O stretching vibration located at 1730 cm^{-1}. This peak could be fitted with a Lorentzian function in the range of 1530 to 1830 cm^{-1} and a minimum coefficient of determination of $R^2>0{,}99$. The density ρ (g/cm^3) can be calculated via (Equation 5-3),

Equation 5-3

$$\rho = \frac{305 - \Delta v_{1/2}}{209}$$

where $\Delta v_{1/2}$ is the full width (cm^{-1}) at half maximum intensity of the peak at 1730 cm^{-1}. The results are independent of the orientation in the sample.

5.3.5 Oxygen permeation measurement

The oxygen permeance values of the flexible lid with EVOH as barrier layer (for more information see previous section) were performed using an Ox-Tran instrument (Modern Controls, Minneapolis, MN, USA), following the DIN 53 380, T3 (gas carrier method) with measurement conditions at 23°C and 0% relative humidity. The permeability tests of the inelastic lid with a thin inorganic barrier layer (SiO_x) performed with an optode, an oxygen measuring device based on fluorescence quenching (Fibox 3 LCD trace, Presens-Precision Sensing GmbH, Regensburg, Germany). Conditions of determination were 23°C and 0% relative humidity. The permeance value of the film samples is given in $cm^3/(m^2$ d bar).

5.3.6 Migration studies

Migration analyses were performed to investigate the influence of supercritical gases on the migration behavior of high pressure treated film packages. For this purpose a high pressure treated film sample was compared to an untreated reference sample regarding the specific migration of two antioxidants (Irganox® 1076 and Irgafos® 168). Additionally, a comparative screening analysis using GC-FID/MS was performed to characterize the migration potential of components from the film materials and the used adhesives.

For the analysis of the specific migration and the screening analysis, pouches (13,5 cm x 19,5 cm) were sealed from a multilayer film (PE-LD/PA/EVOH/PA/PE-LD; See *Pouch* in Table 5-1) and filled with 100 mL of 95% ethanol. The samples were stored upright. The headspace of the pouches over the food simulant was approximately 100 mL and the contact surface of the pouches to the food simulant 95% ethanol was around 3 dm^2.

The gas composition was a mixture of 20% CO_2 and 80% N_2. Information about the pressure system and the applied conditions one can be found in Table 5-1. The external surface of the samples was in direct contact with the pressure transmitting fluid (water). The packages were in contact with the food simulant for 12 days at 40°C and additionally 2 days at room temperature during shipping. All migration tests were performed in duplicate by the accredited Fraunhofer Institute for Process Engineering and Packaging in Freising, Germany. Compliance testing of the film material with EU legislation for food contact materials, e.g. (Commission Regulation (EU) No 10/2011) was not part of the investigations.

A comparative survey of the film samples (Reference to HP sample) was accomplished by cutting 1 dm^2 of each sample into small pieces and subsequent extraction with 10 mL of dichloromethane (DCM) for 1 d at 40°C by total immersion. An aliquot of the 95% ethanol migration solutions was spiked with the internal standard di-tert-butyl-hydroxyanisol (BHA) and Tinuvin 234 and studied by GC-FID/MS (gas chromatography flame ionization detector) for the fingerprint components defined in the dichloromethane extracts. To enhance the detection limit the internal standard was added to the rest of the migration solutions which were then reduced to approximately 1 ml under a gentle nitrogen stream and then analyzed by GC-FID.

The gas chromatographic separation of volatile and low volatile components was performed on a capillary column DB-1 (length 20 m, internal diameter 0.18 mm, film thickness 0.18 µm) and the following temperature program: 50°C (2 min isothermal) to 340°C. With this method, organic components are in a molecular weight range of about 150 to about 700 Daltons. For identification of the main components the extracts were assayed by coupling the gas chromatography and mass spectrometry. The used GC/MS system was ThermoFinnigan SSQ, column: DB-1-MS - 30 m – 0,25 mm i.d. – 0,25 µm film thickness, temperature program: 80°C (2 min), heating rate 10°C/min, 340°C (30 min), full scan, m/z 40-800. The identification of the obtained spectra was carried out by comparing spectra of the NIST library and have not been verified by measuring the pure substances.

Furthermore, the specific migration of two ultraviolet stabilizers was examined. According to the European Plastics Regulation (EU) No 10/2011 the specific migration limit of octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (CAS: 2082-79-3, trade name e.g. Irganox® 1076) is 6 mg/kg food(-simulant). Tris(2,4-di-tert-butylphenyl)phosphite (CAS: 31570-04-4; trade name e.g. Irgafos® 168) including its oxidized form (oxid. Irgafos® 168) is approved as additive for plastics for food contact applications without a specific restriction. These substances were determined with HPLC (high-performance liquid chromatography). The chromatographic separation was performed with a Sphereclone ODS as stationary phase and with 95% ethanol as mobile phase. The subsequent detection by UV was carried out at a wavelength of 230 nm. The quantification was performed using an external calibration. Additionally, a standard addition procedure was performed for the verification of the results.

5.4 Results and Discussion

5.4.1 Crystallinity and density changes of monolayer materials

Apparently, the PE-HD film seems to be unaffected by HPP (Figure 5-5). A tendency of increasing of the amorphous phase in one type low density polyethylene (PE-LD 1) is noticeable, but small (Figure 5-6). The meaning of the used statistical box plot presentation of the data is displayed in Figure 5-4. Slight increasing crystallinity and decreasing amorphous phase with increasing pressure can be detected for the PE-LD 2 sample treated at 40°C (Figure 5-7).This might indicate a temperature effect. Another PE-LD polymer (PE-LD 2, not shown here) does not reveal any morphological changes after a 60 min treatment at 600 MPa at room temperature. Overall, the examination of the crystalline and amorphous phase in single layer polyethylene does not show significant changes due to high pressure, even after several days of treatment.

The investigations of the density of PET reveal a slight decrease for different PET samples. Remarkable is that all these results are of very little order of magnitude (e.g.

changes in the third decimal place for PET density) and therefore no influence on polymer properties is to be expected (Figure 5-8).

Confirming conclusions were made by SANSONE ET AL. (2014). In this study PE-LLD was tested at varying processing conditions (pressure up to 700 MPa and temperature up to 115°C) and some alterations were found but a negligible effect on the functional properties. YOO ET AL. (2009) noticed increasing crystallinity of single layer PE-LD, but in pouches filled with 95% ethanol, which will also have an influence on the results. The review of FLECKENSTEIN ET AL. (2014) lists previous studies which also dealt with pressure induced morphological changes in polymers and came to diverging conclusions. As there are many different ways to determine the crystallinity or density of a sample (among others Raman spectroscopy, DSC, XRD, FT-IR) it is important to make reference measurements with the same method for comparable findings. Therefore all quantitative studies of morphology in this paper were performed using the same methodology with confocal Raman microscopy.

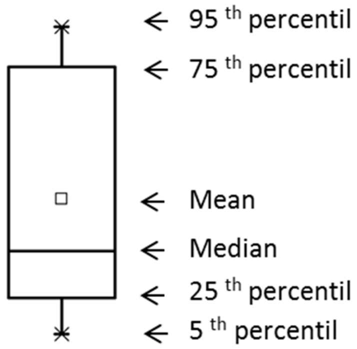

Figure 5-4. Statistical presentation of the data (box plots)

