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Water Content or Water Activity: What Rules Crispy Behavior in Bread Crust?

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A dry crust loses its crispness when water migrates into the crust. It is not clear if it is the amount of water absorbed or the water activity (a_w) that leads to a loss of crispness. The hysteresis effect observed when recording a water sorption isotherm allowed us to study the effects of a_w and moisture content separately. All experiments were carried out on model bread crusts made from Soissons bread flour. The effect of water content and water activity on the glass transition of model bread crusts was studied in detail using two complimentary techniques: phase transition analysis (PTA) and nuclear magnetic resonance (NMR). The results were compared with sensory data and results from a puncture test, which provided data on acoustic emission and fracture mechanics during breaking of the crusts. The water content of the crust was found to be decisive for the transition point as measured by PTA and NMR. However, both water content and water activity had an effect on perceived crispness and number of force and sound peaks. From this may be concluded that the distribution of the water in the samples with a history of high water content is more inhomogeneous, which results in crispy and less crispy regions, thus making them overall more crispy than samples with the same water content but higher a_w.

INTRODUCTION

It is well-known that the crispness of dry cellular foods is lost when the water activity or the water content of the products rises above a critical value. Sensorial evaluations of crispy food products have been performed on, for example, crispy breads (*1*), model bread crusts (*2*), toasted rusk rolls (*3*), and extruded starch products (*4*). In general, above a water content of 9%, loss of crispness is observed in these products. Katz and Labuza (*5*) evaluated potato chips, popcorn, puffed corn curls, and saltines at different water activities with respect to crispness and textural hedonic quality with a sensory panel. Critical water activities ($a_{w,c}$), where the products became organoleptically unacceptable, generally fell in the 0.35−0.50 a_w range. This corresponded to critical water contents of 4.2−7.0% db. Sauvageot and Blond (*6*) found the same for breakfast cereals. Water causes hydration of the components of the crispy products. This results in an increase of the mobility of the macromolecules, which causes a glass to rubber transition of the amorphous regions of the macromolecules present (mainly proteins and carbohydrates) that were initially in the glassy state. Roughly at the same time, a loss of the crispy behavior occurs (*1, 7*). Several authors studied the relation between the glass transition of breadlike products at low moisture contents and the sensorial loss of crispness in more detail (*8–10*). They found that loss of crispness already occurred, while the crispy material was still in the glassy state, which is remarkable because it suggests that increased mobility of the macromolecules does not cause the loss of crispness.

The aim of this study was to investigate the relation between the loss of sensorial crispness in a bread crust model and the water content and water activity. It is important to know whether only the water content or the water activity should be used to explain loss of crispness or if there are other mechanisms involved in loss of crispness. The local water activity determines the direction of water migration, but the water content may finally determine the level of crispness. Samples of bread crust were brought at different water contents and equal water activities by making use of the fact that different water contents at a certain a_w can be achieved by varying the relative humidity (RH) trajectory (hysteresis effect). Here, different water activities at the same water content or vice versa were obtained by either exposing a dry sample to the desired water vapor pressure or by exposing it to 90% air humidity first and then drying it back to the desired water vapor pressure. For example, the crust of a protected atmosphere packaged part-baked bread will follow the trajectory of high RH and then drying back when baked-off, whereas a bread that is baked completely in one step will not show this hysteresis effect. Although other processes may

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Table 1. Composition of the Soissons Flour (Analyzed According to the Methods Mentioned in Ref 16)

moisture (%)	protein (% db)	starch (% db)	lipids (% db)	damaged starch (% db)
14.8	12.9	79.3	1.0	4.9

also take place during storage, baking, and baking-off of this bread, the hysteresis effect might influence the crispness and crispness retention of the crust.

The hysteresis effect implies that products with a similar water activity can have a different water content and visa versa depending on their history. It also means that the system is not in a true thermodynamic but semiequilibrium state, which is stable on the time scale used.

Wolf et al. (*11*) classified the variations in hysteresis loops in foods into three general groups, namely, high-sugar/high-pectin (e.g., apple), high-protein (e.g., pork), or high-starch systems (e.g., rice). Starch gives the largest hysteresis loop of the three groups. Several theories have been suggested to explain hysteresis for porous solid foods. Most were established on the basis of capillary condensation phenomena (*12, 13*), but for starch type products, activation of sorption sites due to the history of high water content was also suggested as a possible explanation (*11, 13, 14*).

