# Extending crispness

## A systematic approach to controlling water migration in bread

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## A systematic approach to controlling water migration in bread

Anita Hirte

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# Abstract

Crispness is one of the most important sensory characteristics of crispy bread, because consumers associate crispness with freshness, wholesomeness, and quality. This sensory sensation, however, is lost within a few hours after baking, because of a fast water uptake of the crust. Therefore, the aim of this thesis was to systematically determine the mechanisms that lead to the fast loss of crispness and to reveal the parameters that are key for crispness retention. We showed that the crust acts as a barrier for water migration, causing water accumulation in the crust. Reducing this barrier property by increasing the water vapor permeability of the crust to an optimal value of $8 \times 10^{-9}$ g/(m s Pa) resulted in breads with crispness retention that was more than eight times longer. These breads had either channels or cracks in their crust. Despite the changes of the crust properties, these breads had similar crumb softness retention compared to standard breads. The properties of the crumb also affected the water uptake of the crust, but less so than the properties of the crust. Bread containing a crumb with a lower water vapor permeability had a significantly longer crispness retention. Based on these findings, we propose a model that provides a comprehensive view of crispness loss and concluded that the increase in crust permeability is the best way to create breads with a noticeably longer crispness retention.

# Contents

# Chapter 1

## General introduction

## 1.1. Bread crust

Bread is a major component of the human diet. On all continents, a variety of different types of breads are baked and consumed. These breads can be distinguished by their unique flavor and texture. One important texture characteristic of several types, e.g. freshly baked baguette, is its crispy crust.

Crispy bread is composed of an inner soft crumb and an outer crispy shell, the crust. These two parts create a pleasant contrast in textures when eaten, which is appreciated by the consumer (Szczesniak and Kahn, 1971). These differences in the texture of crumb and crust are mainly created during dough processing and baking. Both parts originate from the same dough. Yeast cells in the dough produce $CO_2$, causing growth of gas cells and, therefore, the formation of a leavened, cellular structure. At the outside of the dough, a skin is formed that acts as a barrier for the gas produced inside the dough. During baking, the temperature regimes inside the dough and at the dough skin are very different. Typically, temperatures at the level of the dough skin exceed 200°C, whereas temperatures inside the dough are below 100°C. Inside the dough, the increase of the temperature during baking causes the expansion and coalescence of gas cells, transforming the dough foam into a sponge. This structure is then set due to the gelatinization of the starch and the denaturation of the gluten (Cuq et al., 2003). These processes cause that the viscous cell walls in the inner dough are set into an aerated, soft, wet crumb, with interconnected gas cells. The consumer typically appreciates this soft texture of the bread crumb. Therefore, much attention has been paid to understanding and preventing the decrease of the soft texture during storage due to crumb staling.

Already at the start of baking, the temperatures increase the fastest in the bread crust. Therefore, this part is set first, when gas cells are still rather small and less connected. Furthermore, the high evaporation rate in this part causes a drying out of the crust. This dry, rigid skin restricts the further expansion of the dough, the so-called oven rise (Hoseney, 1985). The amount of steam present in the oven determines the drying rate of the crust and therefore the elasticity of the crust, thus affecting the oven rise and the final volume of the bread (Le-bail et al., 2011). Steaming also affects the properties of the crust, e.g., thickness and fracture behavior (Le-bail et al., 2011; Schirmer et al., 2011). After the crust is set during baking, gas cells still expand in the colder, not-set regions of the inner dough. Therefore, additional stress is put on the gas cells, causing coalescence and the creation of an interconnected crumb structure (Hayman et al., 1998). Especially in the outer part, gas cells become compressed against the outer shelf and therefore coalescence. As a consequence, the crust has more elongated, smaller gas cells with thicker beams, and thus a higher density. The water of the crust evaporates completely during baking and temperatures increase mostly over 200°C, depending on the baking conditions. At these high temperatures, Maillard reactions occur, which lead to the development of color and flavors. The fast evaporation of water in the crust causes incomplete gelatinization of the starch in the crust during baking (Moss, 1975; Primo-Martín et al., 2007) and the crust to be in a glassy state after cooling (Cuq et al., 2003).

Due to the different processes that occur during baking, the crust has particular properties that distinguish it from the crumb, as described previously. The crust has a lower degree of gelatinization and is in a glassy state and not a rubbery state like the crumb. The crust also has a different structure, and is browner, denser, drier, harder, and less permeable than the crumb (Grenier et al., 2010; Vanin et al., 2009; Wählby and Skjöldebrand, 2002). The low permeability of the crust restricts water loss during baking, and therefore prevents the drying out of the crumb (Hasatani et al., 1991; Wählby and Skjöldebrand, 2002). Further advantages of the crust are that it contributes to a large extent to the flavor of the bread, gives shape to the bread, and protects the bread against environmental influences, resulting in a longer shelf life. The crumb without the crust is more vulnerable to staling and mold growth.

On the basis of the known differences between crust and crumb, a definition of the crust can be made. However, a clear distinction between crust and crumb is difficult, because the crust is not homogeneous, and specific properties like water content, hardness, color, permeability, structure, and degree of gelatinization change gradually from outer crust to crumb. In the framework of this thesis, we define the crust as the brown, dense, outer shell of the bread, which has a thickness of 1 mm to 3 mm.

## 1.2. Crispness

One particular characteristic of the crust in crispy bread is its crispness. Several different food products hold this important sensory characteristic, as for example, carrots, chips, French fries, and bread. These food products are crispy, according to the definition, because they exhibit successive fracture and acoustic events under low work of mastication (Luyten et al., 2004; Szczesniak, 1988; Vincent, 1998; van Vliet et al., 2007, 2009).

Crispness is related to distinct fracture properties: a fast crack propagation and successive fracture. Fast crack propagation is necessary for acoustic emission, and only occurs if the energy supplied during mastication is primarily used for crack propagation (Luyten et al., 2004). A crispy material can, therefore, contain only a limited amount of energy-dissipating structures that contain free water or mobile macromolecules. If too much energy is dissipated, the crack will either not form or not propagate, and the material can be described as tough. In addition, sensory crispness is based on the occurrence of separate, successive fracture events (Vliet et al., 2007). This successive fracture can only occur in a cellular structure containing thin beams and crack stoppers like air cells (Luyten et al., 2004; Vliet et al., 2007). Luyten and van Vliet (2006) proposed that beams are between 50 µm and 400 µm thick in crispy cellular material. Thin beams and the right characteristics and thickness of the dry cellular structure are required to produce a product that fractures under low deformation. This distinguishes crispy from hard.

In the research literature, crispness is either assessed by humans, or by instruments. Instrumental analysis of crispness includes the fracture of the food material and the subsequent analysis of the acoustic emission and/or the recorded force-deformation curve. Single force parameters showed only a poor correlation to sensory crispness, while acoustic parameters correlated much better (Mohamed et al., 1982; Vickers, 1987). Therefore, the use of acoustic parameters, like sound intensity and number of sound pulses, which relate well to sensory crispness, are a successful tool for the instrumental characterization of crispness (Castro-Prada et al., 2009; Mohamed et al., 1982; Roudaut et al., 1998; Vickers, 1987). Deformation speeds should not be too low and should be approximately similar to biting speed in order to guarantee a good relation to sensory crispness (Castro-Prada et al., 2009).

## 1.3. Loss of crispness

Crispness is lost within a few hours after baking. This loss often causes the consumer to reject the product, because crispness is associated with the attributes of freshness, wholesomeness, and quality that consumers appreciate (Szczesniak and Kahn, 1971). Crispness is lost if the energy supplied during mastication is dissipated by the material and cannot be used for crack formation and crack propagation. In bread crust, this dissipation is strongly related to the amount of water present in the crust (Primo-Martín and van Vliet, 2009). A dry crust is crispy, whereas a wet crust is tough and does not exhibit acoustic emission upon fracture. The relation between the water content and the crispness of baked cereal products was shown by several authors (Primo-Martín et al., 2008c, 2009; Primo-Martín and van Vliet, 2009; Roudaut et al., 1998; van Nieuwenhuijzen et al., 2008). They determined that at a water content between 9% and 11%, the so-called critical water content, half of the crispness is lost. Therefore, crispness is clearly related to the water content of the crust.

Loss of crispness is primarily caused by water migration from the wet crumb to the dry crust. The crumb has a water activity of approximately 0.97, whereas the water activity of the crust is less than 0.6 in the first 30 min after baking. The difference in water activity between crumb and crust is the driving force for water migration. Therefore, the crust takes up water from the crumb, and the water content of the crust increases. The water content of the environment, expressed as relative humidity, will also play a role. Another parameter determining the speed of migration is water vapor permeability, which characterizes the overall resistance of the bread structure to water migration.

Water migration between crumb, crust, and environment causes the loss of crispness after baking. For example, Primo-Martín et al. (2006) determined in a sensory study that bread loses more than half of its crispness within the first five hours after baking, if it is stored at 40% relative humidity. Despite this fast loss of crispness, only few methods have been described that increase crispness retention: the spraying of protease on the crust (Primo-Martín et al., 2006), the application of vacuum cooling (Primo-Martín et al., 2008a; Lösche et al., 2011), the addition of enzymes (Primo-Martín et al., 2008b), and the use of shorter proving times (Primo-Martín et al., 2010). In all these studies the water content of the crust after 4 h storage time was above 10%, and therefore above the critical water content. A further lowering of the water uptake of the crust would be beneficial to increase crispness retention even more.

A description of the mechanism leading to the fast increase of the water content of the crust and the fast loss of crispness is missing in the literature. As a consequence, it is not known whether a change in the properties of crust, crumb, or environment mainly affects crispness retention and which parameters are key for the reduction of the water uptake of the crust. It is difficult to change the parameters of the crumb and the crust separately, because bread making is an all-in-one process. In general, little information is available about the processes that occur during the storage and the cooling of bread. For example, it would be useful to know whether differences exist between the speed of migration through the crumb and the crust, and whether migration in bread during storage can be described by a simple model. Due to this lack of a detailed picture that reveals the reasons for the fast loss of crispness, it is not known how and to what extend the crispness retention of the crust can best be improved.

## 1.4. Aim and outline of this thesis

The aim of this thesis was to systematically determine the mechanisms that lead to the fast loss of crispness and the parameters that are key for crispness retention and that therefore need to be controlled to extend the duration of crispness. This knowledge should lead to guidelines for the industry to produce breads with optimal crispness retention.

These guidelines are based on the information presented in the chapters of this thesis (Fig. 1-1). In Chapter 2, the influence of the permeability of the crust on the water uptake of the crust and on crispness retention was investigated. This information was extended in Chapter 3 through the determination of an optimal water vapor permeability of the crust for sensory crispness and crumb softness retention. In Chapter 4, the focus is on the crumb. This chapter investigated whether different crumb morphologies affect the permeability of crumb and crispness retention. In Chapter 5, it was assessed whether spontaneously appearing cracks on the crust surface can also enhance crispness retention, and which requirements are necessary to create these cracks. Chapter 6, the general discussion, summarizes and discusses all these findings in a model for crispness retention and describes processes occurring during storage and cooling

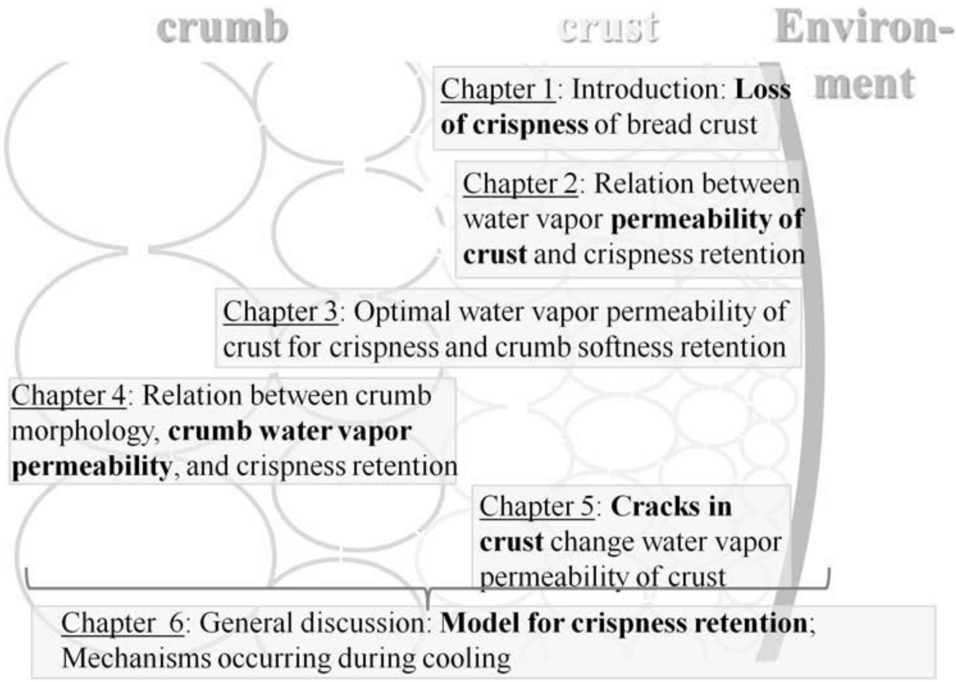


Fig. 1-1: Schematic overview of the thesis

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# Chapter 2

## Permeability of crust is key for crispness

## Abstract

Bread loses crispness rapidly after baking because water originating from the wet crumb accumulates in the dry crust. This water accumulation might be increased by the dense and low permeable character of the bread crust. Our objective was to investigate the influence of permeability of the crust on water uptake in the crust and on crispness retention. To achieve this objective, we increased the permeability of the control bread crust by creating small channels through the crust. The water vapor permeability of the crust with and without channels was measured using a newly developed method for brittle materials. Two further properties were measured over time: crispness of bread by analyzing acoustic properties and water content of the crust. Control bread crust had low water vapor permeability and functioned as a barrier, leading to increased uptake of water in the crust. Water uptake was halved, however, if the water vapor permeability of the crust was doubled. As a consequence, crispness retention increased eight-fold; breads stored for four hours were as crispy as control breads stored for 30 min. We can conclude, therefore, that permeability of crust is key for crispness retention.

## 2.1. Introduction

Crispness is the most important sensory characteristic on which consumers base their appreciation of certain food products (Luyten et al., 2004; Szczesniak and Kahn, 1971). For these products (e.g. French fries, carrots, breads and rolls), crispness is associated with freshness and high quality. Crispness is defined as a textural sensation experienced during eating of a product that fails in a brittle manner under low deformation force accompanied by a characteristic acoustic emission (Luyten et al., 2004; Szczesniak, 1988; van Vliet et al., 2009).

Food products lose crispness if their water activity exceeds a critical value (Katz and Labuza, 1981; Peleg, 1994; Valles Pamies et al., 2000). Most crispy food products do not reach this critical value during storage because their water activity is kept constant, for instance, by packaging. However, maintaining a low water activity in bread crust is not possible because water migrates from the wet crumb to the dry crust (Luyten et al., 2004; Primo-Martín et al., 2006, 2008). This water migration leads to an increase of the water content of the crust, causing a loss of crispness within hours (Dijksterhuis et al., 2007; Luyten et al., 2004; Primo-Martín).

The water sorption capacity of the crust and the water migration through the crust are probably affected by the properties of the crust, e.g. morphology, matrix composition, and density. These properties differ in crust and crumb. Crust contains smaller gas cells, has a more compact and dense structure, a lower degree of starch gelatinization, and lower gas permeability than crumb (Primo-Martín et al., 2007, 2010; Wählby and Skjöldebrand, 2002; Zhang et al., 2005). The low permeability of crust slows down gas transport and mass transfer from the bread to the environment during baking and is therefore responsible for the limited weight loss and dough expansion during baking (Wählby and Skjöldebrand, 2002). The low permeability of the crust could not just restrict water loss during baking but could also lead to decreased water loss and increased water uptake of the crust during storage. Hence, a change in the barrier properties of crust could help to control water uptake in the crust and thereby change crispness retention.

To investigate this hypothesis we changed the water barrier properties and permeability of the crust of rolls by creating channels through the crust. A method to measure water vapor permeability and diffusion coefficient of crust was developed. We also investigated solubility of crust, water uptake in the crust and instrumental crispness of the rolls at different storage times. Our aim was to clarify the mechanisms that are important for crispness retention in bread and to prove the assumption that an increase in permeability of the crust decreases water uptake in crust and increases crispness retention.

## 2.2. Materials and methods

### 2.2.1. Materials

We used a commercial flour, Salvia, without additives prepared by Meneba (Meneba Meel BV, Rotterdam, The Netherlands) to bake rolls (small round breads about 90 mm in diameter and about 50 mm in height). The flour contained 12.0% protein, 5.4% damaged starch, 0.49% ash, and 13.8% water. Dry yeast (Fermipan) was purchased from AB Mauri (Moerdijk, The Netherlands).

### 2.2.2. Baking of rolls

Bread rolls were baked in two stages. The breads were first part-baked and frozen. Half of the frozen part-baked rolls were then punctured to create channels in the crust. Punctured and control rolls were subsequently baked off.

### 2.2.3. Preparation of part-baked rolls

Part-baked rolls were prepared in the TNO baking laboratory (TNO Quality of Life, Zeist, The Netherlands). Wheat flour (3000 g, 7 °C), dry yeast (50 g), and salt (70 g) were blended in a mixer (Kemper SP 15, Kemper, The Netherlands) for one minute at low speed (140 rpm). Water (1779 ml, 10 °C) and ascorbic acid (20 ppm) were then added and the blend was mixed at low speed for two minutes. Subsequently, the dough was kneaded at 280 rpm until it reached a final temperature of 26 °C. The dough was sheeted after mixing and allowed to rest for 15 min. The combination of sheeting and resting was done twice, and the dough was then divided and rounded. Proofing was carried out at 30 °C and 80% relative humidity until a fixed volume of gas had been produced (700 ml) in a SJA Fermentograph (Franken, Goes, The Netherlands). The rolls were part-baked at 180 °C for 10 min and 75 °C dew point in a Becker oven

(Becker BV, Nederweert, The Netherlands). The part-baked rolls were then equilibrated to room temperature for 30 min. The rolls were frozen to –30 °C and stored at –18 °C for less than one week before being treated and baked off to completion.

### 2.2.4. Puncture of crust of part-baked rolls

Two types of rolls were produced: one without channels (control rolls) and one with channels (punctured rolls). Channels in the crust were made by pressing a device containing needles into the frozen rolls before baking off. The penetration depth of the needles was about 2 mm, the distance between the centers of the needles was 3 mm and the diameter of the round needles was 0.62 mm. The rolls were baked off within one minute after removing them from the freezer to avoid defrosting.

### 2.2.5. Baking off and product storage

Rolls were baked off for 5 min at 235 °C in a Bakermat Mastermind oven (Leventi, Gilze, The Netherlands), pre-heated to 250 °C. Five replicates were done for each setting. The rolls were then stored in a climate cabinet (Weiss SB $11^{300}$, Weiss Technik, Ltd, Buckinghamshire, UK) under controlled conditions (relative humidity 40%, 22 °C). The rolls were weighed before baking and at 0 h, 0.5 h, 4 h, and 1 day after baking to measure the water loss.

### 2.2.6. Water vapor permeability, solubility and effective diffusion constant

The measurement of water vapor permeability through films is well described for several materials including starch, wheat gluten and lipids (Bourlieu et al., 2009). This measurement includes a sealing step that is not applicable for brittle materials like bread crust, therefore it was necessary to modify the method.

Water vapor permeability was determined in three steps. First, the upper part of the measuring system shown in Fig. 2-1 was prepared. The crust was separated from the rolls with a knife within 10 min after baking. The distinction between crust and crumb was based on color. Part of the crust was sealed using liquid paraffin (Paraffin type 6, Richard-Allan Scientific, Kalamazoo, MI, USA) and a metal ring (diameter about 17 mm, height about 2 mm, thickness about 0.1 mm). The sealing was done to define a specific open area of the crust (minimum 180 $mm^2$, maximum 250 $mm^2$). The liquid paraffin solidified within 10 s. The sealed crust was then equilibrated at a relative humidity of 40% and a temperature of 25 °C for at least one day.

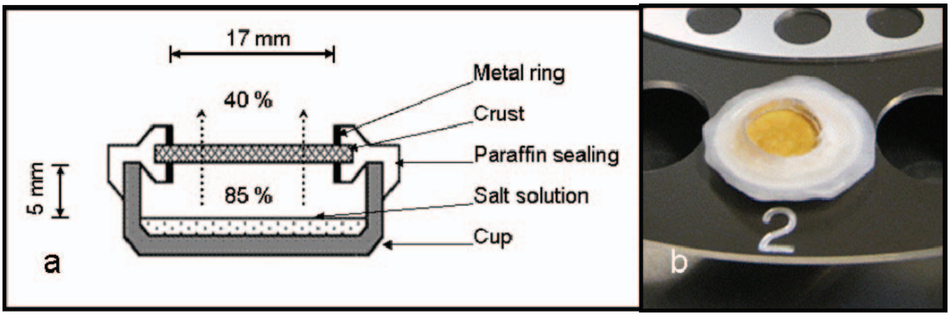


Fig. 2-1: Layout of the water permeability measurement set up. (a) Schematic picture. (b) Cup placed in the gravimetric sorption analyser (SPS). The edge of the crust was sealed using paraffin and a metal ring to define the measurement area. The sealed crust was fixed to a cup containing a salt solution providing an internal water activity of 0.85. The cup was placed in the SPS chamber conditioned at a relative humidity of 40% and a temperature of 25 °C. The weight change as a function of time was measured using a balance.

In the second step, the sealed crust, facing upwards, was fixed with liquid paraffin to an aluminum cup containing 1.5 ml of a saturated potassium chloride solution with an $a_w$ of 0.85. A salt solution with an $a_w$ of 0.85 was chosen to mimic the condition in rolls. The $a_w$ of crumb under the crust is about 0.85. The distance between the bottom side of the piece of crust and the salt solution was about 5 mm. Within two minutes after each crust piece was relocated from the controlled atmosphere, the prepared cup was placed into a gravimetric moisture sorption analyzer (SPSx-1µ, Projekt Messtechnik, Ulm, Germany), which controlled humidity and temperature (40%, 25 °C). The loss of water through the crust was measured as the change in weight every four minutes. After the water permeability measurement was completed (43 h) for four control crust pieces and five punctured crust pieces, the apparatus was disassembled and the thickness of each crust samples was measured with a caliper at five different points and the average value was calculated. The sealed crust was also scanned and the exact measurement area was calculated using ImageJ software (a public domain Java image processing program).

The loss of water through the each sample stored in the SPS was plotted as a function of time and the slope of the curve in the linear region, $G$ (g/s), was used to calculate the water vapor permeability (WVP)

$$WVP = \frac{G \cdot x}{A \cdot \Delta P_v} \tag{2.1}$$

where $x$ (m) is the thickness of the crust, $A$ ($m^2$) is the area of unsealed crust, and $\Delta P_v$ (Pa) is the partial water vapor pressure difference.

A constant water activity gradient across the crust samples of $\Delta a_w = 0.45$ was used; the partial pressure difference was calculated using the following equation:

$$\Delta P_v = P_{v,sat} \cdot \Delta a_w \tag{2.2}$$

where $P_{v,sat}$ is the vapor saturation pressure at a measurement temperature of 25 °C, taken as 3130 Pa.

The water vapor permeability is also expressed as:

$$WVP = D_e \cdot S \tag{2.3}$$

with $S$ the solubility (in g/Pa/$m^3$) and $D_e$ the effective diffusion coefficient (in $m^2$/s). Therefore, both the solubility and the effective diffusion constant affect the water vapor permeability of crust.

The solubility is defined as:

$$S = \frac{\mathrm{d}c_w}{\mathrm{d}P_v} \tag{2.4}$$

where $c_w$ is the water concentration (g/$m^3$). Within our used settings this equation can be written as

$$S=\frac{\mathrm{d}c_w}{\mathrm{d}P_v}=\frac{\rho_\mathrm{s}\cdot\mathrm{d}\dfrac{m_w}{m_s}}{P_{v,sat}\cdot\mathrm{d}a_w}\approx 1058\cdot\mathrm{d}\frac{m_w}{m_s}\qquad \text{in}\ \left(\frac{\mathrm{g}}{\mathrm{Pa\ m^3}}\right)\tag{2.5}$$

where $\rho_s$ ($g/m^3$) is the density of the solid matrix. A density of the solid matrix of 1490 $kg/m^3$ was used for the calculation, because Marousis and Saravacos (1990) determined a particle density of 1490 $kg/m^3$ for starch with a water content of 12.5%. The difference in the mass of water per mass of dry solid sample ($d(m_w/m_s)$) for a given change in the water activity is described by the isotherm. We determined the isotherm of control and punctured crust using the gravimetric moisture sorption analyzer SPSx-11μ (Projekt Messtechnik, Ulm, Germany) at 22°C. The SPSx-11μ increased the relative humidity in 10% steps from 0% to 90% relative humidity. Afterwards the relative humidity was set to 95%. The weight change of the samples was measured every eight minutes to determine the equilibrium water content. We assumed that the equilibrium was reached when the weight change was less than 0.001% within 60 min measurement time or when the step lasted 50 hours. The mass change at equilibrium condition (or maximum residence time) was used to draw the moisture sorption isotherms. The isotherm was modeled with the GAB model to determine the water uptake ($d(m_w/m_s)$) for a water activity increase from 0.40 to 0.85. The solubility was determined for two crust pieces with channels and two crust pieces without channels.

Once the water vapor permeability and the solubility of crust were determined, the effective diffusion coefficient was calculated using Eq. (2.3). The effective diffusion coefficient is the overall diffusion coefficient that describes the transport of water through the total porous cellular solid. Although complex transport mechanisms occur in the porous solid (Fickian diffusion through the solid, matrix relaxation and water vapor transport through the pores) the effective diffusion coefficient is used for simplification.

To set up Eq. (2.3) and (2.5) the following assumptions were made: the density of the solid matrix was constant, the water concentration at the surface of the crust was in equilibrium with the water activity of the adjacent air and $D_\mathrm{e}$ is constant over the measured $a_\mathrm{w}$ range. Bourlieu et al. (2009) mentioned that some of these assumptions are doubtful for hydrophilic materials. We are aware that the calculated $S$ and $D_\mathrm{e}$ are assumptions within our measurement range.