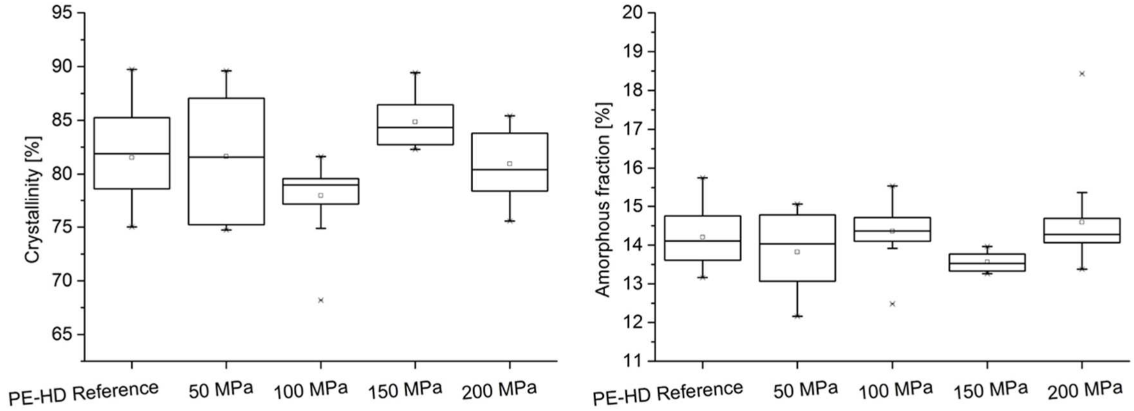

Figure 5-5 Crystalline and amorphous fraction of PE-HD at 23°C (1-5 days) depending on pressure (condition 1A, Table 5-1))

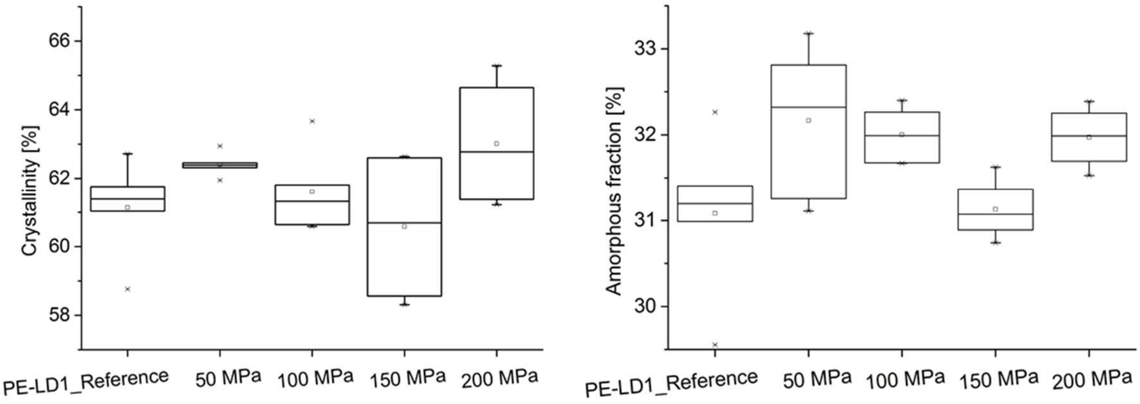

Figure 5-6 Crystalline and amorphous fraction of PE-LD (1) at 23°C (1-5 days) depending on pressure (condition 1A, Table 5-1))

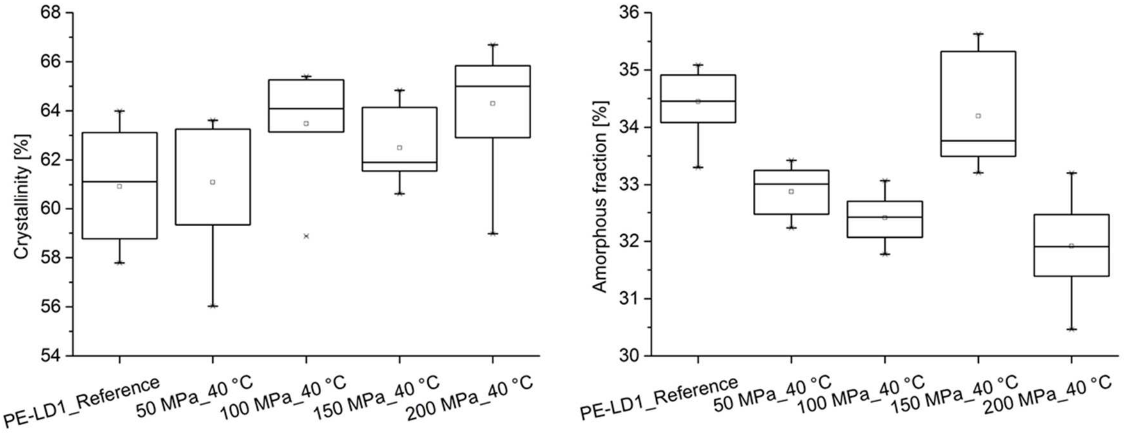

Figure 5-7 Crystalline and amorphous fraction of PE-LD (1) at 40°C (1-5 days) depending on pressure (condition 1B, Table 5-1))

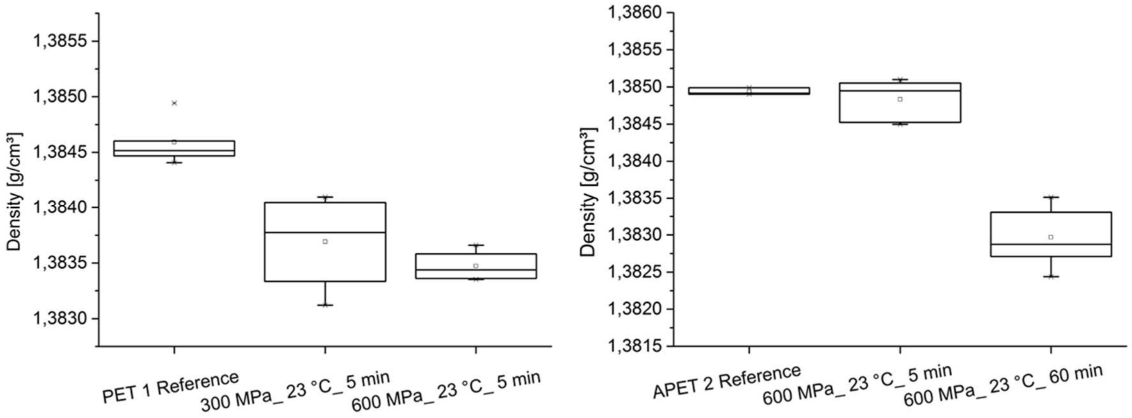

Figure 5-8 Changes of density in PET (1) (left) and APET (2) (right); (condition 2C/D and 2D/E, Table 5-1))

5.4.2 Multilayer films in model packages and real packages

5.4.2.1 Influence of layer thickness

No influence of varying layer thickness to the pressure induced morphology changes could be observed. Figure 5-9 displays the crystallinity of two PE layers (PE-LLD and PE-MD; part of the model tray, pressure condition 2D, see Table 5-1) in a thermoformed tray before and after HPP (600 MPa, 5 min). The crystallinity has a general trend to increase due to high pressure processing, but the results have a low degree of significance. As similar observations were not made for the single layer films pressurized in water, this effect will be probably generated by the additional adiabatic heating created by the compression of the gaseous headspace. Adiabatic heating depends strongly on the kind of material. Patazca et al. (2007) tested the quasi-adiabatic heating of several food products subjected to HPP and observed a temperature increase of about 9°C per 100 MPa for fatty products like oil, whereas the heating effect for water based products (like skim milk) was much lower (3 to 4°C/100MPa). Knoerzer et al. (2010) tested the compression heating of polymers (PE-HD, PP, PTFE) at varying initial temperatures (5 to 90°C) up to 750 MPa. They found that the heating rate of PE-HD is much higher than the rate of water. And the compression heating of gases is likely to be much higher (Ting, Balasubramaniam 2002). Moreover, it has to be taken into account that during pressure build up, holding time and pressure release, the temperature distribution in the film and the layers is not uniform, which explains the scattering of the data. This results agree with studies of ARDIA ET AL. (2004), where a temperature gradient between the center and the boundary of food products could be shown.

The results obtained for an industrial tray packaging (PET/PEcoex) also indicate local thermal effects, to be seen in Figure 5-10. As an effect of HPP on the total package, the crystallinity and measured thickness of three coextruded PE layers has been changed in both directions (decreasing and increasing). It is evident that, in this case, layer thickness and morphology is indeed influenced by HPP, but in a non-predictable way.