The glass transition temperatures of the samples studied were measured by a phase transition analyzer (PTA) (*15*). By this technique, a transition temperature in the mechanical behavior of the material is measured. This technique gives more constant results than, for example, differential scanning calorimetry (DSC), which does not always show a T_g in dry inhomogeneous products (*9*). The PTA is especially suitable for powders. The state of the water in the samples was determined by low field NMR spectroscopy. This is a spectroscopic technique based on the magnetic properties of atomic nuclei and is often used to monitor motional properties of molecules by analyzing the relaxation characteristics of the NMR active nuclei, such as ^{1}H. With respect to protons from water, a difference can be made between bound (short T_2) and free (long T_2) water.

The sensorial difference between the different samples was evaluated by a sensory panel. A texture analyzer was used to evaluate the fracture mechanics and acoustic emissions of the different samples.

MATERIALS AND METHODS

Materials. Bread crusts were prepared using a wheat flour from variety Soissons. The flour was purchased from Meneba (Meneba Meel BV, Rotterdam, The Netherlands). The composition of the flour is shown in **Table 1**.

Methods. *Preparation of the Model Crust.* Dough was mixed in a farinograph mixer (Brabender, Duisburg, Germany) using a 50 g mixing bowl. The formulation included flour, NaCl (2 g/100 g flour), dry yeast (1.7 g/100 g flour), and ascorbic acid (20 ppm). A 55.5% water on flour basis was used to prepare the dough. The temperature of the added water was 22 °C, and the starting temperature of the mixing bowl and flour was 23 °C. The dough was mixed at a speed of 100 rpm until the dough temperature reached 26 °C, which corresponded with the maximum in the torque−time curve. After it was mixed, the dough was separated into three pieces and made into model crusts following the procedure explained earlier (*16*). After they were baked, the model crusts were left to cool to room temperature, wrapped in plastic bags, and frozen and stored at −20 °C until use.

RH Equilibration of Model Crust. The crust samples for NMR and PTA measurements were milled in an analytical grinder (type A10, IKA Labortechnik, Staufen, Germany) 2−3 times for 10 s (to prevent heating of the sample) until a fine powder was obtained. The powder was sieved using a 0.5 mm sieve. Pieces larger than 0.5 mm were discarded. For the sensory test, the model crust samples were presented as such to the sensory panel. The samples were stored in climate chambers (Weiss SB 11^{300}, Weiss technik LTD, Buckinghamshire, United Kingdom) at 22 °C and 90% RH for one night and then put at 40 and 50% RH and 22 °C for 5 days. The reference samples were stored immediately at 40, 50, 57, and 63% RH for 5 days. For NMR and PTA experiments, additional samples were stored immediately at 6, 19, 30, 78, and 85% RH.

Table 2. Enthalpy of the Retrogradation Peak at 55 °C As Measured by DSC at a Speed of 5 °C per Minute

RH sample	ΔH at 55 °C	RH sample	ΔH at 55 °C
40% ($a_w = 0.4$)	0.9	50% ($a_w = 0.5$)	0.8
90 > 40% ($a_w = 0.4$)	0.8 ± 0.2	90 > 50% ($a_w = 0.5$)	0.8 ± 0.0
57% ($a_w = 0.57$)	2.0	63% ($a_w = 0.63$)	1.9 ± 0.2

Amount of Retrograded Starch As Determined by DSC. Around 8 mg of powdered and equilibrated model crust samples (<0.5 mm) were weighed into stainless steel pans. DSC measurements were performed with a Perkin-Elmer Diamond DSC calorimeter (Perkin-Elmer Corp., United States). Indium and galium were used to calibrate the system. The samples were heated from 20 to 100 at 5 °C/min. An empty stainless steel pan was used as a reference during the DSC measurement. The enthalpy (ΔH) of the amylopectin retrogradation was determined (peak at 55 °C) and expressed in J/g of sample (db).