### 2.2.7. Water content of total crust: dry oven method

The water content of the total crust was measured. After storing the rolls for various times the crust was separated from the crumb using a knife. The distinction between crust and crumb was based on color. The thickness of the crust pieces was between 1.0 and 1.5 mm. Crust samples for the 0 h measurement were separated within 5 min after baking. Crust samples separated from the rolls before baking and after 0 h, 0.5 h, 4 h, 24 h and 31 days after baking and crust samples generated after the water vapor permeability measurement were placed in an oven at 105 °C for 24 h. The water content was calculated using the weight before and after drying. The average of at least five replicates per setting was calculated.

### 2.2.8. Water content outer crust: near-infrared method

The water content of the outer crust was measured using a near-infrared ray reflectance moisture meter (KJT-100 handheld model, Kett US, CA, USA). This device measured the water content in the outer crust (about 30 µm). The moisture meter was calibrated as described by Primo-Martin et al. (2008). The average of at least five replicates per setting was calculated.

### 2.2.9. Water activity

The water activity ($a_w$) of the crust and the salt solution was measured using an Aqua Lab Series 3 (Decagon device, Pullman, USA). The average of at least five replicates per setting was calculated.

### 2.2.10. Acoustic analysis to measure crispness

The acoustic characteristics of the crust were measured during fracture of the roll using a texture analyzer (TA-XT Plus, Stable Micro Systems Ltd., Surrey, UK) in an isolated chamber. The top of the roll was fractured vertically at a speed of 20 mm/s using a rectangular cuboid as probe (area touching the sample had a thickness of 1 mm and a width of 10 mm). The sound emitted was recorded simultaneously at a distance of 70 mm using a free field microphone (4189 Deltatron Falcon free field microphone with pre-amplifier 2671, Brüel & Kjær, Nærum, Denmark). Data were digitized and analyzed as described by Primo-Martin et al. (2009). This analysis involved characterization of individual events in the acoustic emission within the first 0.4 s after the device contacted the roll. The number of sound pulses with a sound intensity higher than the threshold of 62 dB was counted. This threshold was used to clear the sound signal from noise. The energy of all pulses was then calculated and divided by the time span of 0.4 s. This value was expressed as mean sound pulse intensity. Twenty acoustic measurements were done for one setting. This number of replication was achieved by fracture five rolls (replicates) four times each.

### 2.2.11. Statistical analysis

Hypothesis testing for the difference in means of two independent samples was performed using a two-sided t-test ($p < 0.05$) using MATLAB 7.5.0 (The MathWorks Inc., Natick, MA, USA).

## 2.3. Results

### 2.3.1. Appearance of rolls

Crispy rolls with and without channels were produced. The rolls with channels were created by puncturing the surface of part-baked frozen rolls with a device containing needles. Using this method, we created well-defined and separated channels through the part-baked crust, because the frozen crust was neither brittle nor elastic (Fig. 2-2). Crust does not exhibit these characteristics before part-baking and after baking off. After baking off, control rolls (without channels) and punctured rolls (with channels) did not differ in volume, height, and crumb morphology; they only varied in the morphology of the crust.

The diameter of the channels decreased during baking to 0.36 mm. Channels represent about 1.1% of the upper surface area of the rolls.

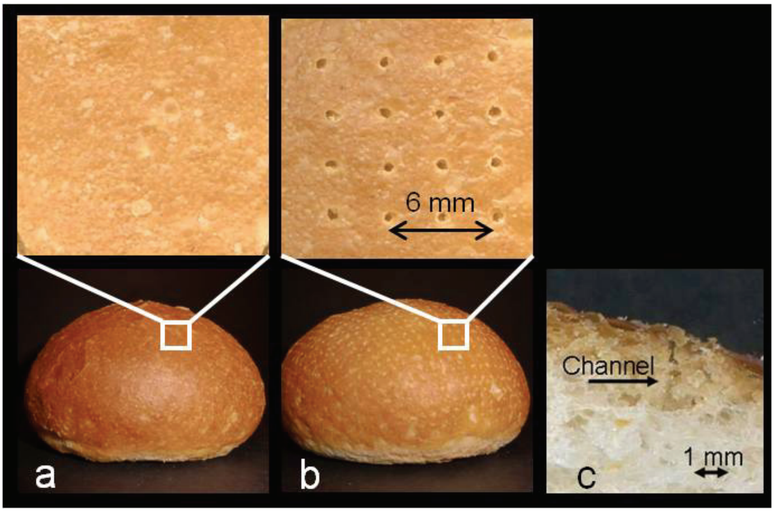


Fig. 2-2: Control roll (a) and punctured roll (b) after baking off. Standard rolls were prepared as described in Section 2.2. Half of the frozen rolls were punctured with a device containing needles. The figure shows the full roll and a detail of the crust for both rolls. (c) A cross section of the punctured crust.

### 2.3.2. Water vapor permeability, solubility and effective diffusion coefficient of crust

Rolls were punctured to increase the permeability of the crust and to study the effect of increased permeability on water migration in the bread. To measure the water vapor permeability and effective diffusion coefficient of the crust we developed a new method in which we sealed part of the crust with paraffin on a cup containing a saturated salt solution. The used sealing procedure was effective; no water penetrated through a sealed metal plate (Fig. 2-3).

The amount of water migrating through punctured and control crust with time is also shown in Fig. 2-3 for two typical measurements. Almost double the amount of water penetrated through punctured crust than through control crust.

Fig. 2-3 shows that the rate of water release became constant after a first lag phase. The duration of this phase, in which the samples equilibrated, differed significantly between control and punctured crust ($p < 0.05$) (Table 2-1). However, after 6 h a constant flux of water vapor migrated through both types of crust. This linear phase was used to calculate the water vapor permeability, which differed significantly between the two types of crust (Table 2-1).

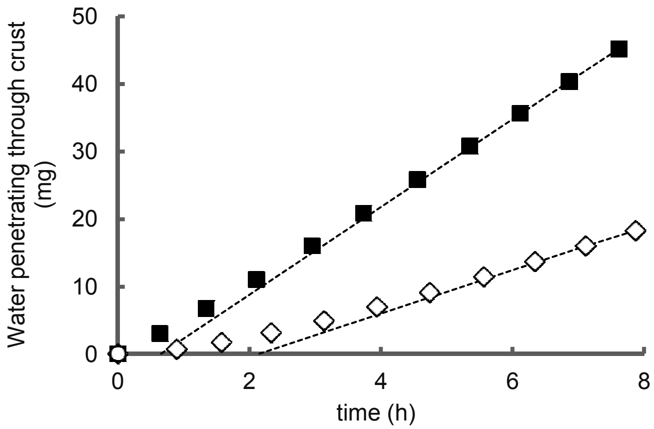


Fig. 2-3: Water vapor penetrating through a metal plate (○), a control crust (◊), and punctured crust (■) as a function of time. Water migrated from a cup (RH = 0.4) to the climate chamber (RH = 0.85). From the two crust samples, the lag phase was calculated by extrapolating the tangent at the linear part of the curve back to the *x*-intercept (dotted lines).

Table 2-1: Water vapor permeability (WVP), solubility, effective diffusion coefficient, duration of lag phase and water content of isolated control crust, isolated punctured crust and metal plate.

| | WVP ($10^{-9}$ g/(m s Pa))[a] | Solubility (g/Pa $m^3$)[b] | Effective diffusion coefficient ($10^{-11}$ m2/s)[c] | Duration lag phase (h)[d] | Water content (%)[e] |
|---|---|---|---|---|---|
| Control crust | 3.5 ± 0.3 | 181.3 ± 2.4 | 1.9 ± 0.3 | 2.2 ± 0.1 | 14.9 ± 3.1 |
| Punctured crust | 6.6 ± 0.9 | 181.2 ± 0.7 | 3.6 ± 0.5 | 0.6 ± 0.1 | 9.7 ± 0.7 |
| Metal plate | 0 ± 0 | n.a.[f] | n.a. | n.a. | n.a. |

[a]The water release through a defined area of crust was measured, given a fixed water activity gradient of 0.45. Given the rate of weight loss, the area of the open crust piece and the thickness, the water vapor permeability can be calculated (Eq. (2.1)).
[b]The solubility was calculated using Eq. (2.5).
[c]The effective diffusion coefficient was calculated using Eq. (2.3).
[d]The duration of the lag phase was calculated as described in Fig. 2-3.
[e]The water content of the crust was measured after 43 h.
[f]Not analysed.

Although the two types of crust differ in their water vapor permeability, they did not differ in their solubility ($p > 0.05$) (Table 2-1). Using both parameters, solubility and water vapor permeability, we calculated the effective diffusion coefficient (Eq. (2.3)). The effective diffusion coefficient is significant higher for punctured crust than for control crust (Table 2-1). In addition, the water content of crust after 43 h was significantly higher for control crust than for punctured crust (Table 2-1)

### 2.3.3. Water content of crust

According to our hypothesis, increased permeability of the crust will slow down the rate of water uptake in the crust. We therefore measured the water loss of the rolls and the change in water content of the crust after three stages: baking off, cooling down, and storage. Fig. 2-4 shows the water content of the total crust (Fig. 2-4a), the water content of the outer crust (Fig. 2-4b), and the weight of the rolls (Fig. 2-4c).

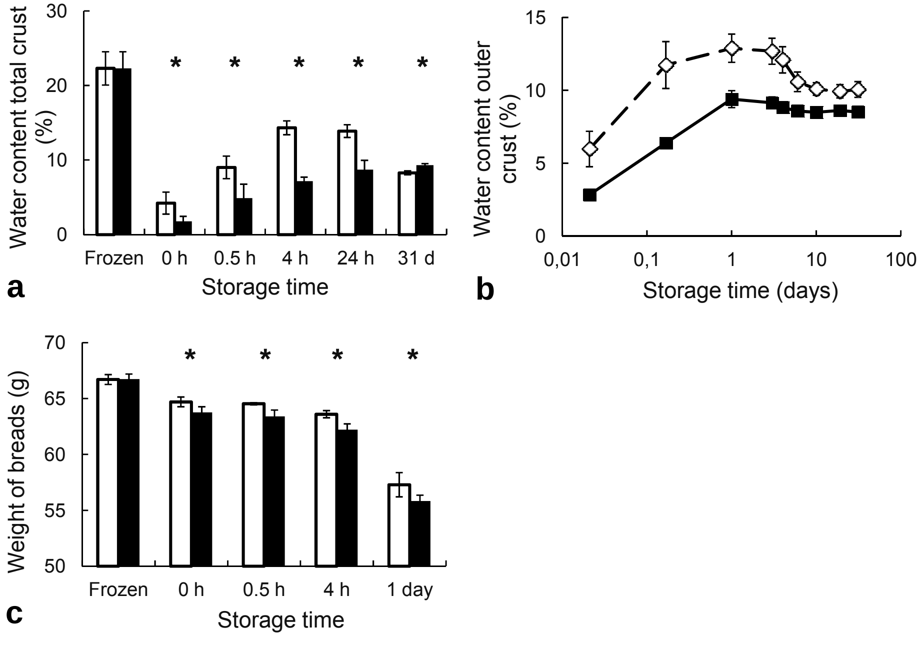


Fig. 2-4: Water content of the total crust (a) and outer crust (b) and bread weights (c) for the control (open symbols/bars) and punctured (solid symbols/bars) rolls as a function of storage time. The rolls were stored at 40% relative humidity directly after baking. *Statistically significant differences ($p < 0.05$).

The water content of the crust significantly differed between control and punctured rolls after baking off and during cooling down (Fig. 2-4a). During cooling down (first 30 min after baking), the water content of the crust increased in both types of rolls; after 30 min storage, the water content of the crust was 9.0 ± 1.5% and the water activity was 0.63 ± 0.04 for control rolls. In contrast, the crust of the punctured rolls had a water content of 4.9 ± 1.9% and a water activity of 0.38 ± 0.01.

During storage of the rolls we not just measured the water content of the whole crust, but also the water content of the outer crust (thickness about 30 µm) using near-infrared spectroscopy (Fig. 2-4b). Both measurements showed a similar trend. The water content of the crust first increased, then decreased, and finally reached equilibrium. For both types of breads, the water content of the outer crust was maximal after storing for 1 day. However, the water content of the outer crust and the total crust was significantly different between both types of rolls at all stages after baking. The crust of the control rolls had a water content of 13.9 ± 0.9% and a water activity of 0.67 ± 0.02, whereas the crust of punctured rolls had a water content of 8.7 ± 1.2% and a water activity of 0.53 ± 0.02 after storing for 1 day. With increasing storage time the water content of the outer crust decreased again and leveled off at slightly different but constant values.

### 2.3.4. Crispness retention

Our hypothesis is that an increase in crust permeability increases crispness retention. To determine whether punctured rolls were actually crispier, we evaluated crispness by measuring acoustic properties during fracture. It is reported in the literature that the number of sound pulses and the pulse intensity evaluated during this measurement relate to crispness (Luyten et al., 2004; Mohamed et al., 1982; Vickers, 1987). If these two parameters are higher, the product is also rated as crispier by sensory analysis. Therefore, we measured these two sound parameters during fracture of both types of rolls after 30 min and 4 hours storage time.

The measurements revealed a significant effect of puncturing on crispness (Fig. 2-5). Punctured rolls had a significantly higher number of sound pulses and significantly higher mean sound pulse intensity than control rolls after cooling down for 30 min ($p < 0.01$). These results indicate a higher crispness after cooling. More importantly, the two parameters were also higher for these rolls after storing for 4 h, indicating longer crispness retention. The trend observed for the acoustic parameters closely resembled the trend observed for changes in the water content of crust.

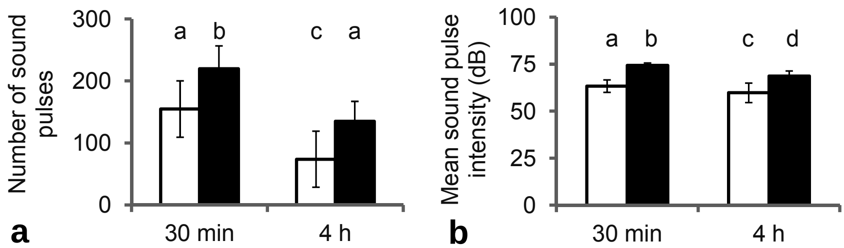


Fig. 2-5: Instrumental crispness parameters, being the number of sound pulses (left) and the mean sound pulse intensity (right) for control (open bars) and punctured (solid bars) rolls. Rolls were fractured after storage for 30 min and 4 h. Different letters indicate significant differences.

## 2.4. Discussion

Crispness is one of the most important sensory characteristics on which consumers base their appreciation of a wide range of breads. However, a rapid loss of sensory crispness in the first hours after baking is inevitable because water originating from the crumb is absorbed in the dry crust (Luyten et al., 2004). It is not known yet, which properties of the bread, e.g. permeability, morphology, ingredient composition and water content, determine the rate of this process. In this paper we focused on the properties of the crust, especially on the permeability of the crust. Our hypothesis is that the crust has low water vapor permeability and acts as a barrier to water vapor migration. An increase in the permeability of crust would facilitate water migration through the crust, minimize water uptake in the crust and decrease loss of crispness.

To test this hypothesis we increased the water vapor permeability of crust by creating small, well-separated channels through the crust by puncturing frozen part-baked rolls (Fig. 2-2). Already Chaunier et al. (2008) suggested that the permeability of baked products is dependent on their porous structure.

To measure the water vapor permeability of crust we had to develop a new method, because the standard method is not applicable for brittle materials like crust (Moore et al., 2004). Our results show that the method is sensitive and reproducible and that the water vapor permeability is almost twice as high for punctured crust as for control crust (Table 2-1). The different water vapor permeability was not due to a different solubility, because this value was alike for punctured and control crust, but due to a different effective diffusion coefficient. The estimated effective diffusion coefficient of crust for control crust ($2.7 \pm 0.2 \times 10^{-11}$ $m^2/s$) and punctured crust ($5.2 \pm 0.7 \times 10^{-11}$ $m^2/s$) are in the same range as the effective diffusion coefficients measured for other processed foods ($10^{-9}$–$10^{-12}$ $m^2/s$) (Labuza and Hyman, 1998). In biscuits higher diffusion coefficients were measured ($10^{-9}$ $m^2/s$) (Guillard et al., 2004), probably because biscuits have a more porous structure than bread crust. This is the first time that the effective diffusion coefficient has been measured experimentally for bread crust. The identification of this value is important, for example, for the modeling of water migration in bread and for the understanding of the pressure increase in bread crumb (Grenier et al., 2009; Zhang et al., 2005).

The water content of crust of punctured rolls stored at 40% relative humidity increased significantly slower than the water content of crust of control rolls (Fig. 2-4a). This difference in water uptake can be explained by the differences in the water vapor permeability and the effective diffusion coefficient. By puncturing the crust, the effective diffusion coefficient was increased because the resistance of the crust to water migration decreased. According to Fick's law this results in an increased water vapor flux through the crust. As a result of the increased water flux, punctured rolls lost more water during baking and the crust had a lower water content after baking (Fig. 2-4). Cuq et al. (2004) and Wählby and Skjöldebrand (2002) already showed that the crust is a barrier against weight loss during baking. However, the different effective diffusion coefficients of both rolls not only led to a different water content of both crusts immediately after baking but also to a different water uptake of crusts during cooling down and storage. During cooling down and storage the difference in water content of both crusts increased further (Fig. 2-4a). The maximum water uptake of the outer crust of punctured rolls (9 ± 1%, 1 day) was similar to the equilibrium water content (9 ± 1%, 31 days) (Fig. 2-4c). The maximum water content of control outer crust (13 ± 1%), however, was significantly higher than the equilibrium water content. The reason for this high water uptake of control crust is that water from the wet crumb migrates towards the crust and that due to the low water vapor permeability of control crust this water does not leave the crust immediately, but accumulates in the crust. Hence our results confirm the hypothesis that the crust functions as a barrier for water migration. After one day of storage the water content of the control crust decreases again (Fig. 2-4b). The decrease in water content occurs, because crust and crumb loose water and dry out with increasing storage time, so that less water is available that could accumulate in the crust. With time crust and crumb reach equilibrium with the environment. If the crust is punctured, however, the water uptake does not exceed the equilibrium water content. This observation is due to the fact that punctured crust has a higher water vapor permeability. Punctured crust acts less as a barrier and channels probably provided a bypass for water migration. Further investigations are however necessary to reveal the detailed mechanism.

In contrast to the significant effect of puncturing on the water content of the crust, only slight effects of puncturing on the water content of crumb were observed. The water content did not differ statistically between the rolls at 4 h after baking for the outer crumb and at 24 h for the central crumb (results not shown). Between 30 min and 24 h after baking the water loss for both types of rolls was not significant different ($p > 0.05$) (Fig. 2-4c). These results suggest that the channels in the crust cause mainly local effects and that the sensory quality of the crumb is not affected. Since sensory studies were not part of this study, these observations need to be confirmed as done in Chapter 3.

On the other hand, the rolls also differed in crispness retention based on acoustic measurements and on the time to reach critical water activity. The critical water content (i.e. the water activity at which sensory crispness has decreased by 50%) was 10.1% for crispy rolls (Primo-Martín and van Vliet, 2009). For control rolls this critical water content was reached in the outer crust after 2.1 h, whereas for punctured rolls this value was not reached within the first day of storage in our study (Fig. 2-4b). Increasing the permeability of the crust, therefore, significantly increased the retention of crispness. This result was also corroborated by measuring acoustic parameters, which are related to crispness. The number of sound pulses from the punctured rolls after storing for 4 h was not significantly different from the number of sound pulses from the control rolls after storing for 30 min (Fig. 2-5). Based on these results we predict an increase of crispness retention by eight-fold at a relative humidity of 40%.

In this study, crispness retention was affected by changing the morphology of the bread crust without changing other variables (e.g. ingredients). We conclude, therefore, that morphological parameters of the crust affect water migration within the bread. In addition, we showed that increased crust permeability enhances crispness retention by eight-fold. We conclude, therefore, that crust permeability is key to crispness retention.

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# Chapter 3

## Control of crust permeability and crispness retention in crispy breads

## Abstract

Crispness of bread crust is rapidly lost after baking. It is known that the speed of this loss is influenced by the water vapor permeability of the crust. A high water vapor permeability benefits crispness retention but could lead to crumb dryness. In this paper we aimed to determine the water vapor permeability that is optimal for both crispness retention and crumb softness retention. The water vapor permeability of crust was changed by creating different quantities and sizes of channels in the crust. The instrumental and sensory evaluation of the breads stored at 40% relative humidity showed that the water vapor permeability for optimal crispness and crumb softness retention was $8 \times 10^{-9}$ g/(m s Pa). Based on this knowledge we suggest possible combinations of the quantities and sizes of channels to create breads with more than eight-fold longer sensory crispness retention without decreasing crumb softness retention. In addition, our data allowed us to develop a model describing the water vapor permeability of crust with channels.

## 3.1. Introduction

Consumers appreciate the combination of different textures in food (Szczesniak and Kahn, 1971). Pleasant contrast in textures occurs, for example, in crispy bread such as a baguette, because these breads contain a soft inner crumb and a dry crispy crust (Luyten et al., 2004). However, this strong contrast is rapidly lost, because the crispy sensation deteriorates within few hours after baking (Luyten et al., 2004; Primo-Martín et al., 2006). To increase crispness retention in bread just a limited number of methods are described: The creation of channels in the crust (Chapter 2), the spraying of protease on the crust (Primo-Martín et al., 2006), the application of vacuum cooling (Primo-Martín et al., 2008a), the addition of enzymes (Primo-Martín et al., 2008b), and the application of shorter proving times (Primo-Martín et al., 2010).

In bread, the loss of crispness is primarily caused by water migration from the wet crumb to the dry crust, which increases the water content of the crust. This water uptake of the crust is dependent on storage conditions, the initial water distribution in the bread, the properties of the crumb (e.g. the speed of water diffusion through the crumb), and the properties of the crust. The present study is limited to the properties of the crust, because our previous study (Chapter 2) showed that in particular the water vapor permeability of the crust has an important influence on the water uptake. Doubling the water vapor permeability of the crust by creating channels through the crust halved the water uptake of the crust. As a consequence, crispness retention increased eight-fold. However, it was not shown whether the chosen water vapor permeability was optimal for sensory crispness retention, and whether the increase of crust permeability had a negative effect on the crumb softness. The softness of the crumb, which is an appreciated attribute of bread crumb, can be negatively influenced by the higher water loss of breads with channels (Chapter 2).

Therefore, the aim of this study was to determine the water vapor permeability of bread crust that is optimal for a low water uptake of the crust and for a long crispness and crumb softness retention of bread. Using different puncture settings, we prepared breads and determined their instrumental and sensory crispness retention, their sensory crumb softness retention and the water vapor permeability of their crust. As well as determining the optimal permeability, we also aimed to describe possible puncture settings to reach this optimal permeability in bread crust and to increase the understanding of water migration through punctured and not punctured crust by modeling.

## 3.2. Materials and methods

### 3.2.1. Baking and freezing of breads

Breads were prepared as described in Chapter 2 with minor modifications. This preparation involved the following steps: mixing, proving (500 ml gas volume in the SJA Fermentograph (Franken, Goes, The Netherlands)), part-baking (180 °C, 10 min) and freezing. During freezing at -0 °C the temperature in the middle of three breads was measured with K type thermocouples (Type 171-8, Testo AG, Lenzkirch, Germany). Breads were cooled with a cooling speed of 0.62 ± 0.05 °C/min from around 33 °C to around -4 °C within 1 h. After freezing at -30 °C for 1 h, breads were stored at -18 °C, punctured, baked off, and analyzed.

### 3.2.2. Creating channels in the crust of part-baked breads

During the experiments, 13 different types of breads were analyzed: breads without channels (control breads), breads sealed with a paraffin layer and 11 breads with variations in the channels (punctured breads). Channels in the breads were made by pressing a channel device containing needles into the crust. The penetration depth and therefore the length of the channels was about 2 mm. The channel devices varied in the distance between the channels (1.5 mm to 12.0 mm) and the diameter of the needles (0.6 mm to 2.0 mm) (Table 3-1). The use of devices with multiple needles was not possible for breads F, G, and H, as these devices separated the crust from the crumb during puncturing in these breads. Therefore, each channel was punctured separately in these breads (Table 3-1). Breads were punctured in the frozen state. The time between sampling from the freezer and baking off was 4 min. The channels did not close during baking, because they were created in a part-baked and therefore already rigid crust. After baking off, several flat crust pieces were separated with a knife and scanned (Epson Perfection V700 Photo scanner, Seiko Epson Corporation, Nagano, Japan). The distinction between crust and crumb was qualitatively made and based on color differences. From the scanned images, the diameter ($d$)

and the area of channels were measured to calculate the punctured surface (punctured surface area relative to the total surface area).

Table 3-1: Properties of analyzed breads. Water vapor permeability and weight loss were determined as described in the methods section.

| Bread | A | B | C | D | E | F | G | H | I | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Diameter of needles (mm) | No[a] | 0.6 | 2.0 | 0.6 | 2.0 | Pa[b] | 0.6 | 0.6 | 1.0 | 1.6 | 0.6 | 0.6 | 2.0 |
| Diameter of channels after baking (mm) | No[a] | 0.5 | 1.8 | 0.5 | 1.8 | Pa[b] | 0.5 | 0.5 | 0.8 | 1.4 | 0.5 | 0.5 | 1.2 |
| Distance between channels (mm) | –[a] | 6.0 | 12 | 3.0 | 6.0 | –[b] | 12 | 4.5 | 6.0 | 6.0 | 2.1 | 1.5 | 3.0 |
| Number of channels per $cm^2$ | 0 | 2.8 | 0.7 | 11 | 2.8 | 0 | 0.7 | 5.6 | 2.8 | 2.8 | 22 | 44 | 11 |
| Punctured surface (%) | 0 | 0.5 | 1.7 | 1.8 | 6.9 | 0 | 0.1 | 0.9 | 1.5 | 4.5 | 3.6 | 7.3 | 12 |
| Water vapor permeability ($10^{-9}$ g/m s Pa) | 3.9 ± 0.6 | 4.2 ± 0.3 | 6.1 ± 1.2 | 8.4 ± 1.5 | 11 ± 1.5 | 0.0 ± 0.0 | 3.6 ± 0.7 | 6.2 ± 1.3 | 7.7 ± 1.1 | 8.5 ± 2.0 | 11 ± 1.1 | 14 ± 2.4 | 19 ± 1.8 |
| Weight loss during baking (%) | 2.4 ± 0.1 | 2.8 ± 0.6 | 3.2 ± 0.1 | 3.7 ± 0.1 | 4.1 ± 0.5 | n.a[c] | 2.7 ± 0.1 | 3.3 ± 0.1 | 3.3 ± 0.1 | 3.9 ± 0.3 | n.a[d] | n.a[d] | n.a[d] |
| Weight loss during storage (%) | 2.3 ± 0.1 | 1.9 ± 0.2 | 2.1 ± 0.2 | 2.9 ± 0.2 | 2.6 ± 0.2 | 0.0 ± 0.0 | 2.1 ± 0.1 | 2.6 ± 0.1 | 2.2 ± 0.1 | 2.4 ± 0.4 | n.a[d] | n.a[d] | n.a[d] |
| Punctured with a device | + | + | + | + | + | + | + | + | + | + | - | - | - |
| Used in sensory | + | + | + | + | + | - | - | - | - | - | - | - | - |

[a]No channels were applied.
[b]Breads were sealed with paraffin.
[c]Not analyzed, because sealing is applied after baking.
[d]Not analyzed, because only part of crust is punctured.