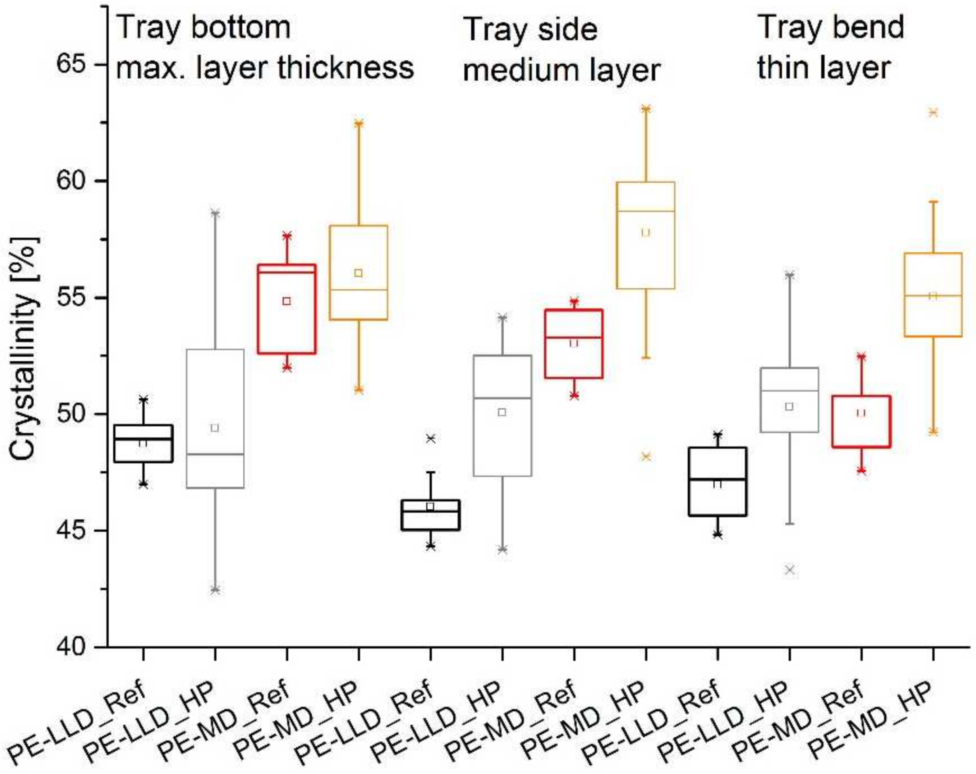

Figure 5-9 Crystallinity changes in different PE-layers (PE-LLD, PE-MD) of a tray, shown in dependence of layer thickness (Model tray, condition 2D, Table 5-1)

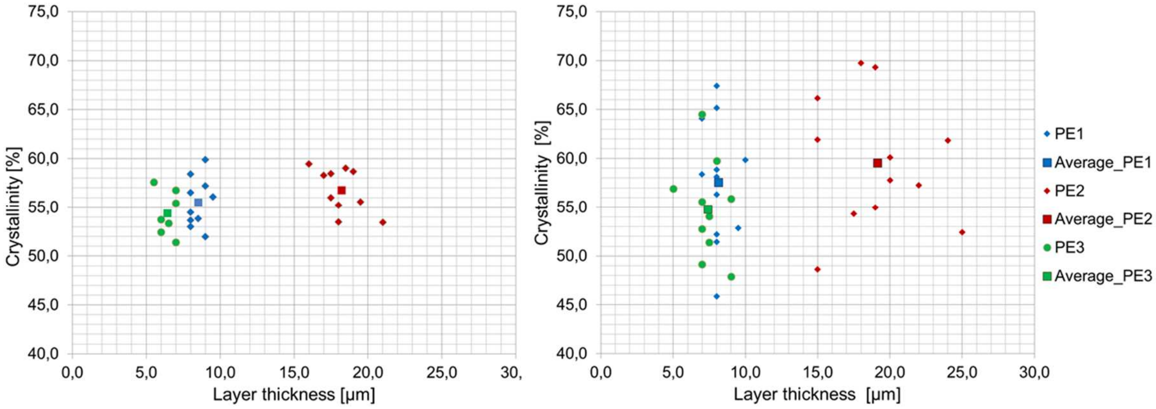

Figure 5-10 Scattering of crystallinity and layer thickness in PET/PEcoex tray after HPP of three different PE types coextruded in one tray (Industrial tray, condition 3F, see Table 5-1)

5.4.2.2 *Influence of headspace volume and gas composition*

The polyethylene as part of an inelastic lid (PET SiO_x /Adh./PE-LD) can be regarded as representative for our findings about the influence of headspace volume and gas composition on polymer morphology. Figure 5-11 demonstrates that changes of the gas composition have no effect on the film. The volume fraction of the gaseous headspace has no effect on the crystallinity, whereas the presence of more gas in the headspace apparently increases the amorphous content. The effect, however, is minimal and will probably have no impact on the final polymer function.

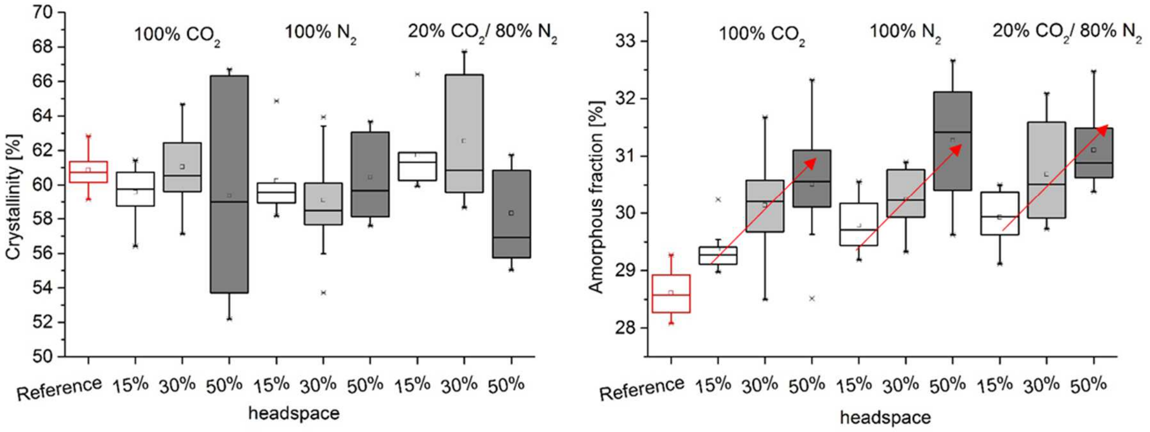

Figure 5-11 Crystalline and amorphous content of an inelastic lid (PET SiO_x /Adh./PE-LD) in dependence of gas composition (100% CO_2, 100% N_2 and 20%CO_2/80% N_2) and headspace volume (15, 30 and 50%), (HP condition 2D, see Table 5-1)

5.4.3 Oxygen permeation of multilayer lid films

5.4.3.1 EVOH barrier layer

After HPP of the related model packages, the oxygen permeability of a multilayer lid with EVOH barrier (Elastic lid, HP condition 2D, see Table 5-1) shows a slight but not significant increase in permeability. The oxygen permeation of the elastic lid was also tested by Mondi Technologies (Gronau, Germany), a company of the project consortium. No significant alterations of the barrier properties 1, 7, 14 or 21 days after the high pressure treatment could be observed (unpublished results). This is in line with findings of several other authors: LÓPEZ-RUBIO ET AL. (2005) tested the oxygen barrier of different PP/EVOH/PP multilayer films at different pressures, exposure times and temperatures, but without gaseous headspace. They found no significant change of the oxygen permeability due to HPP. Similar results were obtained by MASUDA ET AL. (1992) and LARGETEAU (2010). It can be concluded that headspace in packages has (additional to high pressure) only a small influence on the oxygen barrier properties of multilayer films based on EVOH.