The results are shown in **Table 2**. Storage for 5 days at a higher RH (57 and 63%) had more effect on the extent of the retrogradation of starch than storage for 1 day at 90% RH even though the samples had an equal water content after 5 days. There was no difference between the amount of retrograded starch of the samples stored at 40 and 50% RH with a history of 1 day at 90% RH as compared to the samples that were stored at 40 and 50% RH from a dry state.

Water Activity. The water activity of the crust samples was measured using an Aqua Laboratory Series 3 (Decagon devices, Pullman, United States) at 22 °C.

Water Content. The water contents were obtained gravimetrically by drying at 105 °C for 15 h.

Low Field NMR Experiments. Proton relaxation measurements were performed using a Minispec MQ20 20 MHz NMR analyzer (Bruker, Germany) operating at a resonance frequency of 19.95 MHz. After 4 days of equilibration, samples (approximately 0.5 g each) were placed into glass vials (18 cm height and 9 mm diameter) and left in the climate chambers for another day. The vials were then sealed with a cap to prevent moisture loss, and NMR measurements were performed at 25 °C. The transverse relaxation (T_2) time in the ms time domain was measured using the Carr-Purcel-Meiboom-Gill (CPMG) pulse sequence, which consists of a 90° pulse followed by a train of 180° pulses to refocus the NMR signal. The 90−180 pulse spacing was set to 0.05 ms. Relaxation curves obtained from the CPMG sequence were analyzed by fitting a two-exponential to the relaxation curve.

The free induction decay (FID) experiment was performed to obtain information about the ratio between solid and mobile protons. The FID was recorded with a recycle delay of 1.5 s. An average of 64 scans was taken. The following expression was fitted to the FIDs:

$$F(t) = \mathrm{A}e^{(-a^2t^2)/2}\frac{\sin(bt)}{bt} + \mathrm{B}e^{-t/T_{2m}} \quad (1)$$

In this equation, the parameters A and B represent the contributions of the immobile and mobile protons in the sample. Parameter T_{2m} is the spin−spin relaxation time of the mobile proton fraction. The NMR spectrum of the immobile proton fraction is assumed to be a rectangular line shape with a total width 2*b*, convoluted with a Gaussian line shape with a standard deviation given by parameter *a* (*17, 18*).

PTA. The PTA (Wenger, Sabetha, KS) uses a combination of time, temperature, pressure, and moisture to measure the T_g and T_m of a biopolymer sample (*19*). It consists of two sealed chambers, top and bottom, separated by an interchangeable capillary dye. For the experiments presented in this paper, only the closed dye was used (the open dye is only used when evaluating flow behavior). The two

Table 3. Water Content of Soissons Model Crust Samples

RH	sample	water content	RH	sample	water content
40% ($a_w = 0.4$)	A1	7.5 ± 0.0	50% ($a_w = 0.5$)	B1	9.0 ± 0.2
90 > 40% ($a_w = 0.4$)	A2	10.4 ± 0.1	90 > 50% ($a_w = 0.5$)	B2	12.1 ± 0.0
57% ($a_w = 0.57$)	A3	10.3 ± 0.2	63% ($a_w = 0.63$)	B3	12.0 ± 0.1

chambers house electric heaters and contain a hollow cavity that allows a cooling fluid to be used. The pistons, mounted together through sidebars, are held in a fixed position during testing. Air cylinders, mounted to the bottom of the PTA, maintain constant pressure on the sample. The sample was brought in the upper chamber, which was closed by the piston afterward. A linear-displacement transducer measures the sample's deformation, compaction, and flow relative to initial sample height (*20*). In this study, the T_g was measured at 100 bar and a heating rate of 5 °C per minute. The temperature at the start of the measurement was around 20 °C. One gram of sample was used for each measurement. The glass transition temperature was taken as the temperature where the derivative of the displacement temperature plot exhibited a maximum.

Sensorial Testing. A two alternatives forced choice (2AFC) discrimination test was performed with 17 panelists (three males) in duplicate on two different days. The panelists were between 34 and 64 years old. First, they were trained by asking them to order three model crusts with a water activity of 0.4, 0.64, and 0.85 on crispness. During the test, they were asked to point out the most crispy sample of two. They were offered Soissons model crusts of equal a_w but of different water contents and model crusts of equal water content but of different a_w. The water contents and water activities are shown in **Table 3**. The number of selected samples in the 2AFC test was tested for significance by using a normal approximation of the binomial distribution [the results of the 2 days were taken together resulting in a number of panelists (n) of 34].