### 3.2.3. Baking off, product storage and paraffin sealing

Breads were baked off for 5 min at 235 °C in a Bakermat Mastermind oven (Leventi, Gilze, The Netherlands), pre-heated to 250 °C. Five replicates were prepared and analyzed for each storage time. Breads were then stored in a climate cabinet (Weiss SB $11^{300}$, Weiss Technik, Ltd, Buckinghamshire, UK) under controlled conditions (relative humidity 40%, 22 °C). Breads were sealed with paraffin by putting them into liquid paraffin (Paraffin type 6, Richard-Allan Scientific, Kalamazoo, MI, USA) 0 min and 15 min after baking off to ensure complete sealing. All breads were weighed before baking off, after baking off and after storing for 4 h. The weight loss during baking was calculated as the percentage weight loss during baking based on the weight before baking. The weight loss during storage was calculated as the percentage weight loss after storing for 4 h based on the weight before storage (after baking off). We did not determine the weight loss of breads K, L and M. As mentioned earlier, we could not use a device to puncture these breads so that within 4 min just part of the crust could be punctured.

### 3.2.4. Water vapor permeability

The water vapor permeability was measured using the method described in Chapter 2. The measurement involved the determination of the amount of water vapor that migrated through a piece of crust, when a constant water activity gradient from 0.85 to 0.40 at a temperature of 22 °C was applied. From this measurement, which took at least 24 h, the water vapor permeability (WVP) was calculated as

$$WVP = \frac{G \cdot x}{A \cdot \Delta P_v} \qquad (3.1)$$

where $G$ (g/s) is the amount of water migrating through the piece of crust per second, $x$ (m) is the thickness of the crust, which was measured with a caliper, $A$ ($m^2$) is the area of crust, and $\Delta P_v$ (Pa) is the partial water vapor pressure difference (1187 Pa). The measured water vapor permeability is dependent on the used settings.

We also modeled the water vapor permeability for crust with channels. If the crust contained channels, we assumed that part of the water vapor left the system through the channels ($G_1$) and part of the water vapor left the system through the not punctured crust ($G_2$).

$$G_{total} = G_1 + G_2 \qquad (3.2)$$

Using Eq. (3.1), assuming the same partial pressure difference for areas with and without channels, using the diameter of the channels ($d$ in mm), and taking the effective length of channels as $x_{eff} = x+2/3d$, because diffusion through the channel is not just affected by the length of the channel, but also by the size of the hemispheric area above and under the channels (Paul and Clarke, 2002), the total water vapor permeability can be estimated as

$$WVP_{calculated} = WVP_1 \frac{A_1}{A} \frac{x}{x+\left(\frac{2}{3}\right)d} + WVP_2 \frac{A_2}{A} \tag{3.3}$$

where $WVP_1$ is the water vapor permeability of the channels, $WVP_2$ is the water vapor permeability of the not punctured crust that we measured (Table 3-1, bread A), $A_1$ ($mm^2$) is the punctured surface area, $A_2$ ($mm^2$) is the not punctured surface area, and $A$ ($mm^2$) is the total surface area. We assumed that $WVP_1$ is the water vapor permeability of vapor in air because the channels were open. $WVP_1$ can be calculated using the known diffusion coefficient for water vapor in air, Fick's law of diffusion, Eq. (3.1) and the ideal gas law. It follows that

$$WVP_1 = D_a \frac{M_w}{R_g T} = 187 \times 10^{-9} \frac{g}{m \times s \times Pa} \tag{3.4}$$

where $D_a = 2.55 \times 10^{-5}$ $m^2/s$ (Bolz and Tuve, 1973), $M_w$ is the molecular weight of water, $R_g$ is the gas constant and $T = 22$ °C.

### 3.2.5. Water content of crust

The water content (wet basis) of the total crust was calculated using the weight determined with an analytical balance before and after drying at 105 °C for 24 h of at least 5 replicates per setting.

### 3.2.6. Fracture and acoustic analysis to measure instrumental crispness

The mechanical and acoustic characteristics of the crust were measured simultaneously using a texture analyzer as described in Chapter 2 with some modifications. The breads were fractured vertically at a speed of 20 mm/s using a rectangular cuboid as probe (area touching the sample had a thickness of 1 mm and a width of 10 mm). We selected a storage time of 30 min for the measurement of the initial crispness, because after that time the breads had cooled down. We selected a storage time of 4 h for the measurement of crispness retention, because after that time the crust crispness of the control breads had almost disappeared. Acoustic characterization involved the determination of the number of sound pulses, the maximum sound intensity (dB), and the mean sound pulse intensity (dB). Mechanical properties were also determined. We measured the maximum force (N) and the slope of the force–time curve from the first contact of the probe to a force of 3 N (N/s). We selected a force of 3 N, because in each measured sample this force was at least needed to break the crust. In addition, force peaks and force drops were determined by a fast Fourier transform using a low cut-off frequency of 50 Hz. The number of force peaks that occurred within the time span of 0.4 s were counted and expressed as the number of force drops. The average of 20 replicates per setting was calculated.

### 3.2.7. Sensory

Textural properties of the breads were evaluated by a trained sensory panel. The panel members were trained as follows: First, the panelists were introduced to the aim of the study, the purpose of the training and the procedure of testing. In the second part, panelists brainstormed about textural properties of different crispy food products. In addition bread samples were given to the panelists to make them more familiar with the crumb texture. In the third part the definition of the attributes that were used in the sensory test were explained to the panelists and trained with samples.

Five different breads (A, B, C, D, and E; Table 3-1) at two different storage times (30 min and 4 h after baking) were prepared for the actual test. These five breads, which were all punctured using a device, were chosen to represent a wide water vapor permeability range. Samples for tasting were prepared as follows: 1 cm was removed from the bottom of the breads cut in half vertically. The panelists bit into the open side of the bread so that they bit into the crust with their top teeth and into the crumb with their bottom teeth. Therefore, the panelists evaluated crumb softness by biting through crust and crumb together, and not just by biting into the middle of the crumb. This procedure was important for us, because we were especially interested whether the crumb below the crust is less soft. A less soft and dryer crumb could be caused by an accelerated water loss through the channels.

In the actual test the panelists always received two control breads together with four experimental breads. The control breads were breads without channels (bread A) stored for 30 min. The four experimental breads were all stored for the same time (30 min or 4 h). The panelists were asked to evaluate the three attributes considered most relevant to this study. During the first bite they evaluated the crispness of the crust (product fractures in a brittle manner after applying a relatively low force to break the bread crust, with sound emission) and the hardness of the crust (the resistance to break the crust). The softness of crumb (the force needed to bite through the crumb of the bread) was evaluated during a second separate bite. Panelists evaluated each attribute on a linear scale of 20 cm and the control bread had a fixed score at 10 cm. All scores were normalized to a 10-point scale. In general, the breads were evaluated by seven panelists in duplicate on two different days. The sigmoid relationship between sensory crispness and water content was fitted as described by Primo-Martín and van Vliet (2009).

### 3.2.8. Scanning electron microscopy (SEM)

Gold coated crust pieces with channels were visualized with a field emission scanning electron microscope (Tescan Mira, accelerating voltage of 7 keV) equipped with an EDX analyzer (Bruker).

### 3.2.9. Statistical analysis

Analyses of linear correlation (Pearson), least significant difference, and one-way ANOVA were done using SPSS v 11 (SPSS Inc., Chicago, IL). One-way ANOVA was used to compare the means of the ten tested breads used in the sensory test (fixed factor) in their sensory properties crispness, softness of crumb, and hardness of crust (dependent variables).

## 3.3. Results

### 3.3.1. Appearance of crust and channels

In this study we created crispy breads with channels in the crust (Fig. 3-1). The magnification of the crust with SEM revealed that the round channels had shape edges and that the intact crust around the channels did not differ visually from the rest of the crust (Fig. 3-1b). The crust of the created 13 different types of breads differed in the distance between the channels and in the total punctured surface (Fig. 3-1a, Table 3-1). The punctured surface was calculated using the measured diameter of channels after baking, which was slightly smaller than the needle diameter (Table 3-1).

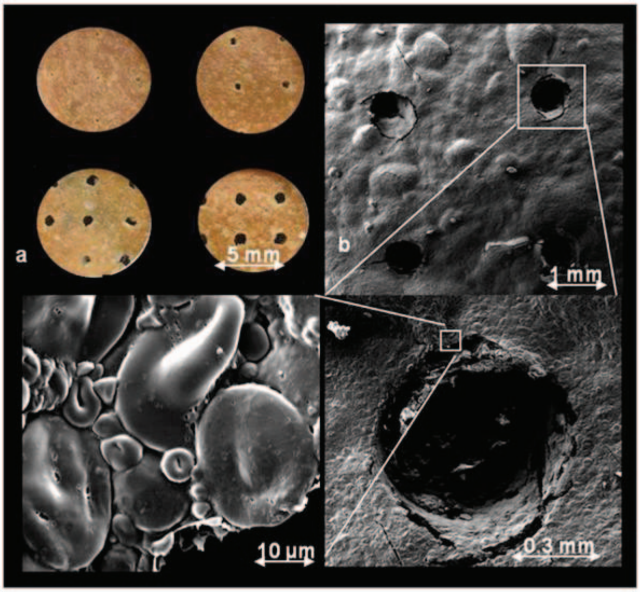



Fig. 3-1: Appearance of bread crusts with channels. (a) Scanned pieces of crust with a diameter of 8 cm. The diameters of the channels are 0.5 mm, 0.8 mm, 1.4 mm and 1.8 mm (from top left to bottom right). Pictures were taken with an Epson Perfection V700 Photo scanner (Seiko Epson Corporation, Nagano, Japan). (b) SEM pictures of breads with a channel diameter of 0.5 mm and a channel distance of 3 mm.

### 3.3.2. Water vapor permeability and water content of crust

Our aim was to determine the water vapor permeability of crust for optimal crispness retention, therefore, we measured the water vapor permeability for all different crust types (Table 3-1). This water vapor permeability was related to the water content of the crust 4 h after baking the breads (Fig. 3-2). The highest water content and the lowest water vapor permeability occurred in breads that were sealed with paraffin (bread F). When the water vapor permeability of the crust increased from 0 g/(m s Pa) up to $8 \times 10^{-9}$ g/(m s Pa), the water uptake decreased and the relationship between the water vapor permeability and the water content of the crust was almost linear. Breads with a higher water vapor permeability had a similar water uptake of approximately 7%.

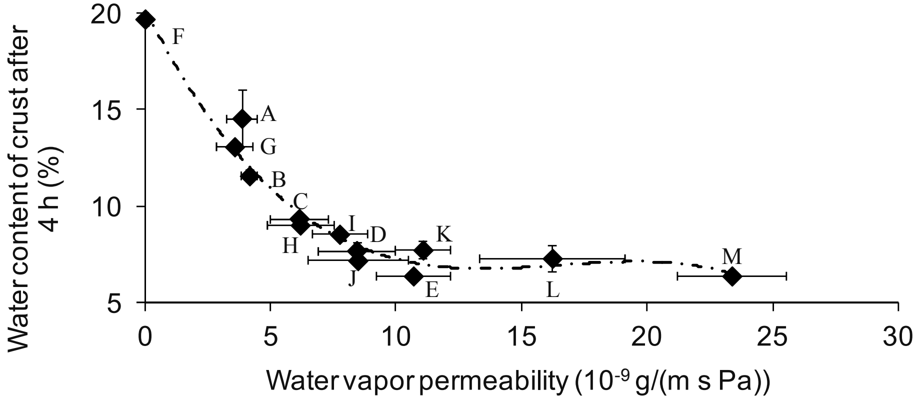



Fig. 3-2: Relationship between the water vapor permeability and the water uptake of crust. The letters indicate the different puncturing settings of the breads given in Table 3-1. $R^2$ of polynomial trendline is 0.96. n≥4.

### 3.3.3. Instrumental crispness

We also measured the instrumental crispness to determine which breads had the highest crispness retention. It is known that sensory crispness sensation is related to the mean sound pulse intensity and the number of sound pulses generated during instrumental evaluation (Castro-Prada et al., 2009; Mohamed et al., 1982; Roudaut et al., 1998; Zampini and Spence, 2004). Therefore, we measured these two acoustic parameters at two storage times and found a clear relationship between them and the water vapor permeability of the crust (Fig. 3-3). Fig. 3-3a shows that the highest mean sound pulse intensity was measured for breads with a water vapor permeability of crust of approximately $8 \times 10^{-9}$ g/(m s Pa) after storing for 30 min and 4 h. For breads with a water vapor permeability higher than $5 \times 10^{-9}$ g/(m s Pa), the measured mean sound pulse intensity after 4 h was higher than the mean sound pulse intensity for breads without channels after storing for 30 min. Fig. 3-3b shows that the number of sound pulses increased with increasing water vapor permeability also for water vapor permeabilities higher than $8 \times 10^{-9}$ g/(m s Pa).

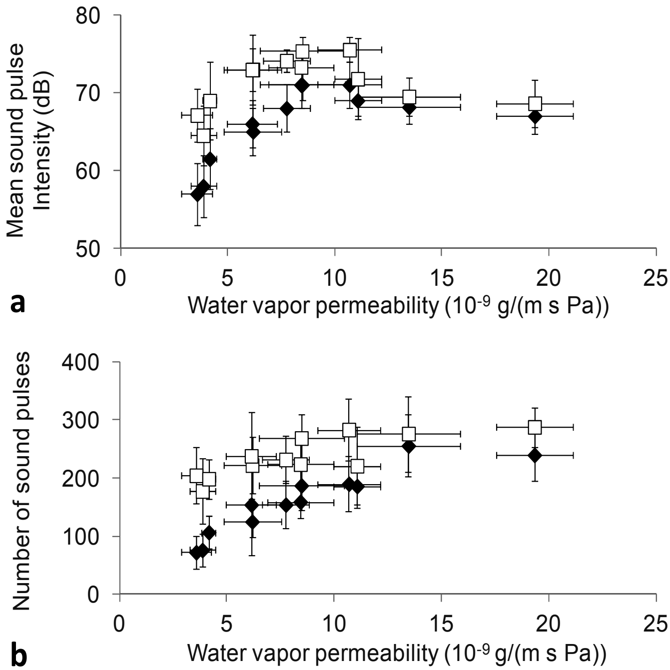



Fig. 3-3: Breads with a certain crust permeability were first stored at 40% relative humidity and then fractured. In the figures the water vapor permeability of the crust is related to the measured mean sound pulse intensity (a) and the number of sound pulses (b) during fracture. Closed symbols, 4 h storage time; open symbols, 30 min storage time. n≥4.

### 3.3.4. Sensory analysis

We also performed a sensory study in which we determined crispness and hardness of the crust, as well as the softness of the crumb. The results for the crispness attribute are presented in Fig. 3-4a. In all five breads tested crispness decreased between 30 min and 4 h storage time. However, the decrease was much lower for breads with a water vapor permeability higher than $7 \times 10^{-9}$ g/(m s Pa), which also had the highest crispness score after 4 h storage time. Comparing the breads stored for 4 h and 30 min showed that the panelists did not perceive a significant difference in crispness between breads with a water vapor permeability above $5 \times 10^{-9}$ g/(m s Pa) stored for 4 h and breads without channels stored for 30 min.

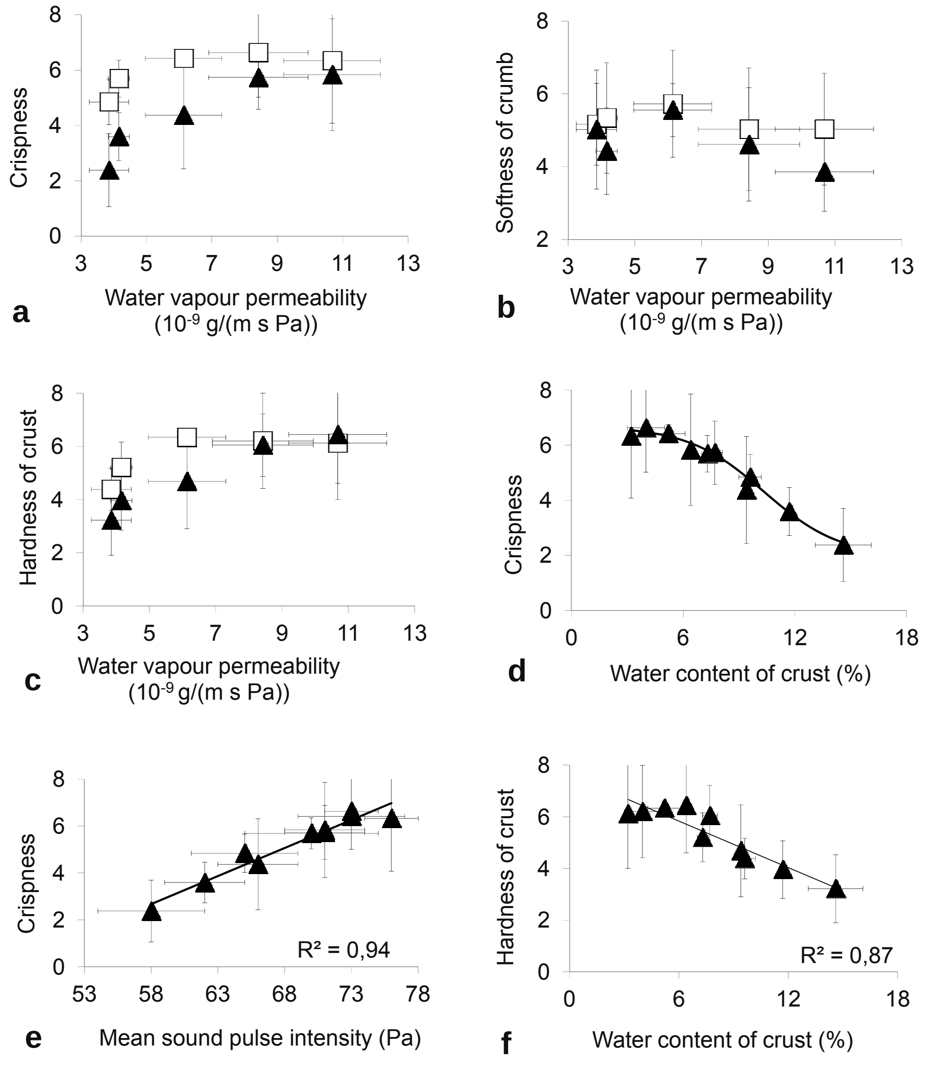



Fig. 3-4: Sensory evaluation of breads with different water vapor permeability of the crust. The sensory rating in crispness, softness of crumb, and hardness of crust of 5 different breads (A, B, C, D, and E, characteristics of bread type given in Table 3-1) with different water vapor permeability is shown in (a) – (c). The breads were tested after storing for 30 min (open symbols) and after storing for 4 h (closed symbols). n = 14, except for breads C and D. The relationship between sensory crispness, water content of the crust after storage for 4 h, mean sound pulse intensity, and hardness for bread A, B, C, D, and E at 30 min and 4 h storage time are shown in (d), (e), and (f). $n \geq 4$.

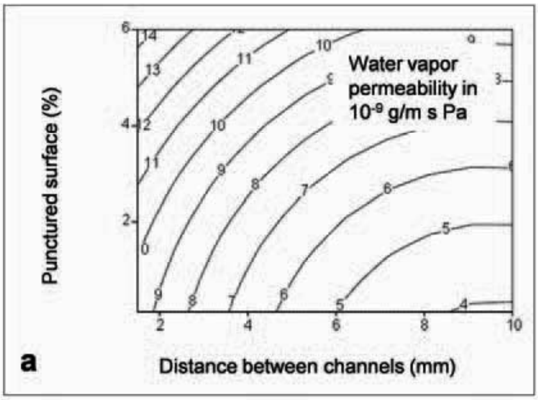
The creation of channels in the crust not only led to a higher crispness retention of the crust but also to a higher total water loss of the breads (Table 3-1) (Chapter 2) and a slightly different water content profile in the outer crumb (Voogt et al., 2011) during storage. This higher water loss could lead to a drying out of the crumb and therefore to a lower softness sensation of the crumb by the panelists. After storing for 30 min, the softness of the crumb did not differ significantly between the breads (Fig. 3-4b). However, after storing for 4 h, breads with a water vapor permeability higher than $9 \times 10^{-9}$ g/(m s Pa) had a significantly ($p < 0.05$) lower crumb softness than breads without channels.

Panelists also evaluated the hardness of the crust (Fig. 3-4c). After 30 min storage time, breads with a higher crust water vapor permeability had a harder crust. However, in these breads hardness did not significantly increase between 30 min and 4 h. Hardness sensation is correlated with a low water content (Fig. 3-4f). Breads with a higher water vapor permeability had a lower water uptake of the crust.

We also related sensory crispness to several instrumental parameters to select parameters that are suitable for predicting sensory crispness sensation in breads. The fracture parameters measured (the number of force drops ($R^2$ = 0.76), the slope of the force–time curve ($R^2$ = 0.70), and the maximum force ($R^2$ = 0.61)) showed significant correlation with the crispness attribute ($p < 0.01$). However, the acoustic parameters (maximum sound intensity ($R^2$ = 0.93), number of sound pulses ($R^2$ = 0.83), and mean sound pulse intensity ($R^2$ = 0.94, Fig. 3-4e)) showed stronger correlations.

### 3.3.5. Relation between puncture setting and water vapor permeability

To create breads with optimal crispness retention, it is important to understand the relationship between the puncture settings (i.e. punctured surface and distance between channels) and the water vapor permeability. This relationship is shown in Fig. 3-5a.



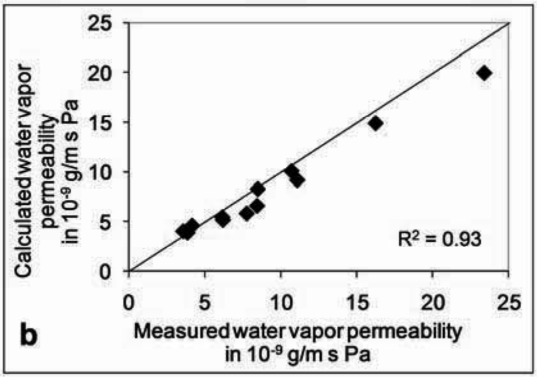




Fig. 3-5: (a) Relationship between puncture settings and the measured water vapor permeability. The relationship between distance between channels, punctured surface and water vapor permeability in $10^{-9}$ g/(m s Pa) (contour lines) is based on a multivariate regression done with Mathcad 13.1, in which the experimental data was used to fit a 2nd order polynomial surface. (b) The measured water vapor permeability is related to the calculated water vapor permeability, which is based on the punctured surface (Eq. (3.3)), n ≥ 4.

We were interested to know if the measured water vapor permeabilities could be predicted from the punctured surface by modeling. Therefore, we calculated the water vapor permeabilities for all puncture settings, summing up the water vapor permeabilities for the punctured surface (channels) and the not punctured surface (Eq. 3.3) and relating both values to each other. Fig. 3-5b shows that the calculated and measured water vapor permeabilities were very well related ($R^2 = 0.93$). In Eq. (3.3), the water vapor permeability is calculated using the punctured surface ($A_1$), but not the distance between the channels. This suggest that the water vapor permeability was dependent on the punctured surface and that the distance between the channels had just an indirect influence: if the distance between the channels was increased keeping the punctured surface constant, the diameter ($d$) of the channels was increased, a variable used in Eq. (3.3).

## 3.4. Discussion

An increase in crispness retention in crispy breads, like baguettes, would be very beneficial, because breads lose their crispy characteristic within a few hours (Luyten et al., 2004). In the instrumental study described in Chapter 2 it was show that increasing the water vapor permeability of the crust provides an effective way to increase crispness retention. However, increasing crust water vapor permeability may also lead to an increased loss of water from the inner crumb, which would lead to unwanted crumb dryness. Based on these findings we aimed to determine the optimal water vapor permeability of crust.

To determine the water vapor permeability that is optimal for crispness retention we established the relationship between water vapor permeability and mean sound pulse intensity. The highest mean sound pulse intensity was found in breads with a water vapor permeability of $8 \times 10^{-9}$ g/(m s Pa) (Fig. 3-3a). This result suggests an optimal crispness retention around that value.

This optimum could be confirmed and explained by the measured water uptake (Fig. 3-2). It is known that the water uptake of bread crust and sensory crispness are very well related (as shown in Fig. 3-4d), and that half of the crispness is lost if the water content exceeds a critical water content of 10% (Fig. 3-4d, Primo-Martín and van Vliet (2009)). Control breads exceeded this critical water content quickly, because the less permeable crust acted as a barrier for water migration (Chapter 2). If the barrier properties of the crust were minimized by increasing the water vapor permeability of crust from 0 to $8 \times 10^{-9}$ g/(m s Pa), however, less water accumulated in the crust (7% versus 20%; Fig. 3-2). This water content of 7% relates to the equilibrium water content of crust at the storage conditions of 40% relative humidity used (results not shown). This equilibrium was reached in all crusts with a water vapor permeability above $8 \times 10^{-9}$ g/(m s Pa), because the water activity of crust cannot be maintained for long below this equilibrium water content.