5.4.3.2 Inorganic barrier layer

The examination of the permeability of an inelastic lid with an inorganic barrier layer (oPET SiO_x/Adh./PE-LD) indicates that at least the inorganic barrier layer is severely damaged. The permeability increases by a factor of ten, i.e. from 8,8 $cm^3(STP)/(m^2\ d\ bar)$ to around 80 $cm^3(STP)/(m^2\ d\ bar)$ which is roughly the permeability of the oPET film alone. (Figure 5-12). Material-specific Raman scans in the film plane at the location of the interface between the adhesive and the SiO_x layer and perpendicular to it (right side Figure 5-12) give more insight into the failure mechanism: They do not only indicate the formation of cracks in the SiO_x layer, but also an intermixing between PE-LD and the adhesive and even a distortion of the PET film at the interface.

In previous studies on films with inorganic layers (without headspace), similar results were obtained: GALOTTO ET AL. (2008) showed that the SiO_x layer within a PP/SiO_x multilayer is negatively affected by HP treatment at 400 MPa. Also CANER ET AL. (2000) tested polymer films with a thin Al metal layer and detected differences in permeability after HPP when compared with their untreated reference. Only MASUDA ET AL. (1992) could not find an effect on the oxygen barrier of a PET SiO_x/PP laminate subjected to HP treatment at 800 MPa for 2 min at 25°C. Probably, the presence of a small gaseous headspace is enough to create severe effects. Moreover, especially in the case of rigid trays the lid must be flexible enough to compensate the compression of headspace gases. It can be concluded that multilayer films with thin inorganic barrier layers are not suitable for high pressure processing, especially for MAP.

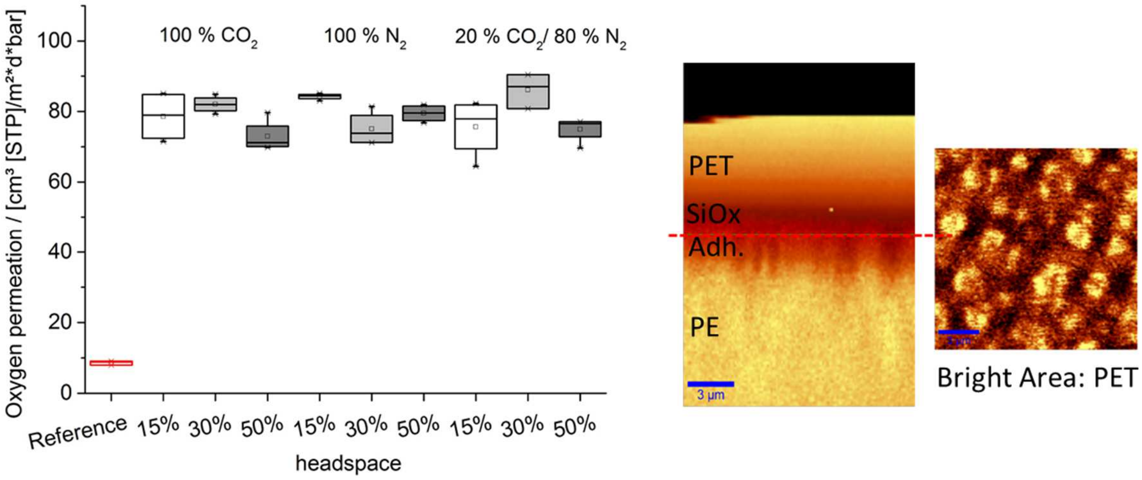

Figure 5-12 Left: Permeability of lid with inorganic barrier layer (SiO_x); Raman scan of destroyed barrier layer (right)

5.4.4 Migration

Comparative screening analyses of dichloromethane extracts and 95% ethanol migration solutions using GC-FID showed no significant differences for the high pressure treated film and untreated reference film sample. The identification of fingerprint components of semi and lower volatility and the semi-quantification results are displayed in Table 5-2. The higher amount of Caprolactam found in the 95% ethanol migration solutions compared to the dichloromethane extracts is related to better solubility in 95% ethanol. Also for the specific migration of Irganox® 1036, Irgafos® 168 and its oxidized form (oxid. Irgafos® 168) no significant differences between a high pressure treated sample and its untreated reference were detected (see Table 5-3).

Table 5-2. Semi-quantification of fingerprint components in the DCM extracts and the 95% ethanol migration solutions, results given in µg/dm² (as mean values of two determinations)

Substance	DCM-Extract Reference [µg/dm²]	DCM-Extract HP [µg/dm²]	Migration Reference [µg/dm²]	Migration HP [µg/dm²]
Caprolactam	499	397	2563	2568
n.i.[4]	< LD	11	< LD	< LD
Isomer(s) of di-tert-butylphenol	< LD	5	14	13
Group of chromatographically non-dissolved isomeric or structurally related substituted phenols	152	186	944	903
hexadecanoic acid	26	46	21	< LD
octadecanoic acid	40	50	14	15
n.i.	< LD	< LD	96	112
n.i.	< LD	< LD	8	19
Erucamide	189	41	472	540
n.i.	< LD	< LD	9	22
n.i.	< LD	28	< LD	14
n.i.	< LD	< LD	13	25
Irgafos®168	571	453	348	371
Irganox® 1076 und oxid. Irgafos® 168	738	796	362	392
n.i.	1568	1359	209	165
Limit of detection (LD) = 5 µg/dm²				

Table 5-3. Specific migration of Irganox® 1076, Irgafos® 168 and oxidized Irgafos® 168

	Area-related migration [mg/dm²]		**Filling-related migration [mg/kg]**[5]	
Sample	Reference	HP	Reference	HP
Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (Irganox® 1036)	0,2	0,2	1,2	1,2
Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos® 168)	0,23	0,22	1,4	1,3
Oxid. Tris(2,4-di-tert-butylphenyl)phosphite (oxid. Irgafos® 168)	0,04	0,04	0,24	0,24
Limit of detection (LD)	0,02		0,11	

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[4] Not identified

[5] Based on a surface-volume-ratio of 6 dm²/kg (according to the EU cube model)

These results stand in good agreement with the studies of SCHAUWECKER ET AL. (2002), who did not observe migration of 1,2-propanediol (pressure transmitting fluid) into PET/PA6/Al/PP (146 µm) pouches compared to migration under atmospheric conditions. LARGETEAU (2010) tested the migration of PA/PE compounds into several food simulating liquids (water, acetic acid, ethyl alcohol, isooctane). In this study also no effect of HP treatment on the migration was observed. Similar results were found by MAURICIO-IGLESIAS ET AL. (2010). Here it could be shown that there is no further extraction of polymer components or additives due to supercritical fluids like CO_2 during high pressure processing and following storage time. When considering the reported overall reduction of diffusion coefficients in polymers subjected to high pressure (RICHTER ET AL. 2010) together with the small amount of CO_2 actually present in MAP packaging, it is very unlikely that an additional extraction of additives will occur in practice.

5.5 Conclusions

The results show small structural changes in relevant packaging polymers subjected to high pressure processing, which are negligible for the macroscopic polymer properties and their industrial application. It could especially be concluded that no relevant structural changes arise from high pressure alone.

The combination of HPP and headspace gases in modified atmosphere packages does not significantly affect the morphology of the inner layers from polyethylene. Small alterations like an increase in the crystallinity of PE can be observed. Generally, however, HPP leads to increasing and decreasing of the crystallinity in the same sample at the same time at different locations. A reason for this observation might be the generation of local variations of the temperature due to adiabatic heating inside the packaging.

The composition of the gas in the headspace does not have an observable effect on the packaging. Only the amount of headspace volume seems to affect the amorphous phase in polyethylene and the overall integrity of a tray packaging.

The results also confirm the absence of possible additional risks for the consumer by migration of polymer additives into the product.

The oxygen permeability of non-treated and high pressure treated multilayer films showed that films on the basis of EVOH layers remained intact, also in combination with headspace gases. Multilayer films with thin inorganic barrier layers are subject to severe damages due HPP. These damages do not only affect the inorganic layers alone, but also the adjacent zones of the polymeric layers. The reason for these effects is still not clear. A simple explanation could be the low elasticity of the inorganic layers which is known to lead to a complete failure of their barrier properties already at a linear strain of several percent. Moreover, high pressure gradients in the vicinity of the inorganic barrier layers might lead to higher rate of formation of gas bubbles. This would mean that extreme local differences in gas permeability should be generally avoided by a proper design of the laminate structure of films to be used in HPP.