Mechanical and Acoustic Measurements. Mechanical testing was performed using a texture analyzer (TA-XT Plus, Stable Micro Systems Ltd., Surrey, United Kingdom). Pieces (different sizes) of model crust were taken for the measurement. The pieces were placed on a solid metal plate and punctured with a cylinder of 2 mm diameter at a speed of 0.1 mm/s. This speed was chosen to discriminate as many fracture events as possible. Ten samples were analyzed for each condition.

The sound emitted during fracturing was recorded simultaneously. For this purpose, an acoustic sensor (Brüel & Kjær 4189 prepolarized free-field 1/2" microphone plus a 2671 Deltatron preamplifier microphone, Nærum, Denmark) with a frequency band of 6.3 Hz up to 20 KHz, and a sensitivity of 50 mV/Pa was used. A fixed distance of 4.5 cm between the model crust and the microphone was used for sound recording. The analogue sound signal and the data of the texture analyzer were digitized using a Brüel & Kjaer Front-end A/D converter system (type number 2827) at a sampling rate of 65 kHz. All fracture and sound tests were performed inside an anechoic acoustic isolated chamber to avoid interference with an external source of sound. Recording and initial signal analyses were performed using Brüel & Kjær Pulse Labshop Software (version 7.0). Both the number of sound pulses and the force peaks were counted, and a linear distance was calculated for the force−time curve according to Meinders et al. (*21*) using Matlab software (Matwork version 7.0.4).

RESULTS

Samples were evaluated with different techniques to check the effect of water content and water activity on the glass transition temperature as measured with the PTA, water mobility as measured with NMR, and sensorial, mechanical, and acoustic properties of crispy model bread crusts. **Figure 1** and **Table 3** show the water activity and water contents of the two series (A and B) that were used for the tests. The reference samples are on the adsorption part of the isotherm, and the high water content samples are on the desorption part of the isotherm.

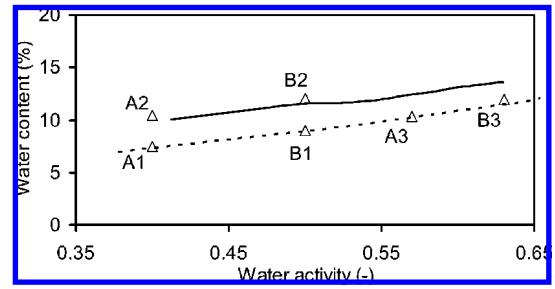

Figure 1. Sorption isotherm of bread crust indicating the samples used in this study. Parts of the sorption (broken line) and desorption (solid line) isotherms are shown. The sorption isotherm was started at 40% RH. The desorption curve was started at 90% RH. A1−A3 and B1−B3 indicate the samples as mentioned in the text.

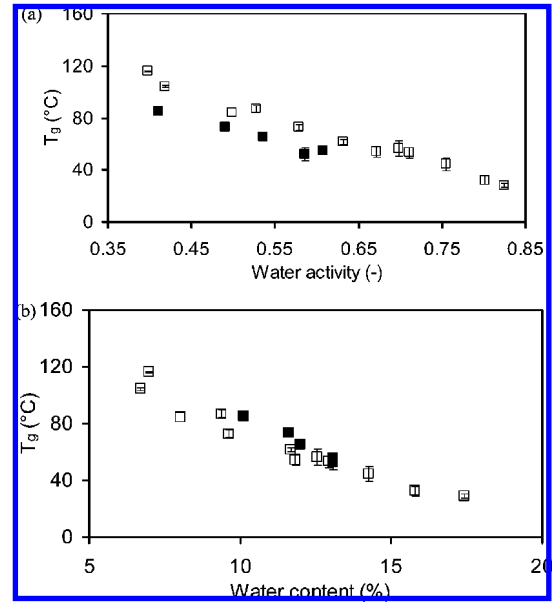

Figure 2. Glass transition temperatures as a function of a_w and water content as measured by the PTA. Results for the reference model crusts (□) and model crusts with a history of high a_w (■) as a function of a_w (**a**) and water content (**b**).