Crispness retention is not just dependent on the water vapor permeability of the crust, but also on the initial water distribution in the bread, the structure of the crust, and the storage conditions. In addition also the properties of the crumb are important, because water migrates from the crumb to the crust. Voogt et al. (2011) suggested that the morphological parameters are more important than the material properties of the crumb. All these factors are most likely dependent on each other, so that an increase of the water vapor permeability at different settings would increase crispness retention with a different extent. If, for example, breads are stored at other storage conditions, the crust will probably also reach the equilibrium water content within 4 h as in this study. If this equilibrium water content exceeds 10%, e.g. at storage condition with a high relative humidity, not just normal breads will lose crispness fast (Primo-Martín et al., 2006; Primo-Martín et al., 2010), but probably also breads with high water vapor permeability of the crust.

The sensory study also confirmed an optimal water vapor permeability of around $8 \times 10^{-9}$ g/(m s Pa), because the increase in water vapor permeability up to this value significantly increased the crispness of breads. In breads with a water vapor permeability of and above $8 \times 10^{-9}$ g/(m s Pa) (bread D and E) crispness sensation did not differ significantly between bread types and between storage times. Such minor differences in crispness sensation for short and long storage times were not reported before (Primo-Martín et al., 2006; Primo-Martín and van Vliet 2009; Primo-Martín et al., 2010). This sensory study was mainly done to investigate, whether puncturing has a negative effect on the crumb properties. We could show that the crumb softness was not significantly lower up to 4 h storage for water vapor permeability values up to $8 \times 10^{-9}$ g/(m s Pa). Slight negative effect were detected, if the water vapor permeability of the crust was above $8 \times 10^{-9}$ g/(m s Pa) and are likely, if breads with channels are stored for a very long time.

In this study, we evaluated crispness using an instrumental and a sensory evaluation and could therefore determine the instrumental parameters that best predict sensory crispness. The parameter that correlated most with sensory crispness was the mean sound pulse intensity ($R^2$ = 0.94). Mohamed et al. (1982), Roudaut et al. (1998) and Zampini and Spence (2004) showed good correlation between sensory crispness and sound intensity. The number of sound pulses, in contrast, was less related to sensory crispness ($R^2$ = 0.83), because crusts with big and/or many channels, exhibited the highest amount of sound pulses which were lower in intensity. Already van Vliet and Primo-Martín (2011) critically discussed the use of the number of sound events as a single factor to rate sensory crispness. Both the number of sound pulses and the mean sound pulse intensity are needed for a more comprehensive description of crispness. However, we propose mean sound pulse intensity to be the best single factor to predict sensory crispness.

The water vapor permeability depends on different properties of the crust, for example the puncture setting. The relationship between the punctured surface and the water vapor permeability at a constant diameter of the channels was approximately linear (Table 3-1). This linear relationship is not valid for fractures in geological materials (Witherspoon et al., 1980; Zimmerman and Bodvarsson, 1996), probably because of the different size, form and surrounding material of fractures in crust and geological material and different transport mechanisms. However, the linear relationship between permeability and open area was also found for perforated packaging films for fruits and bread (Silva et al., 1999; Pagani et al., 2006; Paul and Clarke, 2002). Thus, bread crust behaves similarly to a film. Perforated films are often used as packaging for bread, because the perforations allow accumulating free moisture to escape and therefore ensure longer crispness retention (Setser, 1996). Therefore, not just a certain water vapor permeability of crust is necessary to maintain long crispness retention but also a certain water vapor permeability of the package material. However, a very high permeability of the package material does not decrease the water uptake of crust further (Pagani et al., 2006). We have shown that an optimal water vapor permeability also exists for crust. This optimal water vapor permeability of $8 \times 10^{-9}$ g/(m s Pa) could be reached in our study by different combinations of punctured surface and distance between the channels (Fig. 3-5a). Thus, we can recommend puncture settings to produce breads with optimal crispness and crumb softness retention at the storage conditions used.

The variations of channel diameter and punctured area can help to understand the mechanism of the migration of water vapor through punctured crust. Our modeling shows that the measured water vapor permeability can be predicted by summing the water vapor migrating through the not punctured crust and the water vapor migrating through the air in the channels (Fig. 3-5b). In addition we could show that the water vapor permeability is dependent on the size and shape of the channels, but not on the distance between the channels. This result indicates that the water vapor transport to the environment is dependent on the transport through the open surface of the crust, but not dependent on the transport of water vapor close under the crust towards the channels.

Changing water vapor permeability could also be the mode of action of other methods that increase crispness retention. The six-fold longer crispness retention of crust treated with protease (Primo-Martín and van Vliet, 2009), which makes the gluten network more open (Primo-Martín et al., 2006), could be related to a more permeable crust, as well as the increased instrumental crispness of breads with increased crust porosity (Primo-Martín et al., 2008a). Our observations indicate that the formation of macroscopic cracks in the crust that occur in certain types of breads shortly after baking will also lead to an increased water vapor permeability of crust and therefore longer crispness retention. The effect of cracks on crispness retention is studied in Chapter 5. Thus, the systematic study reported here will provide guidance to other non-mechanical ways of improving crispness retention.

We conclude that by creating channels with different size and distance in the crust we can control the water vapor permeability, the water uptake, and the crispness retention of crust. Using this knowledge we can create breads with optimal water vapor permeability of crust and eight-fold longer crispness retention without negative effects on crumb softness.

## Acknowledgement

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# Chapter 4

## Does crumb morphology affect water migration and crispness retention in crispy bread?

## Abstract

Crispness of bread is rapidly lost because of water migration inside the crumb towards the crust. How crumb properties determine this process independent of crust properties has not been examined before. Therefore, the aim of this study was to analyze and explain the influence of crumb morphology on the overall crispness retention. Crispness retention was determined by analyzing the acoustic emission of breads differing in either crust or crumb morphology. When crumb morphology is coarse with a lower number of large connections between the air cells, the effective diffusion coefficient is reduced. This effective diffusion coefficient of crumb, which equals approximately half the value of air, was estimated using X-ray micro-computer tomography images of crumb pieces. If the crumb has a lower effective diffusion coefficient, bread with similar crust properties has significantly longer crispness retention. Despite this, our data show that variations in properties of crust, which has 30 times higher permeability than crumb, have a larger impact on crispness retention than variations in properties of crumb.

## 4.1. Introduction

Bread is in a non-equilibrium state after baking because of the different water activities of the dry crust and the wet crumb. These differences in water activity lead to water migration in the direction of the crust. If the water content of the crust exceeds a certain value, crispness disappears (Luyten et al., 2004). Because crispness contributes to the total sensory experience and is critical to consumer acceptance and appreciation, loss of crispness should be delayed as much as possible.

In previous papers, we have demonstrated that the water uptake of the crust is strongly influenced by the water vapor permeability of the crust (Chapter 2,3). In these studies, we have taken the transport of water from the inside of the crumb to the crust as a constant. However, large variations in crumb morphology may exist, which in turn could affect water transport and crispness retention.

Properties of crust and crumb are different: crust is dryer, harder, darker and denser and can be separated from the crumb based on these criteria (Vanin et al. 2009). In this study we separated crust from crumb based on the color. These differences will cause a different speed and mechanism of water migration through the crumb and the crust.

The water migration in the crumb is related to different mechanisms: the water transport in the solid, the exchange of water at the gas–solid interface, and the water vapor diffusion through the gas phase. In cellular structures with a high connectivity, such as bread crumb, the water vapor diffusion through the gas phase dominates, because the flux through the gas phase is approximately three orders of magnitude larger than the flux through the solid phase (Esveld et al, 2012a; Voogt et al., 2011). The speed of vapor diffusion through the gas phase can be expressed by the effective diffusion coefficient for vapor and the water vapor permeability and is dependent on the porous structure, in particular on the porosity and tortuosity.

Although the morphology of the crumb could be important for water migration, its impact on the water uptake of crust has never been studied independently of the crust properties. Therefore, the aim of this study was to determine the influence of crumb morphology on the water uptake of crust and the overall crispness retention. To achieve this aim, we developed a composite bread-making process that allows breads to be created with different crumb morphologies and defined crust properties. We studied the water uptake of crust and instrumental crispness of breads stored at 40% relative humidity after 4 h storage time. We also developed two methods to determine the water vapor permeability of the crumb. In addition, we used X-ray imaging to identify those morphological parameters of crumb that most influence the diffusion of vapor.

## 4.2. Materials and methods

### 4.2.1. Baking and storage of breads

Standard breads were prepared as described in Chapter 2 with minor modifications. This preparation involved the following steps: mixing, proving (75 min), part baking (180 °C, 10 min), freezing, baking off and storage (22 °C, 40% relative humidity). Breads were baked off in a convective Bakermark Mastermind oven (Leventi, Gilze, The Netherlands), in which internal fans evenly circulated hot air. In addition to the bread baked using the standard recipe (3000 g wheat flour, 20 ppm ascorbic acid, 46 g dry yeast, named SS), we baked bread containing no ascorbic acid (0 ppm ascorbic acid, 50 g dry yeast, named AA), bread containing DATEM (15 g DATEM (Kerry Bio Functional Ingredients, Zwijndrecht, The Netherlands), 20 ppm ascorbic acid, 35 g dry yeast, named DD) and bread containing potassium bromate (50 ppm potassium bromate (Merck, Darmstadt, Germany), 20 ppm ascorbic acid, 38 g dry yeast, named BB) (Fig. 4-1). Yeast addition was adjusted to get breads with a similar volume. Potassium bromate and DATEM addition should reduce cell size of the crumb as described by Nunes et al. (2009) and Sapirstein et al. (1994).

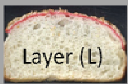
| Crust (Layer?) | Crust (Channels?) | Crumb | | | |
|---|---|---|---|---|---|
| | | Standard (S) | No ascorbic acid (A) | DATEM (D) | Potassium Bromate (B) |
|   |   | LS | LA | LD | LB |
|   |   | CS | CA | CD | CB |
|   |   | SS | AA | DD | BB |

Fig. 4-1: Illustration of the composition of baked breads

In order to vary the crumb independently from the crust, we prepared composite breads by using the same series of dough, and put a separate sheet of standard dough on top of the dough roll before proving (bread LS, LA, LD, and LB; Fig. 4-1). The dough for the layer contained wheat flour (1000 g, 7 °C), dry yeast (16.7 g), salt (20 g), water (593 g, 10 °C) and ascorbic acid (20 ppm) and was mixed in a spiral mixer (model SM 10, Sinmag, Zuienkerke, Belgium) until the dough reached a temperature of 26 °C. After mixing, the dough was sheeted and allowed to rest for 15 min. The combination of sheeting and resting was repeated twice. The dough was then rolled out with a sheeter (Seewer Rondo model SS064 C, Seewer AG, Burgdorf, Switzerland) and round thin dough pieces with a weight of approximately 12 g and a thickness of approximately 2 mm were cut out with a form of 80 mm diameter. These dough sheets were put on the rounded dough made from the four different recipes. The weight of this rounded dough was adjusted so that the total weight of each type of bread was 75.6 g. After freezing, some of these composite breads were punctured as described in Chapter 2 to obtain the channeled breads CS, CA, CD, and CB (Fig. 4-1). These breads contained uniformly distributed channels with a diameter of 0.5 mm and a distance between them of 3 mm. The cross section of the breads was scanned with an Epson Perfection V700 Photo scanner (Seiko Epson Corporation, Nagano, Japan). In the scanned breads a red colorant was brushed on the rounded dough surface, before the dough sheet was put on it, to distinguish both parts in the scanned figures of the baked bread.

### 4.2.2. Water transport

In macroscopic samples such as crumb, water transport is dominated by the transport of vapor through the air phase (Esveld et al., 2012a) going from regions with high vapor concentration to regions with low vapor concentration:

$$J = -D_{v,eff} \nabla \rho_v \tag{4.1}$$

where $J$ is the water vapor flux, $\rho_v$ is the vapor concentration, $\nabla$ is the gradient operator, and $D_{v,eff}$ is the effective water vapor diffusion coefficient for vapor in crumb. The latter is determined by the morphology of the porous sample and can be estimated from X-ray micro-computer tomography (µCT) as described in section 4.2.3.

In bread crumb, not only vapor diffuses through the cells but also water is exchanged between the gas in the cells and the solid beams, resulting in changing water content of the solid matrix. The total water transport in the sample can be described by a Fickian diffusion equation containing the gradient of water concentration (on dry basis, $w$) and the effective water diffusion coefficient $D_{w,eff}$:

$$\frac{dw}{dt} = \nabla \cdot (D_{w,eff} \nabla w) \tag{4.2}$$

The effective water diffusion coefficient $D_{w,eff}$ is given by

$$D_{w,eff} = \frac{D_{v,eff} + \rho_{v,sat}}{(1-\varphi)\rho_{s,dry}(\frac{dw}{da_w})} \tag{4.3}$$

where $\varphi$ is the porosity, $\rho_{s,dry}$ is the density of dry solid of 1490 kg/m$^3$, $\rho_{v,sat}$ the water density in saturated air (which at 22 °C is equal to 0.020 kg/m$^3$), and d$w$/d$a_w$(solubility) is the change in water concentration d$w$ for a given change in water activity $a_w$ (derived from Eq. (8) in Esveld et al., 2012a). The change in water concentration was determined by equilibrating pieces of crumb for at least five days at 92% relative humidity in a gravimetric moisture sorption analyzer (SPSx-1µ, Projekt Messtechnik, Ulm, Germany) or at 96% relative humidity over a saturated $KH_2PO_4$ solution. Therefore, the total water migration through the crumb in bread depends not on the diffusion coefficient in the solid part but on the sorption behavior of the solid part and the porous structure of the gaseous part, and can be expressed as the effective diffusion coefficient for water (Esveld et al., 2012a).

### 4.2.3. µCT, image analysis and modeling of the effective diffusion coefficient

Crust was separated from crumb after baking based on color differences. By visual discrimination, all white crumb material was removed from the brown crust pieces, which were approximately 1.3 mm thick, using a scalpel. Primo-Martín et al. (2010) and Lind et al. (1991) used a similar separation technique based on visual estimation. The more physical based distinction technique described by Jefferson et al. (2006) and Mohd Jusoh et al. (2009) defined crust to be thicker than 4 mm. However, we consider bread parts 4 mm under the surface as crumb, because their color and structure is more similar to crumb than to crust. In addition, the used techniques are more applicable for measuring crust thickness than for separating crumb from crust.

Images of crust and crumb samples (crumb from bread LS, LA, LD, and LB) were taken with a Skyscan 1172 desktop µCT system as described by van Dalen et al. (2007). The three-dimensional (3D) images obtained with a resolution of 6 µm were further used to determine morphological parameters as described by Esveld et al. (2012a). XRT data analysis was performed using Matlab (MathWorks) in combination with the image analysis toolbox DIPlib (Delft University of Technology, the Netherlands). This analysis included transformation into a binary image, determination of the porosity, segmentation into individual cells, measurement of the volume of each cell, determination of the surface area of the cell that is open to other cells, and determination of the size of the connections between the cells. Connections between cells are defined as the area, where the air space of two cells is touching each other. If this touching area is larger than 100 $\mu m^2$ the connection was called large. Connectivity is defined as the percentage of cells connected to other cells. This information was, in a further step, reduced to a 3D picture of connections, in which the diffusion pathway between the pores was depicted. With this network model, the effective diffusion coefficient for vapor through the air phase of the crumb, $D_{v,eff}$, was calculated (Eq. (4.1)). From the 3D µCT images, we determined the morphological parameters and the effective vapor diffusion coefficient for each crumb type (8 replicates of each, in total 32 images).

### 4.2.4. Water vapor permeability

The water flux can also be expressed in terms of the water vapor permeability (WVP):

$$J = -WVP\nabla P_v \tag{4.4}$$

where $P_v$ is the relative water vapor pressure. From the universal gas law and Eq. (4.1), the water vapor permeability can be calculated as

$$WVP_{model} = \frac{D_{v,eff} M_w}{R_g T} \tag{4.5}$$

where $M_w$ is the molar mass of water (18 g/mol), $R_g$ is the gas constant (8.31 J/mol per K) and $T$ is the temperature (here 295 K).

The water vapor permeability of the crust was measured using the method described in Chapter 2. In this method a constant water activity gradient from 0.85 to 0.40 at a temperature of 22 °C was applied to a piece of crust. Due to this water gradient, water vapor migrated from one side of the crust to the other. The quantity (weight) of this water vapor was determined per time (G). From this measurement, which took at least 24 h, the water vapor permeability was calculated as

$$WVP = \frac{G \cdot x}{A \cdot \Delta P_v} \tag{4.6}$$

where $G$ (g/s) is the quantity of water migrating through the sample per second, $x$ (m) is the thickness of the crust, $A$ (m$^2$) is the area of the crust, and $\Delta P_v$ (Pa) is the partial water vapor pressure difference across the sample, which is 1187 Pa for the given conditions. During this measurement, a constant water activity gradient existed in the crust so that no water uptake or release from the solid took place. Therefore, no property of the solid matrix (e.g. $dw/da_w$) was needed to calculate the water vapor permeability.

To determine the quantity of water migrating through a piece of crumb, the setting of the experimental water vapor permeability measurement was adopted to consider the different properties of crust and crumb. For example, a larger piece of sample as well as a different water activity gradient was used. The crumb water activities were set to 0.96 (sample cup) by using a saturated $KH_2PO_4$ solution and to 0.92 (environment). The crumb pieces, were analyzed within 40 min after baking, were 12 ± 1 mm thick with an area of $0.41 \pm 0.01 \times 10^{-3}$ $m^2$ and were sealed and attached to the measurement system using paraffin. The measurement took five days and at least four samples per formulation were measured. The results were used to calculate the water vapor permeability using Eq. (4.6).

### 4.2.5. Water content of crust

The water content (wet basis) of the total crust was calculated using the weight determined with an analytical balance before and after drying at 105 °C for 24 h for at least five replicates per setting.

### 4.2.6. Acoustic analysis to measure instrumental crispness

The acoustic characteristics of the crust were measured as described in Chapter 2. The bread crusts were fractured vertically with a texture analyzer at a speed of 20 mm/s using a rectangular cuboid as probe (area touching the sample was 1 mm thick and 10 mm wide). The acoustic characterization involved the determination of the number of sound pulses and the mean sound pulse intensity.

### 4.2.7. Modeling the water uptake of crust

The Fickian diffusion model of Voogt et al. (2011) (Eq. (4.2)) was used to predict the change in water content in the crust and crumb during storage by assuming different water vapor permeabilities for both parts. This allowed us to model the effect of the morphology of crumb (expressed as permeability) on water uptake in a combined crust–crumb system. In this model several simplifications were made, e.g. the temperature is constant during cooling, the water vapor permeability of the outer crust is constant, despite multiple openings, and the density of the crumb and inner crust is constant, although the density increases towards the crust (Jefferson et al., 2007).

### 4.2.8. Statistics

Two-way ANOVA, correlation analyses (Pearson), and t-test ($p < 0.05$) were done using SPSS v 11 (SPSS Inc., Chicago, IL).

## 4.3. Results

### 4.3.1. Crumb: morphology and water vapor permeability

We aimed to study the influence of different crumb morphologies on crispness retention of bread. Therefore, we prepared breads with fine and coarse morphologies (Fig. 4-2). The morphology of the crumb with no added ascorbic acid was coarser than the standard crumb. This crumb had a lower number of cells, thicker cell walls, a lower connectivity, and fewer connections between the cells (Table 4-1). If, in contrast, DATEM or potassium bromate was added, the crumb became finer. However, these two crumbs also differed in their morphology, because breads prepared with potassium bromate contained a high number of very small cells and very small connections.

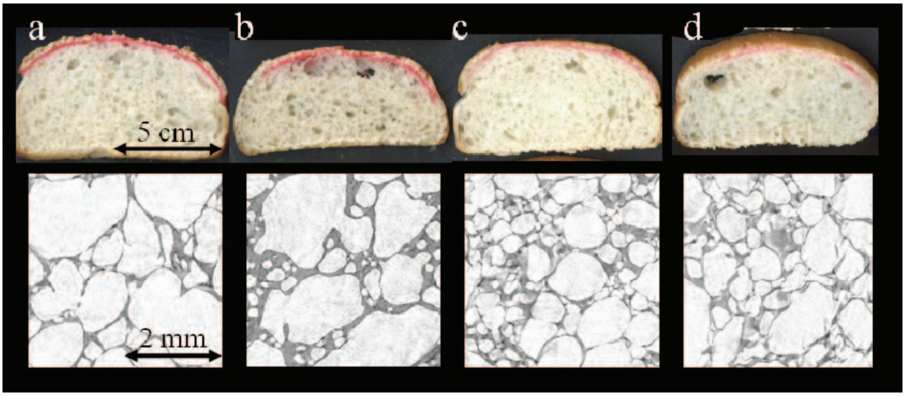



Fig. 4-2: Images of sliced composite bread (upper row) baked with a standard recipe (a), without addition of ascorbic acid (b), with addition of DATEM (c) or potassium bromate (d). Red colorant was put between the dough roll and the dough layer before proving. Cross-sections of the corresponding X-ray images of the crumb are shown in the lower row.

Table 4-1: Properties of crust and crumb: Morphological parameters and water vapor permeability (WVP) of 32 crumb compartments, eight for each crumb type, were determined as described in Section 4.2 and correlated ($R^2_{single}$). The mean values of each crumb type, given with the standard deviation in the table, were correlated to the mean water vapor permeability ($R^2_{mean}$). The water vapor permeability of crumb and crust were determined experimentally as described in Section 4.2. Different letters indicate significant differences.

| | Crumb types | | | | Correlation with crumb WVP | |
|---|---|---|---|---|---|---|
| | Standard | No ascorbic acid | DATEM | Potassium bromate | $R^2_{single}$ | $R^2_{mean}$ |
| **Morphological parameters** | | | | | | |
| Number of cells per mm$^3$ | 32 ± 15[a] | 18 ± 4[b] | 76 ± 9[c] | 146 ±143[c] | 0.15 | 0.64 |
| Median of cell size in 10$^3$ µm$^3$ | 300 | 2189 | 834 | 2 | – | 0.69 |
| Cell wall thickness (µm) | 37 ± 6[a] | 61 ± 4[b] | 20 ± 1[c] | 26 ± 4[d] | 0.54 | 0.87 |
| Porosity | 0.81 ± 0.01[a] | 0.73 ± 0.03[b] | 0.79 ± 0.01[c] | 0.77 ± 0.03[c] | 0.10 | 0.17 |
| Connectivity (%) | 99.61 ± 0.21[a] | 98.09 ± 0.86[b] | 99.98 ± 0.01[c] | 99.94 ± 0.03[d] | 0.41 | 0.71 |
| Surface area of cell open to other cells (%) | 20 ± 10[a] | 11 ± 2[bc] | 16 ± 1[bc] | 19 ± 10[ac] | 0.11 | 0.23 |
| Size of connection (µm$^2$) (median) | 577 | 1761 | 1818 | 245 | – | 0.84 |
| Number of connection per mm$^3$ | 64 ± 37[a] | 24 ± 5[b] | 214 ± 33[c] | 244 ±165[c] | 0.40 | 0.95 |
| Number of large connections (>100 µm$^2$) per mm$^3$ | 52 ± 25[a] | 23 ± 5[b] | 194 ± 32[c] | 162 ± 62[c] | 0.61 | 0.99 |
| **Water vapor permeability** | | | | | | |
| WVP in 10$^{-7}$ g/(m s Pa) (modeling X-ray) | 0.8 ± 0.2[a] | 0.7 ± 0.3[a] | 1.3 ± 0.3[b] | 1.2 ± 0.2[b] | 1 | 1 |
| WVP in 10$^{-7}$ g/(m s Pa) (experimental) | 1.7 ± 0.2[a] | 1.7 ± 0.1[a] | 1.9 ± 0.1[a] | 1.8 ± 0.1[a] | – | 0.97 |
| **Crust[a]** | | | | | | |
| WVP in 10$^{-7}$ g/(m s Pa) of crust (experimental) | 0.034 ± 0.004[a] | 0.025 ± 0.003[b] | 0.036 ± 0.006[a] | 0.029 ± 0.004[b] | – | – |

[a]Water vapor permeability of sheeted crust and crust with channels was (0.033 ± 0.005) × 10$^{-7}$ g/(m s Pa) and (0.058 ± 0.004) × 10$^{-7}$ g/(m s Pa), respectively.

In Table 4-1, the experimentally measured water vapor permeabilities of all four crumb types are given. The values, which were around $1.8 \times 10^{-7}$ g/m s Pa) were not significantly different.

In addition, we tried to measure the water vapor permeability of air by removing the crumb sample from the cell. The water vapor permeability of vapor in air was calculated to be $1.87 \times 10^{-7}$ g/(m s Pa) using the known diffusion coefficient of water vapor in air of $2.55 \times 10^{-5}$ $m^2$/s and Eq. (4.5). The measured value of $(4.01 \pm 0.04) \times 10^{-7}$ g/(m s Pa) is nearly double the calculated value, probably because of air movement over the cup.

We also calculated water vapor permeability from the µCT by modeling the resistance of vapor transport. The modeled effective diffusion coefficients for vapor were between $1.1 \times 10^{-5}$ and $1.9 \times 10^{-5}$ $m^2$/s and the corresponding water vapor permeabilities were between $0.8 \times 10^{-7}$ and $1.3 \times 10^{-7}$ g/(m s Pa) (Table 4-1). These values for crumb are close to the value of vapor transport in air.

Furthermore, we related the water vapor permeability to morphological parameters. On the one hand, we determined $R^2_{single}$ by using the morphological data generated from each of the 32 single compartments for the correlation analysis. On the other hand, we determined $R^2_{mean}$ by comparing the mean values of each crumb type. It was found that the number of large connections correlated best with the water vapor permeability ($R^2_{single} = 0.61$, $R^2_{mean} = 0.99$), whereas porosity, number of cells and surface area of cells open to other cells were not related to this value (Table 4-1). The number of large connections was not only linearly related to the modeled water vapor permeability, but also to the cell wall thickness to the power of –2.045 ($R^2_{single} = 0.86$).

In addition to the estimation of the effective diffusion coefficients for vapor in crumb we also estimated the effective diffusion coefficient of water, which is normally given in the literature (Eq. (4.2)). This value was around $0.16 \times 10^{-9}$ $m^2$/s and similar for all crumbs. This determination involved the calculation of the sorption behaviour for all four crumb types ($\mathrm{d}w = 0.281 - 0.291$) for a change in water activity from 0.92 to 0.96 ($\mathrm{d}a_w$ = 0.04).