A visible negative effect of headspace gases are blisters and white spots inside the packaging material or also inside the food simulant which can be assigned to localized gas decompression. Here, the results still do not allow for systematic approaches. It is, however, possible to reduce the risk of the occurrence of these failures by considering some packaging design aspects: As these defects appear more frequently at weak points of a packaging, e.g. in the edges and thinnest parts of a tray, risks of damage might be decreased by reducing the thickness variation of a tray. A more uniform wall thickness distribution, made possible e.g. by a locally adapted heating regime in the thermoforming process (CLAUS ET AL. 2013) would be a viable approach. Moreover, weak boundary layers between coextruded layers or films and adhesives and inhomogeneities inside the material raise the risk of explosive decompression failures. A zone where the formation of White Spots was often observed is the transition phase between coextruded polyethylene layers. So the formation of localized damages is still an important issue for research in packaging materials for HPP applications.

Overall, however, the use of headspace gases in packages for high pressure treatment is conceivable, as long as proper material combinations are applied.

5.6 Acknowledgments

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6 Discussion and Conclusion

High pressure processing of food in modified atmosphere packaging is part of a hurdle concept for prolonging the shelf life and for improving the quality of temperature sensitive foods. As common gases are in a supercritical state during pressure treatment, special attention must be paid to interactions between the gases and materials. The packaging integrity may be negatively affected. The aim of this study was to identify failure mechanisms and to carry out experiments to acquire relevant data. The following sections discuss and summarise the findings. An overview of the key results is shown in Figure 6-1.

6.1 Influence of high pressure processing of packages with modified atmospheres on packaging integrity

6.1.1 Reversible structural changes

In order to understand the effects on the polymeric packaging, the mechanisms during high pressure treatment must first be understood. Up until now, no in-situ measurements of gas permeation under hydrostatic pressures of up to 2,000 bars have been carried out. The development of a new measurement method based on fluorescence quenching of oxygen has enabled the quantification of oxygen permeation processes in polymers (Chapter 4).

The results of the permeation measurements indicated a decrease in permeability by up to a factor of 70. This was comparable to results concerning the transport processes of aromatic compounds under similar pressure conditions (RICHTER ET AL. 2010). The reduction in permeability was put down to the fact that the free volume of the polymer is markedly reduced under hydrostatic pressure. However, simulation studies of Sarrasin predicted a decrease in the amorphous volume of polyethylene by only a factor of 1.06 at pressures up to 2,000 bars (SARRASIN ET AL. 2015). Hence the detected strong reduction of the oxygen permeability cannot be explained by merely this factor. An explanation might by the marked decrease in chain motion at high pressures which is necessary for the fluctuation of voids in the matrix and therefore responsible for the movement of diffusing molecules. The chains are arranged in a quasi-crystalline state during pressure treatment which diminishes the permeation of gases in polymers. Related comments were made by Gorbachev who blamed "increasing intermolecular interaction, decreasing chain flexibility and increasing packing density of the macromolecules" for the reduced permeability of gases in polymers (GORBACHEV ET AL. 1977).

The results provide an important contribution for understanding the processes taking place under pressure, even though the determination of the solubility and diffusion coefficients is not yet possible. As the breakthrough time of oxygen in a polyethylene film was faster than the pressure build-up time (about 2 minutes), those coefficients could not be determined using the 'lag time' method. The breakthrough time of oxygen in a polyethylene film of 100 µm thickness is about 55 seconds under ambient pressure and temperature conditions, as calculated using an averaged diffusion coefficient in PE (MOISAN 1985). As a decrease both in diffusion and solubility coefficient was observed for other substances (RICHTER, STERR ET AL. 2010), this is likely to have happened also in the case of oxygen.

Future work should use polymers with lower diffusion coefficients to determine the gas solubility under high hydrostatic pressures. Also, the measurement of the permeability of other gases such as CO_2 with optical sensors is desirable.

6.1.2 Irreversible changes

The review in Chapter 3 summarises the irreversible structural changes in polymers due to pressure application. Knowledge of these changes is of great importance for predicting the suitability of a polymer for HPP as the structure, namely the crystallinity and density, influence the barrier and mechanical properties. In the present work, structural changes were determined via Raman spectroscopy (Chapter 5.3.4). The influence of headspace volume and composition, film thickness, initial polymer density, maximum applied pressure and treatment time was investigated. The results clearly show that the changes in crystallinity are not uniform or homogeneous throughout the polymeric matrix but seem to be dependent on thermal gradients. The pressure range, pressure holding time and temperature (under moderate temperature conditions) did not significantly influence the crystalline and amorphous phases of the polymer. In contrast, an increase in headspace volume increased the amorphous content of polyethylene. A possible reason for this is the increased amount of dissolved gas in the polymer and the concomitant plasticising of the intermediate phase. The crystalline phase did not undergo any significant transformation, possibly indicating that the structure of the polymer crystals is in general insensitive to hydrostatic pressures of up to 6,000 bars.

In summary, none of the directly and indirectly induced changes in polymer morphology which were detected will play a crucial role for industrial application of HPP as the changes were small in absolute terms.

6.1.3 Changes in oxygen permeability

The oxygen permeation measurements after high pressure treatment on pouches and tray packaging with headspace (Chapter 5.4.3) showed good agreement with results from literature for experiments on vacuum packaging (LARGETEAU 2010; LÓPEZ-RUBIO ET AL. 2005; MASUDA ET AL. 1992). In these studies ethylene - vinyl alcohol copolymer (EVOH) was used as a barrier layer. Even in the presence of supercritical gases, the barrier properties of EVOH did not show any significant changes after HPP. This barrier material can therefore be particularly recommended for HPP. Only if there is delamination or blister formation, the oxygen transmission will increase significantly. Also, inorganic barrier layers were found to be sensitive to blistering as well as to mechanical stress under HPP conditions. The result is a total loss of barrier properties in most cases. These materials should therefore be avoided for the use in modified atmosphere packaging with HPP.

6.1.4 Migration

No significant additional migration (global or specific) due to a possible extraction of substances with supercritical carbon dioxide (scrCO_2) was detected (Chapter 5.4.4). This was expected due to the small amount of CO_2 present in the packaging. For common extraction processes such as used for decaffeinating coffee, higher amounts of gases are necessary. The findings agree with results in the literature on the global migration of packaging constituents into food simulating liquids after high pressure treatment of vacuum packaging (AYVAZ ET AL. 2016; JULIANO ET AL. 2010). The findings also agree with experiments on the extraction of plasticisers out of polyamide (PA11) using CO_2 at pressures of up to 40 bars and temperatures of up to 120°C (FLACONNÈCHE ET AL. 2001). It can be concluded that if a polymer is in conformity with the migration limits under atmospheric conditions as specified by regulations and if the polymer remains undamaged under HPP treatment, then the requirements will also be met under HPP conditions.

An overview of the results of this work is given in Figure 6-1.

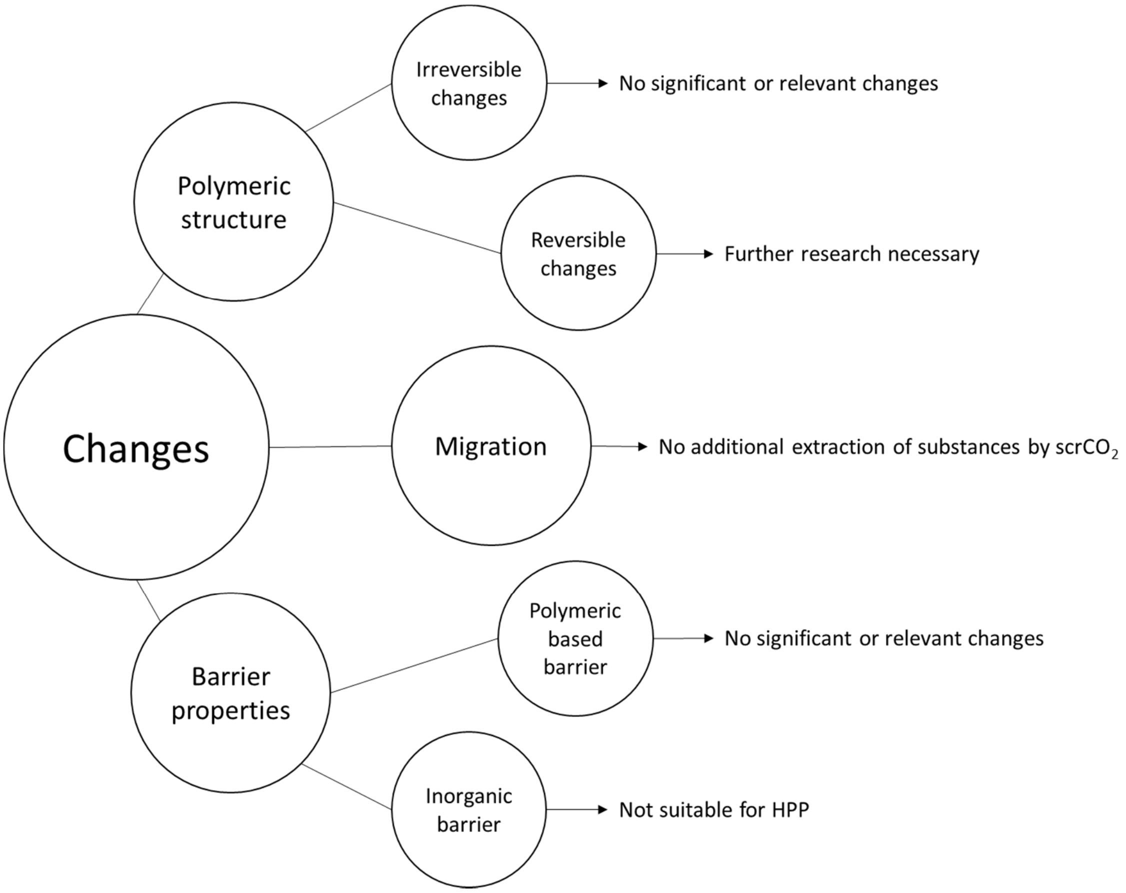

Figure 6-1 Overview of the results of the present study

6.2 General guidelines for packaging design and materials used for modified atmosphere packaging for high pressure processing

The following section is based on the experimental data, the outcomes of the discussion and information available in the literature. The information can be put forward as general guidelines for processing conditions, material properties and packaging design for practical use.

6.2.1 Material properties

The heterogeneity of a material was identified as being one of the parameters having the highest impact on decompression failure. Inclusions in the polymer, such as additives and other components, may act as nucleation points for bubble formation and may result in severe damage in most cases (Chapter 2.4.2.2). By way of example, two pouches with multilayer films of comparable composition are presented in Figure 6-2. The material on the left had inhomogeneities which acted as nucleation points for bubbles, whereas the material on the right was additive free. The materials show clearly differences in the amount of damage.

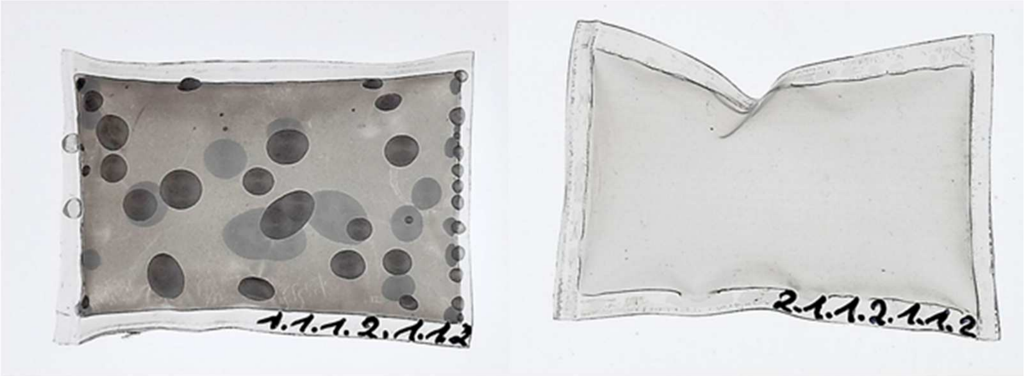

Figure 6-2 Pouches with inhomogeneities (left) and without inhomogeneities (right) and bubble formation after HPP. Own unpublished results from investigations made for industrial clients.

The packaging materials have to be flexible enough to take up the pressure and to reversibly withstand the compression of the headspace and product. The mechanical properties of some rigid materials such as inorganic barrier layers cannot withstand the volume decrease. Irreversible macroscopic damage, for example delamination and flex-cracks, may result. When using rigid materials for tray packaging it is important that at least the lid of the packaging is able to take up the pressure and compensate the volume reduction. Also, packaging components with porous and foam-like structures such as cardboard, paper and expanded polystyrene turned out to be unsuitable for high pressure processing (Figure 6-3 used for illustration) because the voids are irreversibly compressed and are not restored after decompression (CANER ET AL. 2004; OCHIAI, NAKAGAWA 1992).

In Chapter 2, Section 2.4.2 it was shown that factors such as higher molecular weight, higher crystalline fraction, lower elasticity and lower viscosity of the polymers are able to reduce or even prevent the formation of bubbles and blisters.

6.2.2 Packaging geometry and design

The packaging design is important for avoiding decompression failure and damage to the packaging integrity. For example, tray packaging should have large angles in the curved zone between the walls and the base. The profile of an embossing should be avoided. In general the tray and the packaging film should be flat, preventing gas pockets between the material and the food product (see Figure 6-3 exemplary for an unsuitable design). High temperature gradients due to the high heat of compression of the gases are then prevented in these positions (Chapter 5.5). In general, the headspace volume should be as small as possible. Inlays made of cardboard turned out to be unsuitable for the high pressure process (see Figure 6-3, left picture of a cardboard inlay after HPP).

Considering the structure of a multilayer film, it should be kept in mind that widely differing properties of adjacent polymers or materials, such as differences in their mechanical or barrier properties, may lead to considerable gas pressure gradients and hence to bubble formation or delamination (Chapter 5.5).

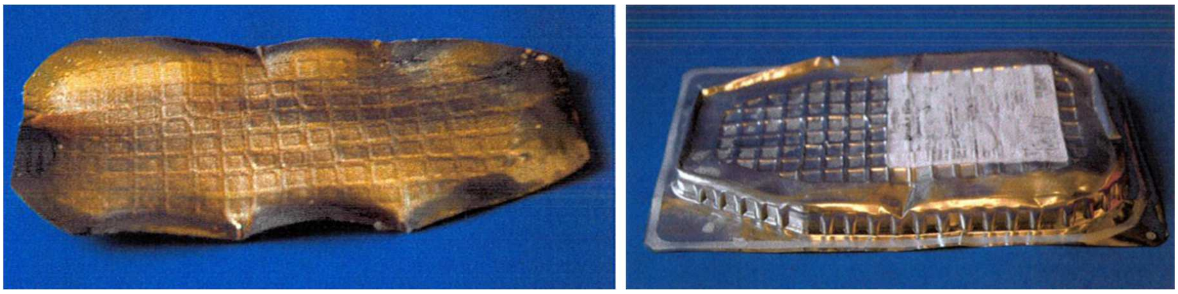

Figure 6-3 Left: Cardboard inlay after HPP. Right: Example of an unsuitable packaging design. Own unpublished results from investigations made for industrial clients.

6.2.3 Processing conditions

The process conditions such as the compression and decompression rates and the process temperature also have a considerable influence. It is recognised that the pressure build-up rate should be as high as possible and the pressure release rate as low as possible in order to get optimum results (Chapter 2.4.2.3). The principle of stepwise and slow decompression has already been realised in industrial applications by MULTIVAC GmbH, Wolfertschwenden (RICHTER 2014). The treatment time also has an influence on polymer-gas combinations with long penetration time. If the time is prolonged more gas is able to dissolve in the polymer and the result is more blisters on decompression. Similarly, an increase in the maximum applied pressure increases the amount of gas which is able to dissolve in the materials (Chapter 2.4.2.3). Anyhow a minimum treatment time combined with a minimum applied pressure is necessary for microbial inactivation and should not fall below the critical values.