### 4.3.2. Crust: Water vapor permeability

The water vapor permeabilities of crust are also given in Table 4-1. Crust of bread baked with no ascorbic acid (AA) or potassium bromate (BB) had significantly lower water vapor permeability than crust from bread baked with a standard recipe (SS). In contrast, the water vapor permeability of sheeted crust was $(0.033 \pm 0.005) \times 10^{-7}$ g/(m s Pa), which was not significantly different from standard crust. The crust with channels had the highest permeability of $(0.058 \pm 0.004) \times 10^{-7}$ g/(m s Pa).

### 4.3.3. Breads: water content and instrumental crispness

The properties of twelve different bread types containing the described crusts and crumbs were studied. All these breads had an almost similar specific volume and height, ranging from 3.3 ml/g to 3.8 ml/g and 45 mm to 53 mm, respectively. If the crust property was kept the same in these breads but the crumb morphology was changed (bread LS, LA, LD, and LB), the water content significantly differed after 4 h storage time (Fig. 4-3a). The same trend was visible if channels were applied to the crust; this resulted in breads with the lowest water uptake and highest mean sound pulse intensity (Fig. 4-3a, 4-3b). However, if crust and crumb were made from the same dough, different trends were observed (Bread SS, AA, DD, and BB). In general, a high correlation degree exists between water content, mean sound pulse intensity, and number of sound pulses (Fig. 4-3).

When all breads were considered, the maximal difference in crispness achieved by crumb variation was lower than achieved by crust variation. If the crust properties were kept the same and the crumb properties were changed, the water uptake could be lowered by 2.7% (from 14.1% (bread LB) to 11.4% (LS)) and the mean sound pulse intensity could be increased by 9.9 dB. Crust variation allowed an increase of 6.0% and 14.0 dB (comparing breads AA and CA), which is considerably more. In addition, a two-way ANOVA revealed that crumb and crust properties alone determined crispness retention. Both crumb and crust properties had a significant influence ($p < 0.05$) on the water uptake, mean sound pulse intensity and number of sound pulses.

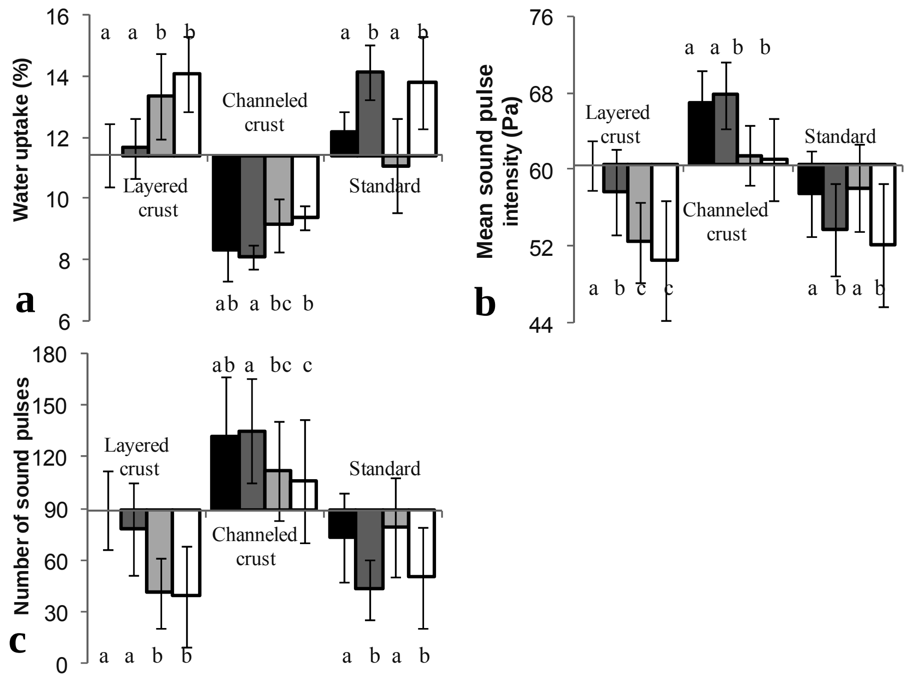



Fig. 4-3: Water uptake and instrumental crispness of composite breads (layered crust or channeled crust) and standard breads. The crumb dough was made by using a standard recipe (S, black), adding no ascorbic acid (A, dark grey), adding DATEM (D, light grey) or potassium bromate (B, white) as described in the methods. After 4 h storage time, the water content of the crust was determined (a) as well as the mean sound pulse intensity (b) and the number of sound pulses of the fractured crust (c) as described in Section 4.4.2. Different letters indicate significant differences ($p < 0.05$) between breads with the same crust type.

### 4.3.4. Comparison of modeled and measured water uptake of crust

In the last part of our study, we challenged our experimental results using modeling. We predicted the water uptake of the crust within the first five hours of storage using a Fickian diffusion model, as described by Voogt et al. (2011) (Fig. 4-4). We used the modeled (X-Ray based) water vapor permeabilities of crumb. The experimental determined water uptake after 30 min and 4 h for all layered breads were almost the same as the modeled values measured after these storage times.

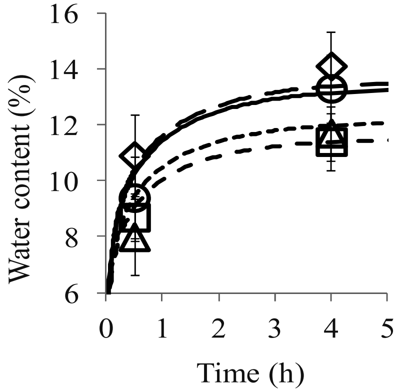



Fig. 4-4: Comparison of modeled and measured water uptake of crust. The water uptake of crust was measured after 30 min and 4 h of layered bread LS (open square, standard crumb), LA (open triangle, crumb containing no ascorbic acid), LD (open circle, crumb containing DATEM), and LB (open diamond, crumb containing potassium bromate). For the same breads (LS, dotted line; LA, short-dashed line; LD, long-dashed line; and LB, solid line) this value was estimated using the model of Voogt et al. (2011).

## 4.4. Discussion

Crispness of bread is lost fast, because water migrates towards the crust through the open cellular system of the crumb. How the morphology of crumb influences water uptake of crust and crispness retention has never been experimentally determined before and was therefore the aim of this study.

To study the influence of morphology of crumb separately, we created composite breads with similar crust but different crumb properties using a layer approach. Composite breads and standard breads had similar properties, because crumb and crust were very well connected and because the water uptake and water vapor permeability of crust did not differ significantly (bread SS and LS, $p < 0.05$, Table 4-1; Fig. 4-2, 4-3).

Analogous to our method for the determination of crust water vapor permeability (Chapter 2), we developed a method for measuring crumb water vapor permeability by determining the water vapor flux through crumb pieces. However, we did not find significant differences between the four crumb structures tested (Table 4-1). The high level of porosity made it virtually impossible to reach a sufficiently stable water vapor gradient in the system. For example, slight differences in other parameters, e.g. air speed on the crumb surface, could influence this susceptible measurement, in which the measured water vapor permeability of crumb was very close to the permeability of vapor in air. We conclude that the measurement of the water vapor permeability of very open structures is not reliable, although it is functional for dense systems like crust.

Due to the limitations of the experimental approach, we determined the water vapor permeability of crumb by modeling the resistance of vapor transport through the open cellular structure using 3D images generated by µCT. With this method, we estimated water vapor permeabilities that were significantly higher for crumb containing DATEM and crumb containing potassium bromate than for standard crumb and crumb containing no ascorbic acid (Table 4-1). The modeled water vapor permeability of crumb is half the value of air, the same factor was found for experimental determined water vapor permeability of crumb and air.

The determination of the water vapor permeability of crumb and crust showed that crust is a more powerful barrier against water migration than crumb. We calculated that crumb has a 30 times higher water vapor permeability than crust. Differences in density (Jefferson et al., 2007) and porosity of crust (approximately 55 % (Primo-Martín et al., 2010)) and crumb (approximately 80 % (Table 4-1)) alone cannot explain these huge differences, because porosity and the effective diffusion coefficient are linearly related. This implies a different connectivity and tortuosity of crumb and crust. Differences in the permeability of crust and crumb have already been assumed by several authors, but never experimentally determined. For example, Zhang and Data (2005) assumed that crust permeability is four times lower than crumb permeability in their baking model. The difference in permeability is the reason for the pressure built up in bread during baking and different diffusion speeds in both parts (Grenier et al., 2009; Zhang and Data, 2005). Crust acts as a barrier against water migration during storage (Chapter 2), whereas the open cellular crumb is very transparent in terms of vapor transport and water vapor migrates half as fast through crumb as through air. For open cellular food, other authors have calculated such high water vapor permeabilities and effective diffusion coefficients based on diffusion experiments at ambient temperatures. The values of 0.1 × $10^{-9}$ $m^2/s$ determined for biscuits (Roca et al., 2006) and 0.8 × $10^{-9}$ $m^2/s$ for crackers ($a_w$ = 0.86, coarse biscuit) (Esveld et al., 2012b) are comparable to the effective water diffusion coefficient of around 0.2 × $10^{-9}$ $m^2/s$ in our study. The differences are related to different porosity and water content of the samples examined.

The X-ray pictures generated were also used to determine morphological parameters of the crumbs, e.g. cell wall thickness, as already done by Babin et al. (2006), Falcone et al. (2004), Lassoued et al. (2007), and Primo-Martín et al. (2010). All these works quantified higher cell wall thickness compared to this work, in which a higher resolution was used during the X-Ray analysis. This comparison indicates that the measured morphology parameters are very dependent on the resolution used. In addition, the analysis of all four crumb types with X-rays showed that the crumb of bread had a high connectivity of over 98% as already shown by Babin et al. (2006) and Primo-Martín et al. (2010). Therefore, more than 98% of the cells are open and connected to each other. However, the four crumbs differed significantly in their morphology. For example, crumb containing DATEM or potassium bromate contained more cells and thinner cell walls. This result is in agreement with the literature (Nunes et al., 2009; Sapirstein et al., 1994).

From the results of the determination of the morphological parameters of the crumb, we can suggest parameters that characterize a crumb with high permeability. The high permeability of crumb containing DATEM or potassium bromate is probably related to the high number of large connections between the cells in these crumbs. If more connections between the cells are present, more routes for water vapor transport are available resulting in faster water vapor transport. We suggest that these large connections occur preferably in thinner cell walls, which probably rupture more easily during proving and baking. Thinner cell walls are more prevalent in crumb containing DATEM or potassium bromate (Table 4-1). It is known that the effective diffusion coefficient is linearly related to the tortuosity and porosity. In our work, porosity of the samples had almost same values, therefore, they likely differed in tortuosity. Chaunier et al. (2008) suggested that the permeability of baked products not only depends on the porosity but also on the pore shape and porous structure. In addition, we did not found a good relationship between the water vapor permeability and the surface area of cell open to other cells, and the number of cells. This result does not support the suggestion of Esveld et al. (2012b) and Primo-Martín et al. (2010) that differences in the surface area of cell open to other cells, the number of big cells, and the size of gas cells are the reasons for differences in the diffusion speed. In both studies, however, other baked porous products with varying porosities were used. In contrast, we could show that a finer crumb enabled faster vapor transport.

The main aim of this paper was to determine how important crumb morphology is for crispness retention. We showed that crispness retention was dependent on crumb morphologies when the crust properties were kept the same. The reason for the longer crispness retention of breads with coarse crumb was probably the lower computed values of water vapor permeability of the crumb of these breads. The lower water vapor permeabilities led to a slower water vapor migration from the crumb to the crust, which led to a slower water uptake of crust and hence to a longer crispness retention. Further proof that a slower water uptake is caused by differences in water vapor permeability is provided by the model developed by Voogt et al. (2011). The modeling of water migration during storage within bread predicted the differences in water uptake of layered crust well if the measured differences in water vapor permeability were assumed (Fig. 4-4).

We assume that in this work the differences in water uptake are mainly caused by differences in water migration during storage and not by different initial water distribution. We did not detect right after baking significant differences in water content of crust (< 1 %) and water content of inner crumb (44% ± 1%) between the four formulations, therefore, we assume for simplification an equal water distribution after baking for breads with different crumb permeability. We also made this assumption, because changes in the water content during baking are mainly dependent on the baking conditions. However, we are aware that differences in permeability could have an effect on the weight loss during baking and on the water distribution within the outer crumb after baking.

Although crumb morphology had an effect on the water uptake of crust, the effect of crust properties was twice as high. Breads with the highest crust permeabilities (CS, CA, CD, and CB) had the lowest water uptake of crust and the highest crispness retention. Therefore, the negative effect on water uptake induced by using fine crumb morphologies could be compensated by crust variation. This result confirms the conclusion made in Chapter 2 that crust permeability is key for crispness retention. The relationship between water vapor permeability of crust and water uptake of crust described in Chapter 3 can explain the differences in water content in breads SS, AA, DD, and BB.

We conclude that defined properties of bread are necessary to increase crispness retention. For long crispness retention, a low permeability of crumb is favorable. This occurs in crumb with a low number of large connections between the cells. In contrast, crust should contain connections throughout the crust, e.g. channels, which increases the water vapor permeability and crispness retention. In our study only variations in crust properties increased crispness retention and the influence of the crust is larger compared to the crumb. Therefore, we suggest focusing on crust properties to create breads with optimal crispness retention.

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# Chapter 5

## Cracks in bread crust cause longer crispness retention

## Abstract

Crispness is among the most important factors that the consumer uses to assess the quality of crispy bread. However, this quality attribute is rapidly lost after baking. It is known that crispness retention can be increased more than eight times by enhancing the water vapor permeability of the crust. Current methods to achieve this, i.e., puncturing the bread before baking, require an extra process step. We hypothesize that cracks that appear spontaneously on the crust surface after baking can also enhance water vapor permeability and therefore improve crispness retention. We were able to confirm this hypothesis by preparing composite breads containing the same crumb but different crusts, with crust recipes of varying starch/protein ratios. Bread crusts with a high gelatinized starch content had many cracks. These cracks led to an increased water vapor permeability of the crust and an eight times longer instrumental crispness retention compared to standard bread. In this paper we also discuss possible causes for crack formation in the crust. We hypothesize that effective cracks are caused by thermal shock in materials with a low ability to dissipate energy.

## 5.1. Introduction

Crispness is an important sensory attribute of crispy breads. However, this pleasant sensation is lost within a few hours after baking, because of water migration within the bread (Luyten et al., 2004). The duration of crispness is associated with quality and freshness of the product and is appreciated by the consumer. In Chapter 3 it was shown that the fast loss of crispness can be prevented by increasing the water vapor permeability of the crust to an optimal value. Optimal permeability was achieved by puncturing artificial channels through the crust before baking off. These channels serve as open areas and reduce the barrier properties of the crust for water vapor. This is especially important when the bread cools, directly after baking. An increased release of water vapor prevents the water from accumulating in the crust, leading to a significantly slower increase of water activity in the crust and thus to a significantly increased retention of crispy features. However, puncturing is an extra process step and also changes the appearance of the crust. Therefore, we aimed to obtain optimal permeability with another method, which is based on ingredient variation.

It is well known that cracks spontaneously form in the crust after the bread exits the oven and cools down (Baardseth et al., 2000; Nebesny, 1995; Qarooni et al., 1988). This prompted the question of whether this process can be used to create sufficient numbers of cracks to increase water vapor permeability and thereby crispy retention. This idea is supported by results of Baardseth et al. (2000), suggesting a relationship between crack formation in the crust and sensory crispness. However, no explanation for this observation was given.

Cracks in bread crust are formed when stresses build up in the crust that cannot be dissipated (Luyten et al., 2004). The stresses responsible for crack creation are either caused by thermal shock or contact loading (Danzer et al., 2008). For example, the contact loading of teeth during eating induces crack creation in dry bread crust, which is necessary for a crispness sensation. The occurrence of these cracks is related to the water content and water activity, because stresses are dissipated as a function of molecular mobility (van Nieuwenhuijzen et al., 2008, 2010). Therefore, around a water content of 10%, the crust changes from an easily fracturing, brittle, crispy material to a ductile material without sound emission (Primo-Martín and van Vliet, 2009).

Directly after baking, temperatures are above the glass transition temperature, and the water content is very low (Cuq et al., 2003; van Niewenhuijzen et al., 2008; Chapter 2). This provides excellent conditions for crack formation. However, polymers present in the crust could also dissipate the stresses that are occurring. We therefore decided to vary the main macropolymer components of the wheat flour: gluten and starch. Baardseth et al. (2000) have already shown that the use of flour with the highest protein content resulted in breads with the lowest number of cracks and the lowest crispness score. Gluten forms a continuous network in the bread crust, in which partly gelatinized starch is embedded (Moss, 1975; Primo-Martín et al., 2006, 2007). Overall, approximately 40% of the starch in the crust is not gelatinized, and the degree of gelatinization increases when moving towards the crumb (Primo-Martín et al., 2007). A change in the composition and/or properties of the main ingredients will probably affect the ability of the network to dissipate stresses, which will result in different cracking patterns of the crust.

A variation of ingredients in the whole bread would result in different volume, water content, and morphology of the crumb. In Chapter 4 it was shown that the morphology of the crumb also affects crispness retention. Therefore, we aimed to exclude the influence of this factor, and baked so-called composite breads as described in Chapter 4. In composite breads, the crumb and the crust are made from different dough. Thus, the composition of the crust layer was changed while keeping the properties of the crumb the same. In Chapter 4 it was shown that composite and standard breads had a similar volume and water uptake of the crust and an inseparable connection between the crust and the crumb when the same standard dough was used for both bread types. Therefore, this provides a unique system that allows us to uncouple crust and crumb properties.

Using these approaches, we aimed to create composite breads with a different number of cracks in their crust. We hypothesize that cracks change the water uptake of the crust and therefore crispness retention. In addition, we aimed to understand how and why the cracks are formed in the bread crust.

## 5.2. Materials and methods

### 5.2.1. Materials

Breads were baked using Salvia flour (12% protein and approximately 80% starch, Meneba Meel BV, Rotterdam, The Netherlands), vital gluten (Protinax® 137, AVEBE, Veendam, The Netherlands, protein content 78%), and wheat starch (Excelsior, AVEBE, Veendam, The Netherlands).

### 5.2.2. Preparation of breads

Composite breads were prepared as described in Chapter 4 with minor modifications and different crust layers. Composite breads were composed of a standard dough (3000 g Salvia flour, 50 g yeast, 70 g NaCl, 20 ppm ascorbic acid) and an added dough layer that formed the crust. The dough layer contained 4.97 g yeast, 5.95 g salt, 20 ppm ascorbic acid, 174 g water, and either flour only or different combinations of flour, vital gluten, and wheat starch, as shown in Table 5-1. The numbers in the bread names indicate the approximate gluten content (dry matter base) of the crust layers, assuming that the flour protein has a gluten content of 85% (Osborne, 1907). The dough was mixed for 6 min, which is the optimal mixing time of the standard dough F10, using 300 g kneading chamber of the Farinograph (Brabender, Duisburg, Germany). These mixing times and water content were, therefore, not optimal for some doughs. However, we standardized these settings to avoid having a higher initial water content that influence crispness retention. After a rest of 15 min, the dough was sheeted and round thin dough pieces were cut, which were 12 ± 1 g in weight, approximately 80 mm in diameter, and approximately 2 mm thick. Each dough piece was placed on a piece of rounded standard dough, whose weight was adjusted, by the weighing and removing excess of dough, so that the total weight of each dough piece before 90 min proving was 75.6 g. After proving, the breads were part-baked (10 min at 180°C), cooled, frozen for less than one week, baked, and stored at 40% relative humidity and 22°C, as described in Chapter 4.

Table 5-1: Properties of bread crust. We added different quantities of flour, wheat starch, and gluten to the dough and calculated the starch content based on the composition. We determined, as described in section 5.4.2, the gelatinized starch using DSC; the equilibrium water content by storing crust pieces at 40% relative humidity; the open area of crust by determining the width and length of cracks per area; and the water vapor permeability by determining the flux of water vapor through crust pieces.

| Bread type | F5 | F7 | F10 | F14 | F25 | GS 5 | GS 7 | GS 10 | GS 14 | GS 25 |
|---|---|---|---|---|---|---|---|---|---|---|
| Flour addition (g) | 149 | 208 | 298 | 281 | 231 | - | - | - | - | - |
| Wheat starch addition (g) | 143 | 86 | - | - | - | 272 | 267 | 258 | 244 | 201 |
| Vital gluten addition (g) | - | - | - | 15 | 61 | 14 | 19 | 27 | 41 | 82 |
| Starch content db % | 90 | 86 | 80 | 76 | 62 | 95 | 93 | 90 | 85 | 70 |
| Gelatinized starch content db (%) | 69 ± 3 | 62 ± 1 | 39 ± 1 | 37 ± 2 | 31 ± 1 | 88 ± 1 | 76 ± 3 | 73 ± 5 | 66 ± 3 | 53 ± 4 |
| Equilibrium water content db (%) | 7.5 ± 0.3 | 7.3 ± 0.7 | 8.2 ± 0.4 | 7.7 ± 0.6 | 7.4 ± 0.4 | 8.9 ± 0.4 | 9.1 ± 0.1 | 8.7 ± 0.3 | 8.9 ± 0.4 | 9.4 ± 0.1 |
| Open area of crust (%) | 1.7 ± 0.3 | 1.3 ± 0.2 | 0.2 ± 0.0 | 0.3 ± 0.3 | 0.0 ± 0.0 | 2.1 ± 0.2 | 2.0 ± 0.4 | 1.9 ± 0.2 | 1.6 ± 0.2 | 0.9 ± 0.2 |
| Water vapor permeability ($10^{-9}$ g/m s Pa) | 6.6 ± 1.2 | 7.5 ± 1.5 | 4.4 ± 1.0 | 4.9 ± 0.5 | 3.5 ± 0.6 | 8.5 ± 1.4 | 7.2 ± 1.2 | 7.4 ± 0.6 | 7.4 ± 0.8 | 3.5 ± 0.6 |

### 5.2.3. Equilibrium water content

We aimed to determine the equilibrium water content of separated crust pieces under the storage conditions used for the breads (40% relative humidity, 22 °C). Therefore, the crusts were first dried over Phosphorus Pentoxide ($P_2O_5$) (Sigma-Aldrich, Chemie GmbH Steinheim, Germany) for one week. Afterwards crust pieces were equilibrated at 40% relative humidity and 22°C in a climate cabinet (Weiss SB $11^{300}$, Weiss Technik, Ltd, Buckinghamshire, UK). Then, they were dried in an oven at 105 °C for 24 h. The equilibrium water content was calculated using the weight before and after drying of at least five replicates per setting.

### 5.2.4. Starch gelatinization

Starch gelatinization was assessed by differential scanning calorimetry (DSC) as described by Primo-Martín et al. (2007). Freeze-dried crust samples, wheat flour and wheat starch were analyzed using distilled water at a ratio of 1:4 (w/v). The quantity of ungelatinized starch was calculated as the quotient of the melting enthalpy of the starch crystallites in the crust sample (peak 70°C) that did not gelatinize during baking, and the enthalpy of starch gelatinization of wheat flour or wheat starch (depending on the formulation of the crust). This value was used to calculate the amount of gelatinized starch in relation to the total dry matter in the crust. Two replicates per formulation were analyzed.

### 5.2.5. Scanning electron microscopy

Gold-coated crust pieces were visualized with a field emission scanning electron microscope (SEM, Tescan Mira, accelerating voltage of 7 keV) equipped with an EDX analyzer (Bruker). These figures were used to determine the width of cracks.

### 5.2.6. CSLM

We performed Confocal Scanning Laser Microscopy (CSLM) to determine the distribution of starch and protein in the crust. Crust samples were incubated with two fluorescent probes, fluorescein 5-isothiocyanate (FITC, 0.85% in water) and Rhodamine B (0.15% in water). FITC stained starch granules more selectively (shown in green color) while Rhodamine B reacted with protein (shown in red color). Samples were incubated for approximately 5 min and then studied with a Leica TCS SP (Leica Microsystems, Heidelberg, Germany) CLSM with an Ar/Kr laser. Two excitation wavelengths, 488 nm and 568 nm for FITC and Rhodamine B, respectively, were used, and the obtained images were overlaid to allow simultaneous visualization of starch and protein.

Protein poor area was determined using ImageJ (a public domain Java image processing software) and defined as the percentage of the green area in the CSLM figures (hue higher than 65, black area was neglected). Five different crust images were analyzed per formulation.

### 5.2.7. Open area of crust

To describe the size of the cracks we determined the width of the cracks and the length of the cracks in a certain area in the crust. The length of the cracks was determined in images of the crust surface (Epson Perfection V700 Photo scanner, Seiko Epson Corporation, Nagano, Japan; resolution 400 dpi; four breads per formulation), which was scanned after 4 h storage time. In these images the length of the cracks was measured in a defined area using the imaging software Cell$^{P}$ (Olympus Europa GmbH, Hamburg, Germany). The width of the cracks was measured using confocal laser scanning microscopy (CSLM) and scanning electron microscope (SEM) figures. The width of the cracks was multiplied by the total length per area of the cracks to estimate the open area of the crust as a percentage of the total area.

### 5.2.8. Water vapor permeability

The water vapor permeability of the crust was measured using the method described in Chapter 4. The measurement involved the determination of the quantity of water vapor that migrated through a piece of crust, when a constant water activity gradient from 0.85 to 0.40 was applied. Five replicates per formulation were analyzed.

### 5.2.9. Water content of crust

The water content (wet basis) of the total crust was calculated using the weight determined with an analytical balance before and after drying at 105 °C for 24 h for at least five replicates per setting.

### 5.2.10. Acoustic analysis to measure instrumental crispness

The acoustic characteristics of the crust were measured as described in Chapter 2. The bread crusts were fractured vertically with a texture analyzer at a speed of 20 mm/s using a rectangular cuboid as a probe (area touching the sample was 1 mm thick and 10 mm wide). Acoustic characterization involved the determination of the number of sound pulses and the mean sound pulse intensity.

#### 5.2.11. Statistics

Analyses of linear correlation (Pearson), and t-test ($p < 0.05$) were done using SPSS v 11 (SPSS Inc., Chicago, IL).