A summary of the parameters and properties which have to be taken into account for high pressure processing is given in Table 6-1.

Table 6-1 Summary of the parameters and properties which should be taken into account for high pressure processing. Results achieved within this thesis are indicated in bold.

<table>
<tr><th colspan="2">Material properties</th></tr>
<tr><th>Dos</th><th>Don’ts</th></tr>
<tr><td>• Flexibility of the film
• High in molecular weight
• High in crystalline fraction</td><td>• Rigid materials
• Foam-like structures (cardboard, expanded polystyrene)
• Inorganic barrier layers
• Inhomogeneities inside the polymers</td></tr>
<tr><th colspan="2">Packaging design parameters</th></tr>
<tr><th>Dos</th><th>Don’ts</th></tr>
<tr><td>• Large angles
• Flat tray bottom
• Low headspace volume</td><td>• Gas pockets between material and food product
• Embossing
• Layer structure:
○ Strong pressure gradients at barrier layers
○ Large differences in mechanical properties</td></tr>
<tr><th colspan="2">Process parameters</th></tr>
<tr><th>Dos</th><th>Don’ts</th></tr>
<tr><td>• High pressure build-up rate
• Slow pressure decrease
• Stepwise pressure decrease
• Moderate process temperatures</td><td>• Spontaneous pressure decrease
• High process temperatures
• Excessive high pressures (keep the pressure to the minimum required)
• Excessive treatment times (keep the treatment time to the minimum required)</td></tr>
</table>

6.3 Final remarks and outlook

It has been demonstrated that commonly used flexible polymeric materials are generally suitable for modified atmosphere packaging for high pressure processing at moderate temperatures. However, some design parameters and material properties must be taken into account when using modified atmosphere packaging for HPP. The fulfilment of standard regulatory requirements by the material with respect to its migration properties should be verified for each case individually.

It was found that explosive decompression failure is a phenomenon influenced by a host of (combined) criteria. Only a limited number of parameters are known to reduce or prevent the occurrence of bubbles and blisters. For better prediction and prevention of decompression failure, further research is necessary focussing on the process parameters applied for HPP. Additional studies are also needed on the high pressure treatment of modified atmosphere packaging at elevated temperatures.

The application of nanotechnology, active packaging and/or packaging with absorbing additives, such as zeolites, should be considered for future work. The in-situ measurement method (Chapter 4) which was developed will facilitate understanding the chemical and physical reactions which take place under pressure. Similarly, analysis of CO_2 reactions and CO_2 transport mechanisms is also conceivable using the recently developed optical device of PreSens GmbH (APOSTOLIDIS, A. 2017) for measuring CO_2 concentrations in gaseous and liquid phases.

6.4 Chapter bibliography

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7 Summary

Over the past twenty years high pressure processing (HPP) has become one of the most important alternative industrial preservation methods to the thermal pasteurization of food products. Pressures up to 6,000 bars and moderate temperatures inactivate vegetative cells, yeast and mould, whereas temperature-sensitive food ingredients remain almost unaffected. This method can therefore be used to give consumers fresh products with fewer preservatives.

In industrial applications the food is packaged prior to high pressure processing in order to avoid recontamination. In most cases, vacuum packaging systems are used. As part of a hurdle concept, modified atmosphere packaging has become ever more common in recent years for applications such as colour stabilisation of fresh meat and the inhibition of microorganism growth by carbon dioxide. Improved product presentation is an additional positive side-effect. The gases commonly used for food packaging are nitrogen, oxygen and carbon dioxide.

Numerous research studies have been undertaken to examine the influence of high hydrostatic pressure on food products, ingredients and microbial species. The impact of pressure on vacuum packaging materials has previously been investigated. However, up to now very few studies have been undertaken on the influence of headspace gases on the integrity of polymers under high pressure.

The resulting effects on packaging under HPP were differentiated into direct and indirect effects, where direct effects are induced by high hydrostatic pressure alone. Indirect effects arise from compression of the polymeric materials or food products and primarily due to compressed gases in the headspace of the packaging. It became clear that both direct effects and indirect effects can cause reversible and irreversible changes to the polymer structure. However, no clear trends could be found in the scientific data. The reversible structural changes induce reversible changes to the transport properties of the gases in polymers and are discussed in the second part of this work.

Irreversible structural changes can influence the barrier properties as well as the mechanical properties of the packaging. Raman spectroscopic studies were performed to analyse the density and the crystalline and amorphous parts of relevant polymers such as polyethylene and polyethylene terephthalate. Key features of this method are non-destructive measurement at very high spatial resolution. The resulting data reveals small but technically not relevant changes to the polymer structure dependent on factors such as the pressure holding time, film thickness, headspace volume and gas composition. Highly inhomogeneous temperature distributions in the packaging due to different adiabatic heating rates of materials, gases or food product constituents under pressure may be an explanation for the inhomogeneous structural changes in the polymer part of tray packaging. However, these small changes were deemed to have a negligible influence on the mechanical or barrier properties for industrial applications.

The oxygen permeability of organic barrier layers (e.g. ethylene-vinyl alcohol copolymer) and inorganic barrier layers (e.g. silicon dioxide) was measured under high pressure conditions. The former were found to be unaffected by HPP whereas the inorganic barrier layers were found to be not stable enough for high pressure applications.

Modified atmosphere packaging (MAP) for HPP must also fulfil all legal requirements concerning the migration of packaging components into foodstuffs, including the additional extraction of constituents by supercritical carbon dioxide. No increase in the specific or overall migration was measured in these studies.

The second part of this thesis deals with the phenomenon of bubble formation in modified atmosphere packaging upon high pressure treatment. Although the development of bubbles and blisters and the delamination of multilayer films, including collapse of the overall packaging integrity, have been reported in previous studies, the factors influencing these effects are not totally clear. The objective of this work was therefore to first of all identify relevant factors causing bubble formation in polymers under HPP conditions.

The occurrence of blisters is also known as explosive decompression failure (XDF) in other areas such as in the petroleum industry. It is due to the outgassing of polymers upon rapid decompression, caused by the rapid change in the thermodynamic equilibrium and the subsequent formation of bubbles in oversaturated materials. It was clear from the literature that the solubility of gases under high pressure increases significantly. This plays an important role because an increased amount of gas dissolves in polymers under high pressure. Besides the solubility, the diffusion and permeation coefficients were also found to influence bubble formation, but no relevant scientific data about the measurement of gas transport under high hydrostatic pressure could be found. Only dynamic permeation measurements under moderate partial pressure differences had previously been performed.

The objective of this part of the work was therefore to develop a new measurement method based on the principle of dynamic fluorescence quenching. This allows the in-situ measurement of the oxygen concentration and oxygen permeation under hydrostatic pressures of up to 2,000 bars. It was demonstrated that the permeation coefficient of oxygen in a polyethylene film is reduced by a factor of between 35 and 70 at 2,000 bars applied pressure compared to the value under atmospheric conditions. The results are in good agreement with findings on the permeation of aromatic compounds through polymers under similar conditions. A reduction in the polymeric free volume and diminished chain motion were deemed to be the cause.

As it was not possible to determine the solubility and diffusion coefficient for gases in polyethylene under high pressure, future work should further develop the method to allow analysis of various other polymers. Also, modifying the experimental setup with an optical sensor system for the detection of carbon dioxide concentration is an option. Simultaneous in-situ tracking of O_2 and CO_2 permeation would then be possible.

This work showed that commonly used flexible polymers are suitable for the high pressure treatment of vacuum packaging and modified atmosphere packaging at moderate temperatures. Regulatory requirements are still fulfilled after HPP, provided the packaging meets requirements under atmospheric conditions. However, some key design features concerning the packaging and film materials should be addressed for industrial applications. These include the avoidance of thin inorganic barrier layers or foamed and rigid materials.