## 5.3. Results

### 5.3.1. Visual properties of crust: Starch and gluten distribution and cracks

We created breads with different numbers of cracks on the surface by changing the composition of the crust. Standard breads (F10) had only a few wide cracks on the surface (Fig. 5-1c). If the crust standard recipe was diluted with starch (F5, F7), many small cracks appeared on the crust surface (Fig. 5-1a, 5-1b). These types of cracks were also visible on bread GS5, GS7, GS10, and GS14 (Fig. 5-1f, 5-1i), in which gluten-starch mixtures were used for the bread crust. The small cracks had a width of approximately 60 µm measured on the CSLM and SEM pictures (Fig. 5-1k, 5-1l, 5-1r, 5-1s, 5-1v). In contrast, the width of the wide cracks, which occurred on breads F10, F14, and GS25, was approximately 120 µm (Fig. 5-1c, 5-1d, 5-1j, 5-1m, 5-1x, 5-1y). Bread F25 did not contain any crack at all (Fig. 5-1e). All small cracks and approximately 50% of the wide cracks were already visible 5 min after baking. Some of the wide cracks appeared later and became wider during storage.

The dimensions of the cracks were described in more detail by the water vapor permeability and the open area of the crust (Table 5-1). The open area of the crust was calculated using the length of the cracks per area, which was, for example, 0.28 mm/mm$^2$ for crust F5 and 0.02 mm/mm$^2$ for crust F10. The length was multiplied by the average width of the cracks to determine the open area of the crust. Since the width of cracks is not constant but varies along the crack, the calculation of the open area of the crust is a qualitative estimate. We, therefore, also determined the water vapor permeability. Water vapor permeability and the open area of the crust were significantly related ($R^2 = 0.77$). If the open area of the crust was larger than 1%, the water vapor permeability was higher than $6 \times 10^{-9}$ g/(m s Pa) and significantly higher than the water vapor permeability of standard crust ($4 \times 10^{-9}$ g/(m s Pa)) (Table 5-1).

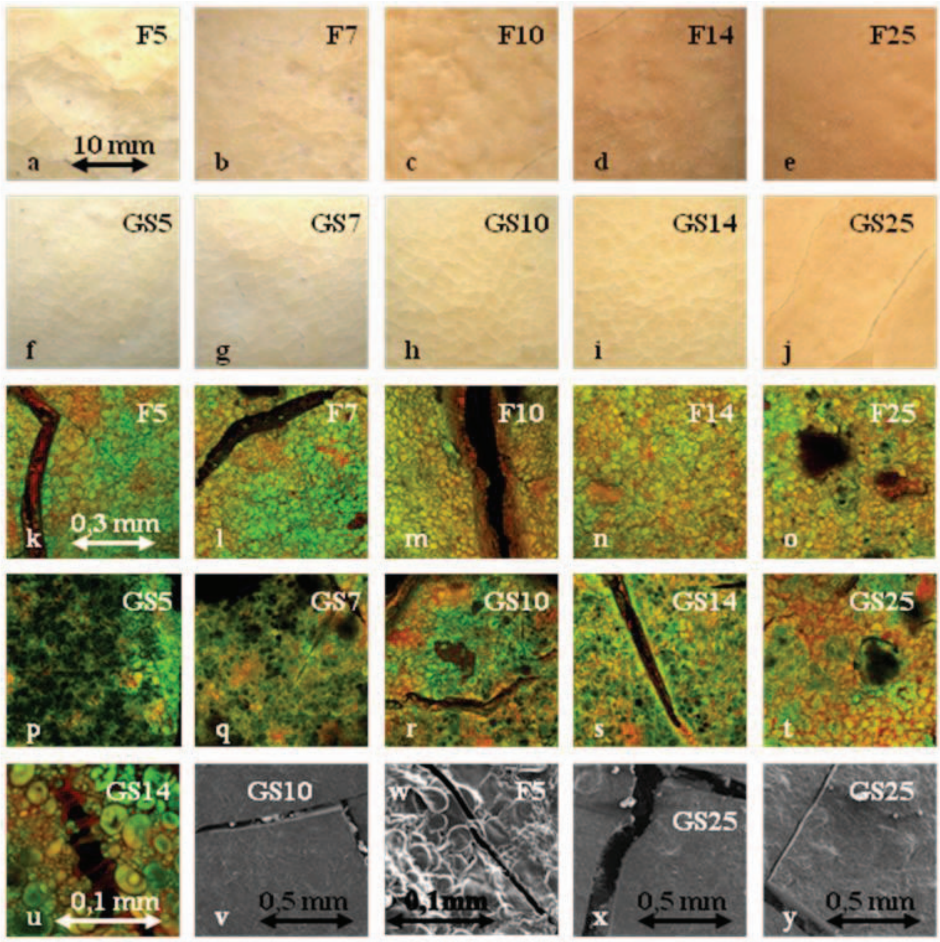


Fig. 5-1: Images of crust surfaces from breads prepared with different gluten-starch contents: (a) - (j) scan of bread crusts, (k) - (t) CSLM figures of bread crust, (u) CSLM image of crust showing a crack with protein strings, (v) - (y) SEM images. For codes of samples see section 5.2.2. Size bar given in figure (a) applies for figures (a) – (j). Size bar given in figure (f) applies for figures (f) - (t).

Crusts also differed in other properties, e.g., the starch content, the equilibrium water content, and the quantity of ungelatinized starch after baking, as shown in Table 5-1. The equilibrium water content at 40% relative humidity was higher for crusts containing a mixture of wheat starch and vital gluten, and was not related to the water vapor permeability ($R^2$ = 0.03). The quantity of gelatinized starch, in contrast, was related to the water vapor permeability

($R^2 = 0.78$), and was higher for bread crust with a low amount of gluten and flour.

With CSLM, the distribution of protein and starch in the crust was visualized (Fig. 5-1k-5-1t). In some crust types, F10, F14, F25, and GS25, starch granules (green) were well embedded into the gluten (red) network, so that the color distribution is more homogeneous and appears as yellow, because of the mixture of starch and protein (red and green). Few single red or green spots are visible (Fig. 5-1m, 5-1n, 5-1o, 5-1t). In contrast, in most crusts from gluten-starch mixtures (GS5 - GS14) and in crusts F5 and F7, the distribution is inhomogeneous, and many green and red spots are visible, indicating local concentrations of gluten or starch (Fig. 5-1k, 5-1l, 5-1p-5-1s). With CSLM two other phenomena could also be visualized: a) cracks that are going through starch granules (Fig. 5-1u) and b) protein strings, which are spanned in cracks (Fig. 5-1w).

### 5.3.2. Water uptake of crust and crispness retention

In Fig. 5-2 the relationship between water vapor permeability and the water uptake of the crust after 4 h storage time is given. By using different ingredients in the crust, the water vapor permeability was increased from $4 \times 10^{-9}$ g/(m s Pa) to $7 \times 10^{-9}$ g/(m s Pa), causing a decrease of the water uptake from 13% to 9%. Around a water content of 10% bread crust becomes un-crispy (Chapter 3; Primo-Martín and van Vliet, 2009). In Fig. 5-2 the results of this study are compared to the found relationship in Chapter 3.

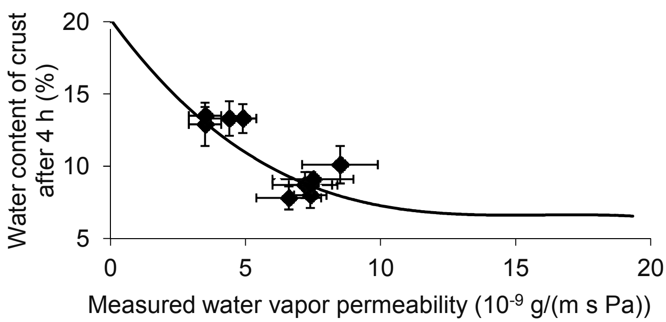


Fig. 5-2: Relationship between measured water vapor permeability and water uptake of crust after 4 h storage time. The line fitted the relationship found for breads with channels (Chapter 3), and the dots represent the data of this study.

These large differences in water uptake caused significant variation in crispness retention (Fig. 5-3). Breads F10, F14, F25, and GS25 (group I) were considered to be not crispy after 4 h storage time, because their mean sound pulse intensity was lower than 64 dB (Fig. 5-2). This mean sound pulse intensity equals the critical water content of 10%, where half of the crispness is lost (Chapter 3; Primo-Martín and van Vliet, 2009). Some breads (group II), in contrast, had intensities much higher than 64 dB, and were therefore considered to be crispy after 4 h storage time. This property applied to bread F5, which had 147 ± 31 sound pulses, with a mean sound pulse intensity of 66 ± 3 dB; bread F7, which had 131 ± 28 sound pulses, with 68 ± 4 dB intensity; and bread GS14, which had 128 ± 27 sound pulses, with 67 ± 7 dB intensity. These values are significantly higher than the 73 ± 43 sound pulses, with a mean sound pulse intensity of 55 ± 7 Pa of standard bread (F10) after 30 min storage time, indicating a crispness retention more than eight times longer. Some breads (group III) also had, besides a high mean sound pulse intensity, a high maximal force. Since this maximal force, which is needed to fracture the breads, is known to relate to the hardness of breads, we consider breads to be hard if the maximal force is higher than 30 N. Breads considered to be hard (GS5, GS7, GS10) had a harder, denser, and less cellular crust.

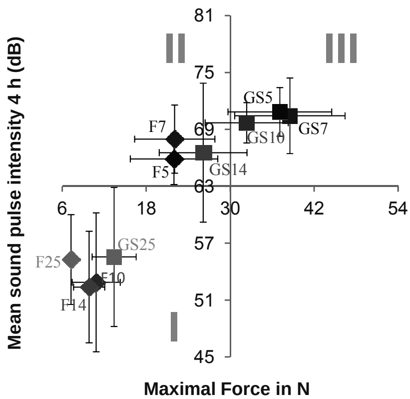


Fig. 5-3: Acoustical-mechanical profiling of bread crusts. Bread crusts were fractured after 4 h of storage time, as described in material and methods. The illustration of the relationship between maximal force and mean sound pulse intensity allows the division into three groups: breads in group I are not crispy, breads in group II are crispy and breads in group III are hard. Codes of samples are given in section 5.2.2 and an explanation for the division into hard, crispy, and not crispy is given in section 5.3.2.

In Fig. 5-4, the relationship between the measured mean sound pulse intensity and the water vapor permeability of all analyzed breads was compared to the relationship of breads with channels (Chapter 3). For both data sets the trend is almost similar as well as the maximum mean sound pulse intensity. In Chapter 3 breads in a wider water vapor permeability range were analysed.

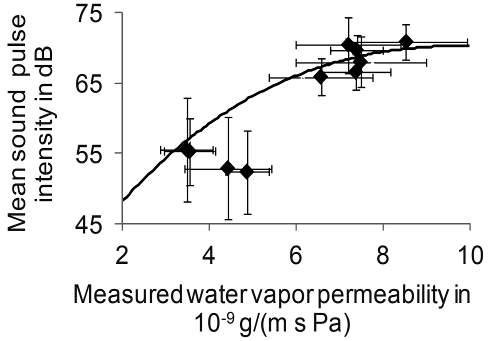


Fig. 5-4: Relationship between the measured water vapor permeability and the mean sound pulse intensity during fracture of the crust after 4 h storage at 40% relative humidity. The line is a fit of the relationship found for breads with channels (Chapter 3), and the dots represent data of this study.

## 5.4. Discussion

Loss of crispness can be prevented by creating breads with a high crust permeability. Current methods to achieve the optimal crust permeability of $8 \times 10^{-9}$ g/(m s Pa) require an extra process step (Chapter 3). Our hypothesis is that cracks occurring spontaneously on the crust surface after baking can also increase permeability of the crust and therefore crispness retention.

We could induce the formation of cracks after baking by varying the crust ingredient composition (Fig. 5-1). Especially breads with an ungelatinized starch content higher than 60% in their crust showed many small cracks on their crust surface (F5, F7, GS14) (Table 5-1, Fig. 5-1). However, an increase of ungelatinized starch content in GS crust over 70% was not beneficial, because these crusts were hard and less cellular (GS5, GS7, GS10). All breads varied only in their crust properties, and the properties of the crumb were similar. This independent variation of crust and crumb properties was possible by using composite breads (Chapter 4).

Bread crusts with many small cracks on their surface had an optimal water vapor permeability, and crispness retention was more than eight times longer than crusts of standard breads (Table 5-1). Therefore high crispness retention can be achieved by ingredient variation in the crust and not only by applying artificial channels into the crust. For both approaches, the underlying mechanism is the same, as described in Chapter 2. Both phenomena decrease the barrier properties of the crust, because they act as open areas. Large open areas induce high permeabilities. For both approaches, an open area of the crust of approximately 1.5% resulted in optimal water vapor permeability. In addition, for both approaches, the relationship between water vapor permeability, water uptake, and mean sound intensity was almost similar, demonstrating the clear interconnection of these three values (Fig. 5-2 and 5-4).

In this second part of the discussion, we hypothesize why cracks are created in the crust after baking. When bread leaves the oven, the rapid temperature change causes stress accumulation in the crust. We hypothesize that this thermal shock is the reason for cracking. Thermal shock is also responsible for the cracking of glass and ceramic materials (Danzer et al., 2008). In order to test this hypothesis, we studied whether cracks occurred in the crust if the breads stayed in the warm oven after baking. This was not the case (results not shown).

Cracks are created in the crust if the accumulated stresses cannot be dissipated. Dissipation requires the presence of mobile molecules, either water or polymers. At a water content higher than 9%, the molecular mobility of water molecules in crust in the glassy state is responsible for increased stress dissipation (van Nieuwenhuijzen et al., 2010). However, the water content within the first 5 min after baking is below 5% (Chapter 2), and hence dissipation of energy will be low and probably depends on the mobility of polymers. Therefore cracks will especially occur in networks containing polymers with a low ability to dissipate stresses.

We hypothesize that the amount of gelatinized starch in the crust determines the amount of cracking. Crust that had more gelatinized starch was more prone to crack and had a higher open area of crust (Fig. 5-5a, $R^2 = 0.97$). In Fig. 5-5, the three groups are observed (I, II, and III) that were already indicated in

Fig. 5-3. In group I, the amount of gelatinized starch is less than 60%, and these breads had a low amount of cracks. Breads of group II have an amount of gelatinized starch between 60% and 70%, and breads of group II have an amount of gelatinized starch above 70%. The breads also differ in the amount and properties of the gluten. In crusts of group I, the gluten network was more homogeneous than in crusts of groups II and III, and therefore fewer protein-poor areas appeared in the crusts (Fig. 5-1, 5-5b). We hypothesize that a network containing evenly distributed viscoelastic gluten and a low content of gelatinized starch has the ability to dissipate stresses occurring after baking. This assumption is supported by the following: On the one hand, fracture strain is higher in crumb with a higher gluten content and in films made of gluten instead of gelatinized starch (0% water content) (Attenburrow et al., 1992; Zghal et al., 2001). On the other hand, gluten has a lower glass transition temperature than gelatinized starch (Cuq et al., 2003). Our hypothesis is in line with Young (2003), who acknowledged that the thicker the gelatinized starch layer in the crust created during steaming, the greater is the cracking of the crust when the bread leaves the oven and begins to cool. A content of gelatinized starch higher than 70% resulted in hard and less cellular bread crust (Fig. 5-5, group III). In these crusts, the creation of a homogeneous gluten network was probably less facilitated. Therefore, the network had a lower gas-holding capacity and the crust became dense and hard. The use of an optimum amount of gelatinized starch (60% - 70%) resulted in crispy and cellular crust with cracks (group II). We recommend creating crust with gelatinized starch content between 60% and 70% to get optimal crispness retention. Protein content alone is probably not the factor that determines the occurrence of cracks, because the weak correlation between both factors that was found by Baardseth et al. (2000) is consistent with the poor relationship ($R^2$ = 0.53) found in this study. However, in the study of Qarooni et al. (1988) the occurrence of cracks in bread crust was negatively correlated to the protein content.

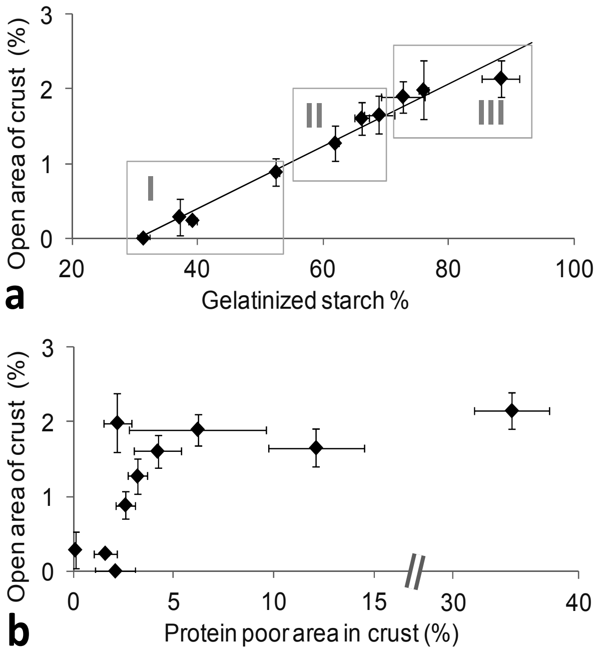


Fig. 5-5: a) Relationship between amount of gelatinized starch in bread crust determined by DSC and open area of crust caused by cracks. b) Relationship between protein-poor area in bread crust and open area of crust. Protein poor area is defined in materials and methods as the percentage of area in CSLM figures that is green. Green spots have a high content of starch and a low content of protein. Open area of crust is defined in materials and methods as the product of crack length and crack width.

In this study, breads with optimal crispness retention were composite breads. The creation of composite breads requires an extra process step. However, we hypothesize that effective cracks in the crust can be also created in standard breads, in which the crust and the crumb are made from the same dough. Cracking can be induced by increasing the thermal shock, for example, by increasing crust temperature during baking or by using liquid air for cooling. Another possibility is to weaken the crust network, for example, by increasing the degree of gelatinization in the crust. This is possible by spraying a gelatinized starch solution on the crust or by increasing the water content in the crust during baking, e.g., by steaming.

We therefore conclude that by exposing a bread crust material, which is prone to crack, to enough stress creating thermal shock, optimal water vapor permeability can be reached, which ensures longer crispness retention of bread. In this study, crust with an optimal content of gelatinized starch had the highest amount of cracks and the longest crispness retention.

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# Chapter 6

## General discussion

## 6.1. Introduction

Crispness is one of the most important sensory characteristics of crispy bread, because consumers associate crispness with freshness and quality (Szczesniak and Kahn, 1971). Freshly baked bread of high quality is characterized by a soft moist inner part, the crumb, and a dry outer crust, which is crispy. Bread crust is defined as crispy if it exhibits successive fractures and acoustic events under low work of mastication (Luyten et al., 2004; Szczesniak, 1988; van Vliet et al., 2007, 2009).

Whether crust is crispy or not depends on its water content. After baking, the water content of the crust is very low, allowing crispy facture. Rapidly after baking, however, water migration between crumb, crust, and environment increases the water content of the crust. This fast increase of the water content leads to a fast loss of crispness within a few hours after baking. Therefore, it is beneficial to extend crispness retention. However, only a few approaches have been described so far (Primo-Martín et al., 2006, 2008a, 2008b, 2010). Also, there is scarcely any literature that provides a deeper understanding of the mechanisms leading to the fast water uptake of crust.

Therefore, in this thesis, we describe a number of studies systematically aimed at understanding the influence of certain parameters on crispness retention. In this general discussion, these results will be further reviewed and underlying mechanisms discussed with the aim of constructing a comprehensive view on crispness loss and retention. In this respect, we were interested in which time frame, which structures, and which parameters are key for crispness retention and therefore need to be controlled to extend crispness retention. Based on our studies, we constructed a model (Fig. 6-1) for crispness retention and determined the relation between crispness and water content (section 6.2), the time frame that is most important in the water uptake of crust (section 6.3), and the role of water migration (section 6.4).

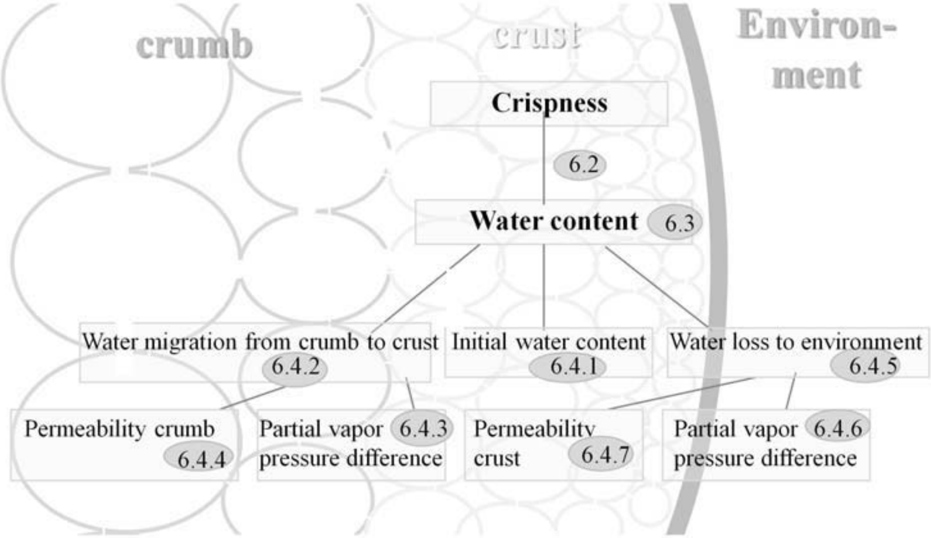


Fig. 6-1: Outline of general discussion. Numbers indicate the section in which the topic is discussed.

## 6.2. Loss of crispness related to water content of crust

It is known that crispness is lost because of water uptake (Katz and Labuza, 1981). Several authors already related crispness to the water content or water activity of the material (Peleg, 1994; Roudaut et al., 1998; van Nieuwenhuijzen et al., 2010). However, only a few studies have investigated bread crust (Primo-Martín and van Vliet, 2009). Therefore, we aimed to discuss the use of either water content or water activity in relation to the crispness of crust. We endeavored to capture this relation by modeling. Results in Chapter 3 suggest that crispness can be calculated based on the following sigmoid equation:

$$\boldsymbol{C} = \boldsymbol{C}_0 + \frac{\boldsymbol{C}_\infty - \boldsymbol{C}_0}{\mathbf{1} + \boldsymbol{EXP}(-\mathbf{0.5} * (\boldsymbol{w_c} - \mathbf{10}\ \%))}. \quad (6.1)$$

where C is the sensory crispness score, $C_o$ is the sensory crispness score at 0 % water content (higher asymptote), $C_\infty$ is the crispness score at infinitive water content (lower asymptote), and $w_c$ is the critical water content. In Eq. (6.1) we have inserted a critical water content of 10%. The critical water content is defined as the water content by which half of the crispness is lost. Several authors have determined a critical water content using the sigmoid relationship between sensory crispness and water content or water activity, as proposed by Peleg (1994) and used in Eq. (6.1). For baked cereal products, this value is between 9% and 11% (Primo-Martín et al, 2008c, 2009; Roudaut et al, 1998; van Nieuwenhuijzen et al., 2010) and for bread crust 10% (Primo-Martín and van Vliet, 2009; Chapter 3). This supports the use of a critical water content of 10% in Eq. (6.1). Eq. (6.1) contains a slope factor of 0.5, characterizing the steepness of the change from crispy to not crispy. This factor is based on the fitted slope factor of 0.5 in Primo-Martín and van Vliet (2009) and Chapter 3. We conclude, therefore, supported by the literature, that the water content of crust during storage is the parameter determining the loss of crispness and that the critical water content of bread crust is 10%.

Crispness can also be related to the water activity (Peleg, 1992). Water activity and water content are related by the isotherm and water activity is the driving force for water migration in bread. However, we focused on water content as the parameter, because of the following limitation. Water activity can only be measured in equilibrium conditions. However, bread crust is not in equilibrium, due to differing water activities within the crust and due to the slow reaction rates in complex systems with low water content (Franks, 1991; Primo-Martín 2008a, 2009, Chapter 2). Van Nieuwenhuijzen et al. (2008) used equilibrated model crusts to determine the effect of water activity on crispness sensation. Their results suggest that the combined measurement of the water content and the water activity of the crust is necessary for the determination of crispness, if the water activity of the crust was raised and lowered to a large extent. The observed hysteresis effect occurs, for example, if a model crust is stored successively at 90% and 40% relative humidity (van Nieuwenhuijzen et al., 2008).

## 6.3. Cooling phase is crucial for crispness retention

The increase in the water content of the crust during storage differs between breads with short and long crispness retention. Breads with short crispness retention are not crispy after 4 h storage time, because their water content is above 10%, whereas breads with long crispness retention have significantly lower water content after this storage time. For both types of breads, we measured the water content at certain time points during storage. Our results show that most differences in water content already occur within the first 30 min of storage, and that the water contents of the crust after 30 min and after 4 h are linearly related (Fig. 6-2).

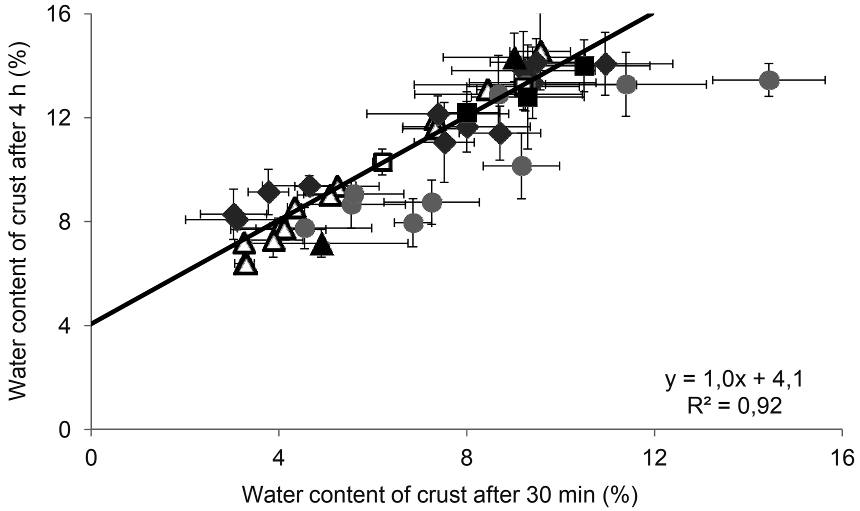


Fig. 6-2: Relation between water content of crust after 30 min and 4 h storage at 40% relative humidity using data from experiments described in Chapter 2 (closed triangles), Chapter 3 (open triangles), Chapter 4 (closed diamonds), Chapter 5 (grey circles), and in Primo-Martín et al. (2008a) (storage at 50% relative humidity; open squares), and Primo-Martín et al. (2010) (closed squares). Correlation analysis done for all data except data from Chapter 5.