In conclusion it can be stated that this work contributes to the safe use of vacuum packaging and modified atmosphere packaging for the high pressure treatment of food.

8 Zusammenfassung

In den letzten zwanzig Jahren hat sich die Hochdruckbehandlung (HPP) zu einer der wichtigsten alternativen Konservierungsmethoden für die thermische Pasteurisierung von Nahrungsmittel in der industriellen Anwendung entwickelt. Bei Drücken bis zu 6.000 bar und moderaten Temperaturen werden vegetative Zellen, Hefen und Schimmelpilze inaktiviert, während wertvolle temperaturempfindliche Lebensmittelinhaltsstoffe so gut wie unverändert bleiben. Diese Methode ermöglicht es dem Handel, frische Produkte mit weniger Konservierungsstoffen anzubieten.

Für industrielle Anwendungen wird das Lebensmittel vor der Hochdruckbehandlung verpackt, um eine Rekontamination zu vermeiden. Bei den meisten Anwendungen werden Vakuumverpackungen verwendet. In den vergangenen Jahren jedoch wurden im Hochdruckprozess immer häufiger Verpackungen mit modifizierter Atmosphäre im Kopfraum (MAP) eingesetzt, da es zusätzliche Vorteile bietet, wie die Farbstabilisierung von frischem Fleisch oder die Hemmung des Mikroorganismenwachstums durch Kohlendioxid. Gase, die für Lebensmittelverpackungen (MAP) am häufigsten eingesetzt werden, sind Stickstoff, Sauerstoff und Kohlendioxid.

Zahlreiche Untersuchungen wurden durchgeführt, um den Einfluss von hohem hydrostatischem Druck auf verschiedene Lebensmittel, Inhaltsstoffe und Mikroorganismen zu untersuchen. Auch die Auswirkungen auf Verpackungsmaterialien als Teil von Vakuumverpackungen wurden untersucht. Aber nur sehr wenige wissenschaftliche Arbeiten betrachteten den Einfluss von Gasen im Kopfraum der Verpackung auf die Integrität von Polymeren bei der Hochdruckbehandlung.

In dieser Arbeit wurden daher, auf Basis relevanter wissenschaftlicher Arbeiten, mögliche Auswirkungen von HPP auf die Verpackung in verschiedene Effekte eingeteilt. Dabei wurde zwischen direkten und indirekten Effekten unterschieden. Direkte Effekte werden durch hohen hydrostatischen Druck allein induziert und indirekte Effekte durch komprimierte Kunststoffe oder Lebensmittel, vor allem aber durch komprimierte Gase im Kopfraum der Verpackung. Es wurde deutlich, dass sowohl direkte als auch indirekte Effekte die Polymerstruktur reversibel und irreversibel verändern können. Ein eindeutiger Trend konnte jedoch nicht beobachtet werden. Die reversiblen Änderungen der

Polymerstruktur spiegeln sich in reversiblen Veränderungen der Transporteigenschaften von Gasen in Polymeren wieder und werden im zweiten Teil dieser Arbeit diskutiert.

Irreversible Strukturveränderungen können sowohl die Barriereeigenschaften als auch die mechanischen Eigenschaften der Verpackung beeinflussen. Raman-spektroskopische Untersuchungen wurden durchgeführt, um die Dichte sowie den kristallinen und amorphen Teil relevanter Polymere quantitativ zu analysieren. Die Vorteile dieser Methode waren die zerstörungsfreie Messung bei gleichzeitig sehr hoher räumlicher Auflösung. Die resultierenden Daten zeigen kleine, aber technisch nicht relevante Änderungen der Polymerstruktur in Abhängigkeit von Faktoren wie der Druckhaltezeit, der Schichtdicke, dem Kopfraumvolumen und der Gaszusammensetzung. Es wird erwartet, dass insbesondere inhomogene Temperaturverteilungen in der Verpackung aufgrund der unterschiedlichen adiabaten Erwärmung von Materialien, Gasen und/oder Produktbestandteilen eine Erklärung für inhomogene Strukturveränderungen in Polymeren von Tray-Verpackungen sein können. Eine Relevanz dieser minimalen Änderungen für die mechanischen Eigenschaften oder der Barrierefunktion bei der industriellen Anwendung konnte nicht beobachtet werden.

Die Sauerstoffpermeabilität von organischen sowie von anorganischen Barriereschichten wurde untersucht. Erstere zeigten sich von HPP nicht beeinflusst, wohingegen sich anorganische Sperrschichten für Hochdruckanwendungen als unzureichend herausstellten. Die mechanischen Eigenschaften sind nicht ausreichend um eine Kompression (insbesondere des Kopfraums) auszugleichen. Außerdem entsteht an diesen Schichten ein hoher Partialdruckgradient im Vergleich zu benachbarten Polymeren, der die Bildung von Blasen forciert.

Eine zusätzliche Extraktion von Verpackungskomponenten in Lebensmittel durch überkritisches Kohlendioxid konnte in dieser Arbeit nicht nachgewiesen werden. Die Untersuchungen ergaben keine erhöhten Werte der spezifischen Migration oder der Gesamtmigration während und nach der Hochdruckbehandlung.

Der zweite Teil dieser Arbeit beschäftigt sich mit dem Phänomen der Blasenbildung in MAP nach der Hochdruckbehandlung. Obwohl die Entwicklung von Blasen und Delaminationen von mehrschichtigen Filmen bereits in früheren Studien diskutiert wurden, konnten die beeinflussenden Faktoren nicht vollständig geklärt werden. Ziel dieser Studie war es zunächst, relevante Faktoren für die Blasenbildung in Polymeren bei HPP zu identifizieren.

Das Auftreten von Blasen ist in anderen Anwendungsgebieten wie der Erdölindustrie als "explosive decompression failure" (XDF) bekannt. Das Phänomen wird durch die Übersättigung von den in Polymeren gelösten Gasen erklärt. Die schnelle Veränderung des thermodynamischen Gleichgewichts nach rascher Dekompression ermöglicht die Bildung von Blasen in übersättigten Materialien. Aus der Literatur wurde deutlich, dass die Löslichkeit von Gasen bei hohen Drücken deutlich zunimmt. Neben der Löslichkeit wurde auch der Diffusions- und Permeationskoeffizient, also die Transporteigenschaften von Gasen in Polymeren unter hohen Drücken als Einflussfaktoren für die Blasenbildung genannt. Allerdings existierten keine relevanten wissenschaftlichen Daten zur Bestimmung der Gaspermeation bei hohem hydrostatischem Druck.

Ziel dieses Teils der Arbeit war es daher, ein neues Verfahren zu entwickeln, das auf dem Prinzip der dynamischen Fluoreszenzlöschung basiert und die in situ Messung der Sauerstoffkonzentration und Sauerstoffpermeation bei hydrostatischen Drücken bis zu 2.000 bar ermöglicht. Es konnte gezeigt werden, dass, verglichen mit Werten bei atmosphärischen Bedingungen, der Permeationskoeffizient von Sauerstoff in Polyethylen um einen Faktor zwischen 35 und 70 bei 2.000 bar verringert wird. Eine Verringerung des polymeren freien Volumens und eine verminderte Kettenbewegung werden als ein Grund für diese Ergebnisse gesehen.

In dieser Arbeit konnte gezeigt werden, dass handelsübliche flexible Polymere grundsätzlich für die Hochdruckbehandlung von Vakuumverpackungen sowie für Verpackungen mit modifizierter Atmosphäre bei moderaten Temperaturen geeignet sind. Unter Annahme, dass die verwendeten Materialien bei atmosphärischen Bedingungen den gesetzlichen Anforderungen genügen, kann davon ausgegangen werden, dass die Anforderungen auch nach der Hochdruckbehandlung erfüllt sein werden. Allerdings sollten einige entscheidende Parameter für die Verpackungen und Folienmaterialien bei der industriellen Anwendung berücksichtigt werden.

Zusammenfassend kann diese Arbeit zur sicheren Anwendung von polymeren Packstoffen für die Hochdruckbehandlung von Lebensmitteln beitragen.

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