In Fig. 6-2, only data points from Chapter 5 are slightly off trend. This is due to the fact that the crusts in these samples also contained wheat starch and vital gluten. The use of these ingredients often resulted in dense and thick crusts. With the crusts made of only flour, the following trend was visible:

$$\boldsymbol{W_{c,4h} = W_{c,30min} + 4.1}\ \%. \tag{6.2}$$

where $w_{c,4h}$ is the water content after 4 h storage time and $w_{c,30min}$ the water content after 30 min storage time. This equation points to the relevance of the first 30 min, which corresponds to the cooling phase. Clearly this is the time frame in which the main differences in crispness retention occur and in which the water uptake of the crust is the highest. During the first 30 min, the water content of the crust increases for almost all breads with more than 4%, if an initial water content of 0% is assumed. During the next 3.5 h the water content increases by 4.1% (Eq. (6.2), Fig. 6-2). We therefore hypothesize that the understanding of processes that occur during cooling and the knowledge of the key parameters that influence the water uptake of the crust during cooling are very important in increasing crispness retention.

In general, cooling is inevitable in the baking process to lower the temperature in the bread before packaging or freezing and to prevent condensation and mould growth in the package. Therefore, cooling is an important process step. The duration and the conditions of the cooling process determine the total water content of the bread, the duration of the total bread preparation process, the shelf life, and the crispness retention of the bread. However, the influence of cooling conditions on the bread quality has hardly been studied. Grenier et al. (2002) determined that surrounding temperatures affect cooling time and water loss, and Le Bail et al. (2005) concluded that relative humidity during cooling is the most important factor influencing crust flaking in frozen part-baked breads. Due to this limited knowledge, we aimed to describe the processes that occur during cooling in more detail.

**Vacuum cooling**

Fast cooling can be achieved by vacuum cooling. The reduction of the pressure close to a vacuum, as done by Primo-Martín et al. (2008), quickly removes both heat and water. Consequently, vacuum-cooled breads have a lower water content in the crust after 30 min storage time: 6% instead of 9%. This difference causes a significantly different crispness retention: normal cooled bread reaches the critical water content of 10% after 1 h, vacuum-cooled bread after 3 h (Primo-Martín et al., 2008). Longer crispness retention was also achieved by the combined use of vacuum cooling and high proving humidity (Lösche et al., 2011). Vacuum cooling reduces the boiling point of water. Therefore, the high loss of water during cooling, approximately 3% per bread in the study of Primo-Martín et al. (2008), is caused by water evaporating from the solid crumb. This high water loss could also change the properties of the crumb. Le-Bail et al. (2011) determined a faster staling of the crumb of vacuum-cooled bread after one day of storage, and in Chapter 3 we showed that breads that lost 2% more water during processing had a sensory less soft crumb after 4 h storage time. Therefore, the control of the vacuum cooling process is necessary to avoid too much water loss and the reduction of crumb softness

## 6.4. Water content of crust changes because of water migration

After baking, the water distribution within the bread is inhomogeneous. The water content of the crust is low, whereas the water content of the crumb is high. The crumb serves as a water reservoir because of the high water content of 47%, which corresponds to a water activity of 0.97 at 22°C. This water is present in the solid part of the crumb as liquid water, and in the gas phase as vapor. Of the 30 g total water present in the bread we used, vapor accounts for less than 0.3 g, because gas can hold less water than a solid. This values are based on a volume of the total bread of 0.5 l and a temperature of 100°C. During cooling, the temperature decreases, resulting in a further decrease of vapor being present in the gas phase. Therefore, most water is present in the liquid phase.

Due to the different water content and the water activity of crust, crumb, and environment, water migrates between these parts. Consequently, the water content of the crust increases during cooling. We modeled this water migration between crumb, crust, and environment to determine the key factors for the water uptake of the crust. The water content at a certain storage time is the sum of the initial water content, the water that is taken up from the crumb, and the water that is lost to the environment. This relation is shown in Eq. (6.3)

$$\boldsymbol{W_c = W_{c,i} + \Delta m_{w,cb} - \Delta m_{w,e}} \tag{6.3}$$

where $w_c$ is the water content of the crust, $w_{c,i}$ the initial water content, $\triangle m_{w,cb}$ the water uptake of the crust due to water migration from crumb to crust, and $\triangle m_{w,e}$ the water loss to the environment. In most breads, the water supply from the crumb ($\triangle m_{w,cb}$) is higher than the water loss to the environment ($\triangle m_{w,e}$) resulting in the fast increase of water content in the bread crust during cooling. Supplied water that is not lost to the environment accumulates in the crust.

This principle becomes clearer when we use an example from Chapter 2. Standard breads lose 0.17 g water during the first 30 min of storage. In that time the water content of their crusts increases to 9%. Assuming a crust weight of 7 g and an initial water content of 0%, the crust takes up 0.6 g water in that time that is delivered by the crumb. Therefore, more water accumulates in the crust than leaves to the environment. In addition, the crust takes up more water than is present as vapor after baking (0.3 g). This implies that vapor is generated by evaporating liquid water from the solid. This water evaporation is more pronounced at higher temperatures. Therefore, more vapor is supplied during the cooling phase than during the later storage phase. If we now compare standard breads with channeled breads, we recognized that channeled breads lose more water during cooling, namely 0.36 g (Chapter 2). Consequently, crust with channels has a lower water content. The additional 0.19 g water that is lost by breads with channels does not accumulate in the crust. This amount of water equals to a decrease of water content of the crust by 3%. This corresponds well with the difference in water content of 4%, as determined by the experiment. Standard breads had a water content of the crust of 9% after 30 min, and breads with channels had a water content of 5%, which corresponds to a total water content in the crust of 0.3 g (Chapter 2).

### 6.4.1. Initial water content

To model the water uptake of the crust during cooling using Eq. (6.3), it is important to know the initial water content of the crust after baking. So far, we have assumed an initial water content of 0%. The measured initial water content was less than 1% for breads analyzed in Chapter 3. For this measurement, bread crust was separated immediately after baking. However, the whole procedure still lasted around one minute. Therefore, we assume that bread crust in the first seconds after baking has a water content of 0% (Eq. (6.4)).This low water content is caused by the high temperatures during baking; the exposure of crust to temperatures above 200°C induces a complete drying of the crust.

$$\mathbf{W_{c,i} = 0} \tag{6.4}$$

The water content distribution of the bread below the crust in the crumb after baking was determined by Voogt et al. (2011). Starting from the crust, the water content increased linearly in the first 8 mm of the crumb. At 80 mm distance the water content is 47%, the same as in the whole inner crumb. The first 80 mm below the crust are, therefore, the region, in which water migrates towards the crust.

### 6.4.2. Vapor migration from crumb to crust

The water content in the crust increases, because vapor migrates from the crumb to the crust, as described in the previous paragraphs. This migration of vapor through the open cellular crumb was modeled by Voogt et al. (2011) with the following Fickian diffusion model

$$\boldsymbol{\Delta m_{w,cb} = -A\Delta J dt} \tag{6.5}$$

$$\boldsymbol{J = -WVP_{cb}\frac{\Delta P_{v,cb}}{\Delta x}} \tag{6.6}$$

where $A$ is the area, $J$ the water flux, $WVP_{cb}$ the water vapor permeability of the crumb, and $\triangle P_{v,cb}$ the change in partial pressure of the vapor in the crumb. The model that was used assumed a temperature during the cooling phase. Although this is not the case, this Fickian diffusion model from Voogt et al. (2011) could predict the experimentally determined changes in the water content of the crumb surprisingly well. Therefore, despite the known limitations, we used this model as a starting point to describe water migration in crumb. This model proposes that the migration of water from the crumb to the crust is determined by the water vapor permeability of the crumb and the partial vapor pressure differences in the bread (Eq. (6.6)).

### 6.4.3. Temperature and partial vapor pressure differences (T, $\triangle P_v$)

The driving force for water migration is the partial vapor pressure difference, as shown in Eq. (6.6). A higher partial pressure difference between the crumb and the crust will cause a faster water migration between the crust and the crumb, and therefore a faster water uptake of the crust. To visualize the extent of the driving force, we calculated the partial pressure of vapor for crust, crumb, and environment during storage, based on the temperatures of these parts (Table 6.1).

The temperature within the bread varies during cooling (Table 6.1). In the crumb, the temperature drops fast after baking, because of vapor transport and conduction. This temperature drop causes condensation of the saturated vapor predominantly in the outer crumb and crust, because the temperature drops the fastest in these parts. Condensation leads to a slight pressure decrease during the first 5 min of cooling (Grenier et al., 2010). However, condensation does not cause a visible condensation front, because the available water in the saturated gas phase is less than 0.3 g.

Based on the measured temperatures, the partial water vapor pressure in the air phase of the different compartments was calculated (Table 6.1). After baking, the partial pressure differences are 40 times higher between the crumb and the crust than after 4 h storage time, resulting in much more water transport during the first minutes after baking. This comparison supports the importance of the cooling phase for the water uptake of the crust. During the first 30 min after baking, differences in partial pressure reduces; therefore, the first part of the cooling phase is more important for the water uptake of the crust than the later phases.

Table 6-1: Temperature and partial vapor pressure of crumb, crust, and environment. Temperature of the crust after baking (0 min) was measured in the oven with IR; the other temperatures of crust and crumb were measured with K type thermocouples (Type 171-8, Testo AG, Lenzkirch, Germany), which were fixed in the middle of the bread (crumb) and in the crust (1 mm distance to the surface). Grenier et al. (2010) and Primo-Martín et al. (2008a) measured four different bread types slightly different temperatures of the crust and the crumb. Partial pressure of vapor depends on the temperature and the water activity. Water activity of the crumb is 0.97 (in the solid and therefore also in the air phase) and of the environment 0.4. For the crust, the water content and the water activity were measured of the breads analyzed in Chapter 2. For a short storage time (5 min, 15 min), water activity was calculated from the water content using the isotherms of the crust at the different temperatures of Lind and Rask (1991).

| | | Crumb | Crust | Environment |
|---|---|---|---|---|
| Temperature (°C) | 0 min | 90 | 207 | 22 |
| | 5 min | 55 | 50 | 22 |
| | 15 min | 40 | 30 | 22 |
| | 30 min | 25 | 23 | 22 |
| | 4 h | 22 | 22 | 22 |
| Partial pressure of vapor (kPa) | 0 min | 68 | 0 | 1.0 |
| | 5 min | 15 | 3.1 | 1.0 |
| | 15 min | 7.2 | 1.7 | 1.0 |
| | 30 min | 3.1 | 1.7 | 1.0 |
| | 4 h | 2.6 | 1.8 | 1.0 |

The water content of the crumb is another parameter, which affects the partial pressure in the crumb and could, therefore, affect water migration. A higher water content of the inner crumb, however, does not directly affect water activity and partial pressure, because of the steepness of the isotherm at high water activities. We suggest that the water content matters for other reasons. On the one hand, the cooling rate can be affected by the water content, while on the other hand, the water content distribution in areas below the crust can be of importance. In these areas a slight difference in the water content has a large effect on the water activity according to the isotherm, and the water vapor present in these zones is able to reach the crust fast. For example, after baking, breads with channels have a lower water content in the first 2 mm under the crust (Voogt et al., 2011), which could also be a reason for the reduced water uptake of the crust during cooling. The second factor that is dependent on the water content is the cooling rate, because of the different heat capacity of water and dry crumb. If the temperature within the bread is higher, more water vapor migrates from the crumb to the crust. Therefore, a higher water content of the bread could affect water migration. The water content could also be of importance, because the liquid water in the solid beams is the source of vapor production. However, the presence of water in the crumb and the migration of vapor toward the crust is just one factor. We consider it more relevant for crispness retention that water does not accumulate in the bread crust, but rather is lost to the environment. Therefore, we assume that a faster migration of water from the crumb to the crust hardly influences crispness retention, if the water does not accumulate in the bread crust, which is the case for crust with optimal crust permeability.

### 6.4.4. Water vapor permeability of crumb (WVPcb)

The transport of water vapor to the crust is important for crispness retention (Eq. (6.2), (6.3)). This transport is affected by the water vapor permeability of the crumb, as modeled in Eq. (6.6). This relation was experimentally confirmed in Chapter 4: breads with a higher permeability of the crumb had a significantly faster water uptake of the crust and significantly lower crispness retention.

The experiments in Chapter 4 also lead to a deeper understanding of the water migration in the crumb. The crumb is very transparent for water vapor. The water vapor permeability of the crumb is 30 times higher than of the crust and is approximately half the value of air (Chapter 4). For the first time, we could experimentally determine the permeability of the crumb and the crust and compare both (Chapter 4). Crust permeability was experimentally measured with a newly developed method that is applicable for brittle material like bread crust (Chapter 2). The permeability of the crumb was also determined using a modification of this method, but at the high levels measured, the method was not able to distinguish between different crumb morphologies. We, therefore, also estimated the water vapor permeability with the modeling method described by Esveld et al. (2012). With this method we determined a very high water vapor permeability of the crumb. This supports the conclusion of Esveld et al. (2012) that water is mainly migrating through the open, highly connected gas phase, and that the migration through the solid is negligible. Therefore, properties of the solid phase, e.g., beam thickness, do not affect the speed of water migration. In contrast, the speed of migration and the water vapor permeability of the crumb depend on the porosity and the number of large connections between the air cells in the crumb (Chapter 4) (Eq. (6.7))

$$WVP_{cb} = (4.56 \times 10^{-10} LC + 8.18 \times 10^{-10}) \times \varphi \quad \text{(in g/m s Pa)} \qquad (6.7)$$

where LC is the number of large connections per mm$^3$ and φ the porosity. Therefore, the water uptake of the crust can be reduced by decreasing the porosity or the number of large connections between the air cells in the crumb.

### 6.4.5. Water loss to environment

The water migrating towards the crust either stays in the crust or is lost to the environment (Eq. (6.3)). This water loss to the environment is a complex process, including, for example, accumulation, diffusion, evaporation, and convection. At this stage we cannot quantify the influence of each process. In addition, the use of the simple Fickian diffusion model, as used for the crumb (Eq. (6.5), (6.6)) to predict water migration through the crust to the environment, is not recommended, because this model could not sufficiently predict the water uptake of the crust (Voogt et al., 2011). However, we can describe parameters influencing the water migration from the crust to the environment: the partial vapor pressure difference between the crust and the environment ($\triangle P_{v,e}$), which is the driving force for water migration, and the water vapor permeability of the crust ($WVP_{ct}$), which we identified as a key parameter for the water uptake of the crust (Chapter 2). We, therefore, propose that these two parameters are the two most important ones affecting water loss to the environment.

$$\Delta \boldsymbol{m}_{\boldsymbol{w},\boldsymbol{e}} = \boldsymbol{f}(\Delta \boldsymbol{P}_{\boldsymbol{v},\boldsymbol{e}}, \boldsymbol{WVP}_{\boldsymbol{ct}}) \qquad (6.8)$$

In Eq. (6.8) it is stated that the water migration from the crust to the environment is dependent on the partial vapor pressure difference and the water vapor permeability of the crust. Other parameters, e.g., the air speed, could also influence water loss to the environment. However, we expect their influence to be of less importance.

### 6.4.6. Partial vapor pressure differences, environment ($\triangle P_{v,e}$)

The loss of water to the environment is related to the partial vapor pressure difference between the crust and environment, because this will be the driving force for water migration (Eq. (6.8)). Therefore, the given partial pressure differences in Table 6.1 relate to the water loss of breads, as measured in Chapter 2. During the first 15 min of cooling, in which the partial pressure differences are the highest, the water loss rate of 0.72 ± 0.14 mg/min is higher than from 15 min to 30 min storage time (0.41 ± 0.05 mg/min) and from 30 min to 4 h storage time (0.45 ± 0.03 mg/min).

The vapor pressure of the environment is lower than the vapor pressure of the crust during cooling (Table 6.1). Therefore, water is lost to the environment. Only in the first seconds after baking can the partial vapor pressure of the crust be slightly higher than of the environment, but the water loss in this phase is negligible (Table 6.1). Thus we state that the environment of the bread is important, not because it acts as a source of water, but because it affects the speed at which water is lost from the crust.

It was not studied in this thesis how different conditions of the environment like vapor pressure, temperature, water activity, and air speed, will affect water loss and therefore crispness retention. In the practices of the consumer, environmental conditions are typically uncontrolled and dependent on the natural conditions present in the storage room or in the packaging used. Package material for crispy bread is mostly perforated or highly permeable, to ensure sufficient water loss to the environment and to minimize water accumulation in the bread crust. Primo-Martín et al. (2006) showed that breads stored in plastic bags had, after 5 h storage time, a water content of the crust of 21%, as opposed to 14% for breads stored at 40% relative humidity. Primo-Martín et al. (2006) and Grenier et al. (2002) analyzed the effect of different temperatures and humidities of the environment. Grenier et al. (2002) determined that higher cooling temperatures cause less water loss. Primo-Martín et al. (2006) determined that the increase of the relative humidity from 40% to 80% after 30 min storage time resulted in breads with a water content of the crust of 20%, instead of 15% after 2 h storage time and a lower sensory crispness score. Storage conditions of 80% relative humidity were chosen to study extreme conditions; however, such conditions are seldom reached in normal households.

In this thesis, a constant relative humidity of the environment of 40% was used. Li and Kendrick (1995) measured in households an average relative humidity of 41% existing in a humid continental climate, with extremes of 33% and 55%. In buildings that exist in other climate regions, the average relative humidity can be different. However, we selected one fixed relative humidity in this thesis to ensure the comparability of results.

The chosen relative humidity of 40% determined the water content of the crust for breads with optimal crust permeability after 4 h storage time. After that storage time, these crusts reached the equilibrium water content for a relative humidity of 40% of 7% (Chapter 3, Fig. 6-3a). This water content is below the critical water content of 10%. Therefore, these breads were crispy after 4 h storage time. The critical water content of 10% corresponds to a water activity of 50% (Primo-Martín et al., 2009; Chapter 3). Therefore, we propose that crispness can be extended for several hours by increasing the permeability of the crust, provided that breads are stored below a relative humidity of 50%. If breads are stored at higher relative humidities, crispness will be lost faster. We propose that breads stored at humidities higher than 65% will lose crispness within 1 hour, even if the permeability of the crust is increased in these breads. In these breads, the water content of the crust will increase fast to values of 12%, which is the equilibrium water content at 65% relative humidity (Primo-Martín et al., 2009). At a water content of 12%, 90% of the crispness is lost (Chapter 3).

### 6.4.7. Water vapor permeability of crust ($WVP_{ct}$) and properties of crust

Perhaps the most important factor controlling crispness retention is the permeability of the crust. The crust has a rather low permeability of $0.04 \times 10^{-11}$ g/(m s Pa), because of its dense structure (Chapter 2). This barrier property of the crust in combination with the low partial vapor pressure difference between the crust and the environment (Table 6.1) leads to a slow water migration through the crust to the environment. Therefore, water accumulates in the crust, resulting in large differences between the water activity of the crust and the environment (Chapter 2).

A reduction of the barrier properties of the crust can therefore help reduce the water accumulation in the crust. As shown in Chapters 2, 3, 4, and 5, the increase of the water vapor permeability of the crust leads to a decrease in the water uptake of the crust and an increased crispness retention. The clear relation between these factors is illustrated in Fig. 6-3, which includes results from Chapters 2, 3, 4, and 5. This figure shows that there is an optimum for crispness retention at a water vapor permeability of $8 \times 10^{-9}$ g/(m s Pa). At this water vapor permeability, mean sound pulse intensity, sensory crispness, and softness of the crumb are the highest after 4 h storage time (Fig. 6-3b; Chapter 3). A further increase of the water vapor permeability does not decrease water uptake of the crust further (Fig. 6-3a), because the crust water content cannot be maintained for long below the equilibrium water content at 40% relative humidity of 7% (Chapter 3). Therefore, water content and mean sound pulse intensity after 4 h storage time are similar for breads with a water vapor permeability of and above $8 \times 10^{-9}$ g/(m s Pa) (Fig. 6-3). Furthermore, breads with a vapor permeability above $9 \times 10^{-9}$ g/(m s Pa) have a significantly lower crumb softness, confirming the optimal value of $8 \times 10^{-9}$ g/(m s Pa) (Chapter 3). The doubling of the water vapor permeability from $4 \times 10^{-9}$ g/(m s Pa) to $8 \times 10^{-9}$ g/(m s Pa), by increasing the open area by 1.5%, leads to a more than eight times longer crispness retention (Chapters 3, 5). Such effects on crispness retention could not be achieved by changing the permeability of the crumb (Chapter 4). The permeability of the crust was increased either by applying channels through the crust (Chapters 2, 3) or via the creation of cracks in the crust (Chapter 5). Cracks were caused by a thermal shock in the crust material, with a low ability to dissipate stresses, e.g., crust containing 60% - 70% of gelatinized starch (Chapter 5). Consequently, conditions can be chosen to induce a sufficient amount of cracks, thus causing optimum crispness retention.

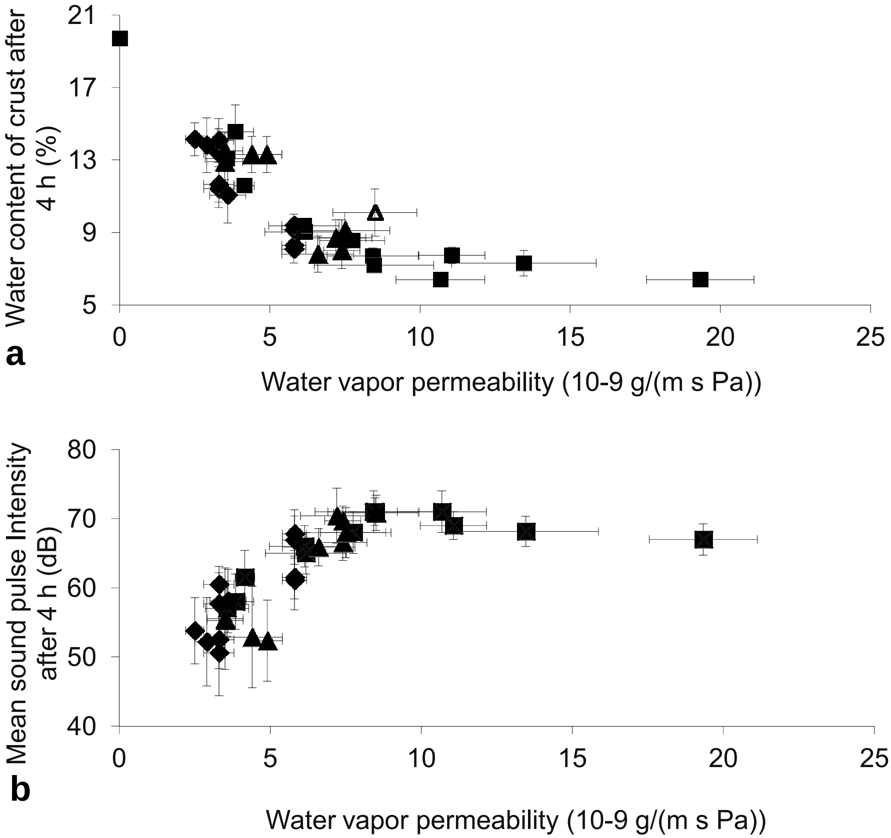


Fig. 6-3: Relation between water vapor permeability of the crust and a) water content of the crust and b) mean sound pulse intensity after 4 h storage time. Squares represent data of Chapter 3, diamonds data of Chapter 4, and triangles data of Chapter 5 (empty triangle sample GS5 with thick crust).

Bread crust typically has an outer dense solid layer. This outer crust is not cellular and does not contain openings that are visible with the naked eye (Primo-Martín et al., 2010; Fig. 6-4). We propose this closed structure to be the largest barrier for water migration and mainly responsible for the low water vapor permeability of the crust. Therefore, water migrates very slowly through the outer crust, causing the large differences in water activity between the environment and the total crust.

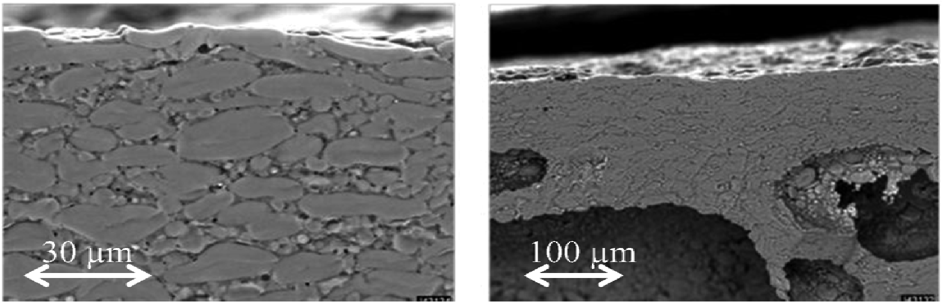


Fig. 6-4: SEM figures of bread crust. Method described in van Dalen et al. (2011).

The close-up view of the crust (Fig. 6-4) reveals that the crust contains small openings (Fig. 6-5a). These openings are randomly distributed over the crust and account for less than 1% of the crust surface. Nevertheless, the water vapor leaves the bread through these openings (Fig. 6-5a), because the migration of water vapor is much faster than via condensation and vaporization through the closed solid parts of the outer layer (Esveld et al., 2012). We, therefore, propose that the outer crust does not behave like a porous cellular structure like the crumb does, but rather like a perforated film. This assumption is also based on the fact that bread crust and perforated packaging films behave similar: a linear relationship between permeability and open area exists (Chapter 3; Pagani et al., 2006; Paul and Clarke, 2002; Silva et al., 1999). The permeability of this outer crust is, therefore, dependent on the area and size of the perforations. The random distribution of the perforations will also lead to different migration in different parts of the crust. In regions with no perforations, water accumulates in the crust during storage. In regions near perforations, the water vapor migrates fast to the environment. Therefore, the water content in this region stays lower during storage. This inhomogeneous water migration in the crust hinders a simple modeling of the water uptake of the crust. Therefore, the simple Fickian diffusion model of Voogt et al. (2011) cannot predict the water uptake, especially of a crust with channels or cracks. An accurate model requires a 2D approach to model water migration in closed crust areas and open crust areas separately. This 2D approach is especially important in crust with channels. In these crusts more water leaves the crust, especially through the homogeneously distributed channels (Fig. 6-5b).

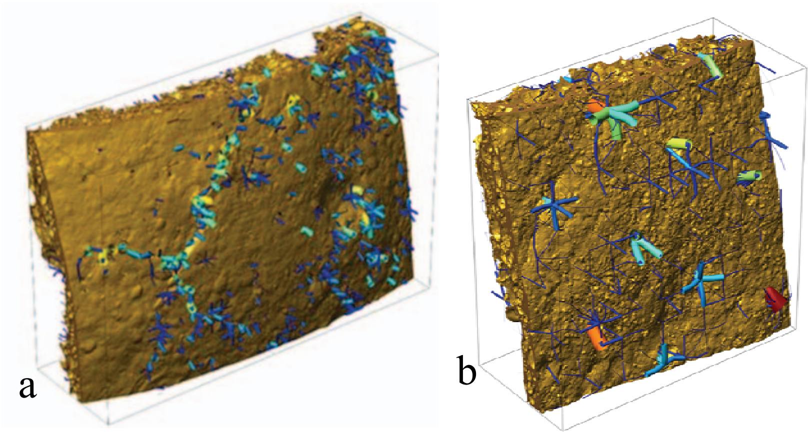


Fig. 6-5: Modeling of vapor transport through crust: a) normal crust and b) crust with channels (from ongoing studies). Crust was visualized with X-Ray and water vapor flux was modeled as described in Chapter 4. Thicker tubes indicate a higher water vapor flux.

## 6.5. Physical modeling versus experiments: two approaches to develop a model for crispness retention

In the previous paragraphs we combined physical models and experimental results to propose a model for crispness retention, which is visualized in Fig. 6-6. This model shows that crispness is related to the water content of the crust, and that the water content of the crust is determined by water vapor migration. Water vapor migration is especially important during the first 30 min after baking, because at this time, vapor transport is the fastest and, consequently, the water uptake of the crust is the highest.

Water migration from crumb to crust can be reasonably well described using the Fickian diffusion model of Voogt et al. (2011). Based on this model and the experimental results, we state that water migration within the crumb is determined by the partial vapor pressure difference and the water vapor permeability of the crumb (Fig. 6-6).

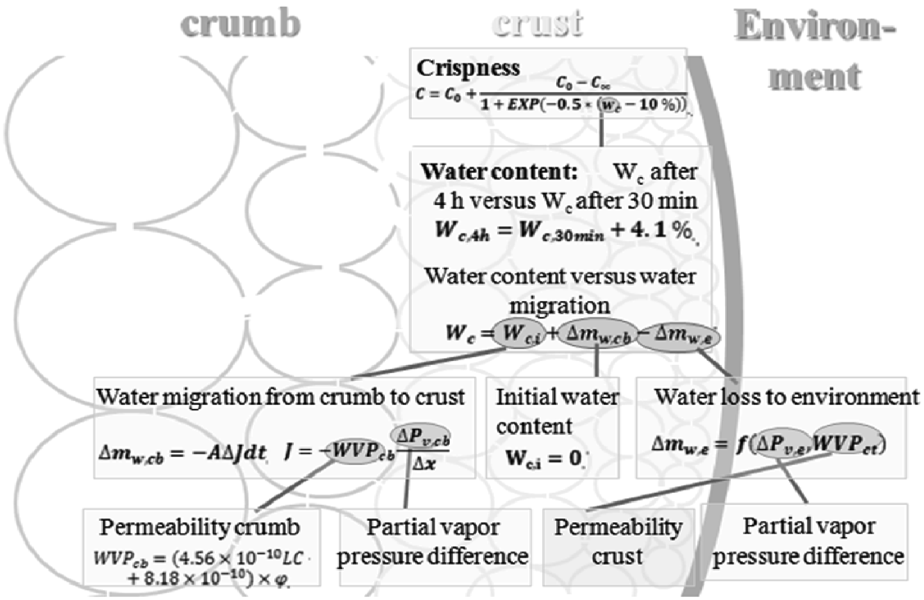


Fig. 6-6: Model for crispness retention. Description is given in the text.

Experiments demonstrating the importance of the water vapor permeability of the crumb were done using composite breads. In composite breads, the properties of either the crumb or the crust can be set independently (Chapters 4, 5). This approach allowed us to develop the model in Fig. 6-6.

The physical model from Voogt et al. (2011) used to describe water migration through the crumb could not be used to predict water migration through the crust to the environment and the water uptake of the crust. Therefore, we recommend developing an extended model that includes these aspects. In such a model it is necessary to include the parameter temperature and a 2D model of the crust. This extended model should be, furthermore, validated by experimental results, showing the influence of several parameters, e.g., water content distribution in the crumb, distribution of openings in the crust, as well as relative humidity and temperature, and air speed of the environment. Such a model has the advantage of being able to determine the effect of several parameters separately, most importantly parameters that cannot be varied separately in experiments, e.g., the water content of the crumb. This combination of a physical model and further experimental results would lead to a deeper knowledge of the water migration that occurs during cooling and storage.

## 6.6. Application in industry and recommendations

In this general discussion we systematically discussed the parameters influencing the water migration in bread with the aim of identifying the parameters that are key to increasing crispness retention. We suggest that the permeability of the crust is one key parameter. The increase in water vapor permeability of the crust can extend crispness by more than eight times. In contrast, changing other parameters has limitations, either technologically or quality wise. The proven effect of vacuum cooling on the water uptake of the crust is smaller (Fig. 6-3), and the negative effects on crumb softness have already been reported. The possibilities for changing the properties of the crumb are limited: the properties of the crumb are restrained by the bread type used. Therefore, a change in the crumb morphology, which had a small impact on crust crispness in this thesis, is often not possible. A number of further parameters, e.g., water content of the crumb and conditions of the environment, were not varied experimentally in this thesis. However, based on theory we made an estimate of their potential impact. This, of course, needs to be experimentally validated. Such a study should be combined with an extension of the model, as recommended in section 5.

The optimal water vapor permeability of crust for crispness retention can be achieved with several methods. In Chapter 2, we created crust with optimal permeability by pressing needles into the crust to create channels. This approach requires an extra mechanical process step as well as the use of a part-baked process. In unfrozen breads, artificial openings could also be created by using a laser. In addition, we demonstrated the potential of “natural” cracks in reaching the optimal water vapor permeability (Chapter 5). These cracks are created in the crust with a low ability to dissipate the stresses that occur due to the thermal shock after baking. In our approach, especially breads with a crust layer containing between 60% and 70% gelatinized starch were prone to crack. The approach used in Chapter 5 requires the creation of composite breads. This demands an extra process step. However, we assume that a sufficient amount of cracks can also be created in standard breads, either by increasing the thermal shock (e.g., higher crust temperature during baking, cooling with liquid air), or by weakening the crust network with different means, e.g., increasing the degree of gelatinization in the crust by increasing the water content in the crust during baking, for example by steaming. The four times increase of crispness retention by protease addition (Hamer et al., 2006; Primo-Martín et al., 2006) could be also related to an increased permeability of the crust. Based on these suggestions, we recommend developing bread with optimal water vapor permeability of the crust without the need for channel application or composite bread making.

A higher water vapor permeability of the crust increases the water loss to the environment and therefore prevents the rapid wetting of the crust. A potential side effect could be excessive drying of the outer crumb. Our studies show that after 4 h storage time, sensory crumb softness was not significantly lower in breads with optimal crust permeability (Chapter 3). However, further studies of the effects of an increased permeability of the crust after 4 h storage time would be beneficial. We propose that bread with a rather high permeability of its crust will have a less soft crumb and a harder crust after a longer storage time. Therefore, it is necessary to choose the right permeability of the crust to ensure the longest possible retention of both crust crispness and crumb softness. In our view the retention of both is not possible for more than 10 hours, because water migration will either cause water accumulation in the crust, or the drying out of the crumb. This amount of time is sufficient for crispy breads, which are sold in bakeries and normally baked and consumed the same day.

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# Summary

## Summary

Crispness is one of the most important sensory characteristics of crispy bread. Consumers associate crispness with freshness, wholesomeness, and quality. This sensory sensation that consumers appreciate, however, is lost within a few hours after baking. Despite this fast loss of crispness, only a few methods have been described that prevents this fast change after baking. In addition, a description is needed of the mechanism leading to the fast increase of the water content of the crust.

The aim of this thesis was, therefore, to systematically determine the mechanisms that lead to the fast loss of crispness. This approach should reveal the parameters that are key to crispness retention and that, hence, need to be controlled to extend the duration of crispy sensation. It is known that the fast water uptake of crust causes the loss of crispness. However, it was not shown before, whether properties of crust or crumb mainly determine the water uptake of the crust. This knowledge should provide guidelines with which the industry can produce breads with optimal crispness retention.

Our research showed that the crust acts as a barrier for water migration, because of its low permeability (Chapter 2). Water from the inner wet part of the bread, the crumb, migrates fast to the crust, but cannot quickly pass into the environment. Water, which does not leave to the environment, accumulates in the crust. This water accumulation in the crust is the reason for the fast loss of crispness (Chapter 2). Water accumulation is especially pronounced during the first 30 min after baking. In this cooling phase, the differences in partial vapor pressure, which is the driving force for water migration, are the highest. The resulting fast water migration causes differences in crispness retention to be created during this cooling phase as shown in Chapter 6. This result confirms that the cooling phase is crucial for crispness retention.

The permeability of the crust is the parameter that controls the loss of crispness. Both parameters are very closely related (Chapters 2, 3, 4, 5, 6), and the doubling of the water vapor permeability from $4 \times 10^{-9}$ g/(m s Pa) to $8 \times 10^{-9}$ g/(m s Pa) leads to a more than eight times longer crispness retention (Chapters 2, 3, 5). There is a clear optimum here as well. At $8 \times 10^{-9}$ g/(m s Pa), sensory and instrumental crispness, and the softness of the crumb are the highest after 4 h storage time (Chapter 3). Based on these findings, we propose

that the increase of the crust permeability is the best way to create breads with the long crispness retention that is appreciated.

Different methods to reach the optimum permeability of the crust were applied: the application of channels through the crust (Chapters 2, 3), or the creation of spontaneous cracks in the crust (Chapter 5). Cracks are caused by a high thermal shock in crust material, with a low ability to dissipate stresses. In this thesis crust containing between 60% and 70% of gelatinized starch was prone to crack (Chapter 5). Specific crust properties could be created by using so-called composite breads, in which only the crust properties were varied. This newly established method allowed us to vary crumb and crust properties independently, which is a requirement for the separate study of the influence of crumb and crust.

In chapter 4 it was shown that crispness retention is not only affected by the water vapor permeability of the crust but also by the permeability of the crumb. A higher permeability of the crumb leads to a faster water migration from the crumb to the crust, and therefore to a significantly faster water uptake of the crust. This relation was found in Chapter 4, both experimentally and via modeling. Bread with a finer crumb had a higher water vapor permeability of the crumb and consequently a faster water uptake of the crust. However, the negative effect on the water uptake induced by fine crumb morphologies could be fully compensated for by changing the permeability of the crust (Chapter 4). Therefore, the water vapor permeability of the crust is more important for crispness retention than the permeability of the crumb. Both permeabilities were measured with particular methods: crust permeability was measured using a newly developed method for brittle materials, and crumb permeability by modeling the water flux though X-ray micro-computer tomography images of crumb pieces. The experiments in Chapter 4 also lead to a deeper understanding of the water migration in the crumb. The crumb is very transparent for water vapor; the water vapor permeability of the crumb is 30 times higher than of the crust and half the value of the air (Chapter 4). The water migration in the crumb is ruled by the water vapor transport through the interconnected gas cells and can be described by a simple Fickian diffusion model.

All of the findings were combined in a model that is discussed in Chapter 6. This model highlights the mechanisms, parameters, and time frames that cause changes in the crispness of bread. Changes in the crispness are determined by the water migration within the bread, which causes water accumulation in the bread crust. The water migration within the crumb could be well modeled, whereas the physical description of processes that lead to water loss and water accumulation in the crust is not complete. Nevertheless, this model combines experimental work and modeling to come up with an integrated view on crispness retention and shows that properties of the crust are key to crispness retention.

# Samenvatting

Knapperigheid is een van de belangrijkste sensorische eigenschappen van knapperig brood, omdat consumenten knapperigheid associëren met versheid, gezondheid en kwaliteit. Echter, deze sensorische beleving die consumenten waarderen gaat binnen enkele uren na het bakken verloren, hetgeen wordt veroorzaakt door een snelle opname van water door de korst. Ondanks dit snelle verlies van knapperigheid zijn er slechts enkele methoden beschreven om deze snelle verandering na het bakken te voorkomen. Daarnaast is er een beschrijving nodig voor het mechanisme dat leidt tot de snelle toename van het watergehalte.

Het doel van dit proefschrift is daarom het systematisch bepalen van de mechanismen die leiden tot het snelle verlies van knapperigheid. Deze aanpak zou de belangrijkste parameters die zouden moeten worden beheerst voor het behoud van knapperigheid uit moeten wijzen, zodat de duur van het behoud van de knapperige beleving kan worden verlengd. Deze kennis zou richtlijnen moeten opleveren, met welke de industrie brood kan produceren met optimaal behoud van knapperigheid.

Ons onderzoek laat zien dat de korst door zijn lage permeabiliteit als een barrière voor watermigratie functioneert (Hoofdstuk 2). Water uit het binnenste, vochtige deel van het brood, het kruim, migreert snel naar de korst, maar kan niet snel verloren gaan naar de omgeving. Water dat niet naar de omgeving verloren gaat accumuleert in de korst. Deze wateraccumulatie is de reden voor het snelle verlies van knapperigheid (Hoofdstuk 2). De meeste wateraccumulatie vindt plaats 30 minuten na het bakken. In deze afkoelingsfase zijn de verschillen in partiële dampdruk, welke de drijvende kracht voor water migratie is, het grootste. De resulterende snelle watermigratie veroorzaakt verschillen in behoud van knapperigheid tijdens deze afkoelingsfase (Hoofdstuk 6). Dit resultaat bevestigt dat de afkoelingsfase cruciaal is voor het behoud van knapperigheid.

De permeabiliteit van de korst is de parameter die het verlies van knapperigheid beheerst. Beide parameters zijn nauw verwant (Hoofdstukken 2, 3, 4, 5, 6), en het verdubbelen van de waterpermeabiliteit van 4 x $10^{-9}$ g/(m s Pa) naar 8 x $10^{-9}$ g/(m s Pa) leidt tot een meer dan acht keer zo lang behoud van

knapperigheid (Hoofdstukken 2, 3, 5). Ook hier is er een duidelijk optimum. Bij $8 \times 10^{-9}$ g/(m s Pa) zijn de sensorische en instrumentele knapperigheid en de zachtheid van het kruim het hoogste na 4 uur bewaartijd (Hoofdstuk 3). Gebaseerd op deze bevindingen, opperen wij dat toename van korstpermeabiliteit de beste manier is om brood te maken met het gewaardeerde lange behoud van knapperigheid.

Verschillende methoden om optimale korstpermeabiliteit te bereiken werden toegepast: het aanbrengen van kanalen door de korst (Hoofdstukken 2, 3), of het maken van spontane barsten in de korst (Hoofdstuk 5). Barsten worden veroorzaakt door een grote temperatuurschok in het korstmateriaal, met een lage capaciteit om stress te doen verdwijnen, bijvoorbeeld een korst die 60 tot 70% gegelatineerd zetmeel bevat (Hoofdstuk 5). Specifieke korsteigenschappen kunnen worden verkregen door gebruik te maken van zogenaamde composietbroden, waarin alleen de korsteigenschappen werden gevarieerd. Deze nieuwe methode liet ons toe de korst- en kruimeigenschappen onafhankelijk te variëren, hetgeen een vereiste is voor het afzonderlijk bestuderen van de invloed van korst en kruim.

Behoud van knapperigheid wordt niet alleen beïnvloed door waterdamppermeabiliteit van de korst, maar ook door de permeabiliteit van het kruim. Een hogere permeabiliteit van het kruim leidt tot een snellere watermigratie van het kruim naar de korst, en daardoor tot een significant snellere wateropname van de korst. Deze relatie was bevestigd in Hoofdstuk 4, zowel experimenteel als door modelleren. Brood met een fijner kruim, met meer grote verbindingen tussen de gascellen, had een grotere waterdamppermeabiliteit van het kruim en daardoor een snellere wateropname door de korst. Echter, het negatieve effect van de wateropname veroorzaakt door de fijne kruimmorfologie kan volledig worden gecompenseerd door het veranderen van de permeabiliteit van de korst (Hoofdstuk 4). De waterdamppermeabiliteit van de korst is dan ook belangrijker voor de behoud van knapperigheid dan de permeabiliteit van het kruim. Beide permeabiliteiten werden gemeten met afzonderlijke methoden: korstpermeabiliteit werd gemeten met een nieuw ontwikkelde methode voor broze materialen, kruimpermeabiliteit door het modeleren van waterflux door röntgentomografie afbeeldingen van stukken kruim. De experimenten in Hoofdstuk 4 leidden ook tot het beter begrijpen van watermigratie in het kruim. Het kruim laat waterdamp goed door:

de waterdamppermeabiliteit van het kruim is 30 maal hoger dan die van de korst en half zo groot als die van lucht (Hoofdstuk 4). De watermigratie in het kruim wordt beheerst door waterdamptransport door onderling verbonden gascellen en kan worden beschreven met een eenvoudig Fickiaans diffusiemodel.

Alle bevindingen zijn gecombineerd in een model dat in Hoofdstuk 6 wordt besproken. Dit model belicht de mechanismen, parameters en tijdsbestekken welke veranderingen in knapperigheid van brood veroorzaken. Veranderingen in knapperigheid worden bepaald door de watermigratie in het brood, welke wateraccumulatie in de korst veroorzaakt. De watermigratie in het kruim kan goed worden gemodelleerd, terwijl de fysische beschrijving van processen die leiden tot waterverlies en wateraccumulatie in de korst niet compleet is. Desalniettemin combineert dit model experimenteel werk en modellering om te komen tot een integrale blik op behoud van knapperigheid, en laat het zien dat eigenschappen van de korst cruciaal zijn voor het behoud van knapperigheid.

# Zusammenfassung

Knusprigkeit ist eine der wichtigsten sensorischen Eigenschaften von knusprigen Backwaren. Konsumenten assoziieren mit Knusprigkeit Frische, Genuss und Qualität. Backwaren, wie Brötchen und Brot, verlieren diese Eigenschaft jedoch innerhalb weniger Stunden nach dem Backen. Nur wenige Methoden sind beschrieben, die diese Qualitätsverluste vermindern. Des Weiteren steht eine ausführliche Beschreibung der Prozesse, die zu dieser schnellen Abnahme der Knusprigkeit führen, noch aus.

Das Ziel dieser Doktorarbeit war es, systematisch zu bestimmen, welche Mechanismen zum schnellen Verlust der Knusprigkeit führen. Durch diesen Ansatz sollten Faktoren bestimmt werden, die entscheidend beeinflussen, wie lange Backwaren knusprig bleiben. Es ist bekannt, dass die schnelle Wasseraufnahme der Kruste der Grund für den Verlust der Knusprigkeit ist. Jedoch wurde noch nicht gezeigt, ob Eigenschaften der Kruste oder der Krume die Wasseraufnahme der Kruste maßgeblich beeinflussen.

Im 2. Kapitel dieser Arbeit wird gezeigt, dass die Kruste von Brot und Brötchen eine Barriere für den Transport von Wasser darstellt. Wasser, welches aus dem Inneren Teil des Brotes, der Krume, zur Kruste migriert, wird verzöget an die Umgebung abgegeben. Die geringe Permeabilität der Kruste bewirkt, dass sich dieses Wasser stattdessen in der Kruste ansammelt. Diese Akkumulation von Wasser ist der Grund für den schnellen Verlust der Knusprigkeit (Kapitel 2). Die Akkumulation von Wasser in der Kruste ist besonders ausgeprägt während der ersten 30 Minuten nach dem Backen. Wir konnten zeigen, dass diese Abkühlungsphase entscheidend dafür ist, wie lange Backwaren knusprig bleiben (Kapitel 6).

Die Permeabilität der Kruste ist der Faktor, der den Verlust der Knusprigkeit maßgeblich beeinflusst (Kapitel 2, 3, 4, 5, 6). Brötchen mit einer doppelt so hohen Permeabilität der Kruste ($8 \times 10^{-9}$ g/(m s Pa) anstatt $4 \times 10^{-9}$ g/(m s Pa)) blieben viermal länger knusprig (Kapitel 2, 3, 5). Eine Permeabilität von $8 \times 10^{-9}$ g/(m s Pa) war optimal, um möglichst lange Krusten knusprig und Krumen weich zu bewahren (Kapitel 3). Diese Ergebnisse legen nahe, dass die

erfolgversprechendste Methode zur Herstellung von Backwaren mit langanhaltender Knusprigkeit, die Erhöhung der Permeabilität der Kruste ist.

In dieser Arbeit werden verschiedene Methoden zur Erreichung der optimalen Permeabilität der Kruste beschrieben: die mechanische Durchlöcherung der Kruste (Kapitel 2,3) und die Erzeugung von Rissen in der Kruste (Kapitel 5). Risse entstehen durch einen hohen thermischen Schock in Krusten, die aufgebauten Stress nicht ableiten können. In Kapitel 5 wurde gezeigt, dass Risse vor allem in Krusten mit einem Anteil von verkleisterter Stärke zwischen 60% und 70% auftraten.

In Kapitel 4 wurde gezeigt, dass der Verlust der Knusprigkeit nicht nur abhängig von der Permeabilität der Kruste ist, sondern auch von der Permeabilität der Krume. Eine höhere Permeabilität der Krume führte zu einer schnelleren Migration von Wasser durch die Krume zur Kruste, und somit zu einer signifikant schnelleren Wasseraufnahme der Kruste. Dieses Ergebnis wurde in Kapitel 4 experimentell und durch Modellierung gefunden. Brötchen mit feinerer Krume zeigten eine höhere Permeabilität ihrer Krumen und somit eine schnellere Wasseraufnahme ihrer Krusten. Jedoch wurde die bei Verwendung feiner Krumen erhöhte Wasseraufnahme, vollständig kompensiert durch die Veränderung der Permeabilität der Kruste (Kapitel 4). Die Permeabilitäten von Kruste und Krume wurden mit speziellen Methoden gemessen. Die Permeabilität der Kruste wurde mit einer neu entwickelten für brüchige Materialien geeignet Methode charakterisiert. Für die Bestimmung der Permeabilität der Krume wurden zunächst mit Hilfe der Mikro-Computertomographie Bilder der Krume erstellt, und anschließend der Fluss an Wasserdampf durch das 3D System modelliert. In Kapitel 4 wird des Weiteren der Wassertransport durch die Krume charakterisiert. Die Krume ist sehr transparent für Wasserdampf: die Permeabilität der Krume ist 30-mal größer als die Permeabilität der Kruste und nur um den Faktor zwei kleiner als die Permeabilität von Wasserdampf in Luft. Wassermigration durch die Krume wird bestimmt durch den Transport von Wasserdampf durch die miteinander verbundenen Poren und kann durch ein einfaches Fick´sches Diffusionsmodel beschrieben werden.

Im Kapitel 6 wurden die beschriebenen Ergebnisse in einem zusammenfassenden Model vereint. Dieses Model hebt Mechanismen, Parameter und Zeitspannen hervor, die für den Verlust der Knusprigkeit maßgeblich sind. Eine Unterscheidung zwischen Prozessen in der Kruste und der Krume wird dargestellt. In der Krume wurde die Wassermigration modelliert, wohingegen die physikalische Beschreibung der Prozesse in der Kruste nicht vollständig ist. Nichtsdestotrotz vereint das Model experimentelle Ergebnisse und Modellierungen um den Verlustes der Knusprigkeit von Backwaren ganzheitlich darzustellen. Diese Zusammenfassung verdeutlicht nochmals, dass Veränderungen der Eigenschaften der Kruste der Schlüssel zu einer verlängerten Knusprigkeit sind.

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# About the author

Anita Hirte was born 25th of December, 1982 in Berlin, Germany. After finishing secondary school in 2002, she started to study Food Technology at the Technical University in Berlin. The same field of study she followed up at the Wageningen University in 2005 and 2006. After her graduation in 2008 from the Technical University in Berlin she returned back to Wageningen. In Wageningen she started as a Ph.D. fellow at the Food Chemistry group of Wageningen University and at the Top Institute Food and Nutrition (TIFN). She was part of the TIFN project “Water migration in solids”. In 2012, Anita Hirte started as a specialist for food application at SE Tylose in Wiesbaden, Germany.

## List of publications

Hirte, A., Hamer, R.J., Meinders, M.B.J., Primo-Martín, C., 2010. Permeability of crust is key to crispness retention. Journal of Cereal Science 52, 129–135.

Voogt, J. A., Hirte, A., Meinders, M.B., 2011. Predictive model to describe water migration in cellular solid foods during storage. Journal of the Science of Food and Agriculture 91, 2537–2543.

Hirte, A., Hamer, R.J., Meinders, M.B.J., van de Hoek, K., Primo-Martín, C., 2012. Control of crust permeability and crispness retention in crispy breads. Food Research International 46, 92–98.

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Hirte, A., Hamer, R.J., Hoffmann, L., Primo-Martín, C. Cracks in bread crust cause longer crispness retention. Submitted for publication.

# Overview of completed training activities

**Conferences and workshops**

European young cereal scientists workshop, Viterbo, 2009

Delivery of functionality in complex food systems, Wageningen, 2009

Euro food water, Reims, 2010

Structure and rheology of cereal-based foods, Ghent, 2010

European young cereal scientists workshop, Budapest, 2010

AACC conference, Savannah, 2010

Cereals & Europe spring meeting, Freising, 2011

**General courses**

Ph.D. competence assessment, Wageningen, 2008

Ph.D. introduction week, Eindhoven, 2008

Basic statistics, Wageningen, 2008

Project and time management, Wageningen, 2009

Techniques for writing and presenting a scientific paper, Wageningen, 2009

Career assessment, Wageningen, 2011

Publishing research articles, Berlin, 2011

**Optional activities**

Ph.D. study trip, China, 2008

Ph.D. study trip, Switzerland and Italy, 2010

Cereal meetings

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