PTA. With the PTA, the glass transition temperature of the bread crust particles was evaluated. Samples of different water contents (between 7 and 18%) and a_w (between 0.4 and 0.82) were tested. The water content difference between two samples at the same water activity varied from 3.4 (at the lower RH) to 2% at 65% RH (**Figure 1**). In **Figure 2**, the resulting transition temperatures of the different samples are shown. **Figure 2a** shows the PTA transition temperatures against water activity, and in **Figure 2b**, the same transition temperatures are plotted against water content. The glass transition temperature as measured with PTA decreased with increasing water content and water activity. The PTA results were comparable with the DSC results as obtained for model crusts of Soissons flour before (*2*). **Figure 2a** shows that the samples with a higher water content had a significantly lower glass transition temperature at equal a_w. **Figure 2b** shows that the difference in water activity of the sample had no influence when comparing the glass transition temperatures of samples with equal water content but different a_w.

NMR. NMR was used to obtain information about the mobility of the (water) protons in the model crust in relation to

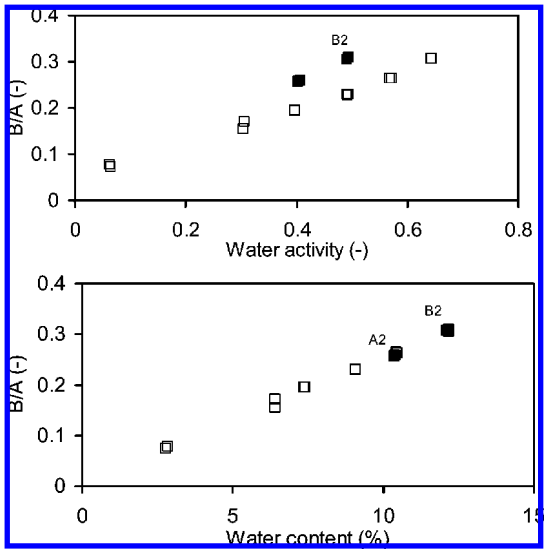

Figure 3. Ratio of mobile (B) over solid (A) protons as measured by FID NMR as a function of a_w and water content. Results for the reference model crust (□) and model crust with history of high a_w (samples A2 and B2) (■) as a function of a_w (**top**) and water content (**bottom**).

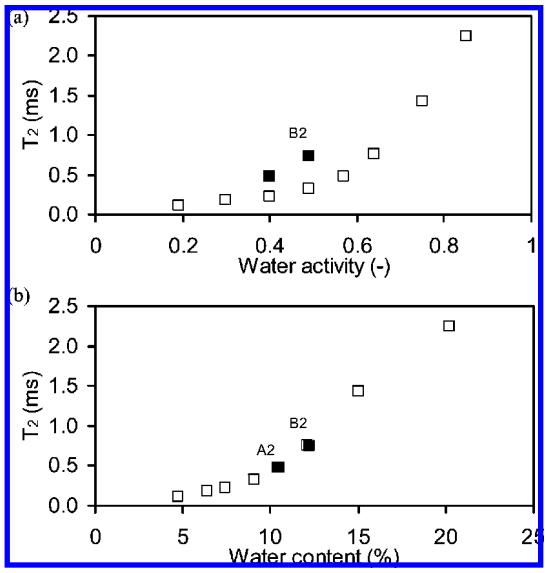

Figure 4. CPMG NMR T_2 relaxation time as a function of a_w and the water content. Results for the reference model crust (□) and model crust with a history of high a_w (samples A2 and B2) (■). A larger T_2 indicates a higher mobility of the water protons. Samples as a function of water activity (**a**) or water content (**b**).

water content and water activity. A single-pulse FID experiment was used to study the ratio of mobile protons (B) over immobile protons (A). The mobile protons are associated with water, and the immobile protons are associated with the solids (e.g., starch) (*22*). The results are shown in **Figure 3**. This ratio increases with increasing water content and a_w. At a fixed water content, this ratio turned out to be unaffected by a variation in water activity.

For the single-pulse experiment, a T_{2m} relaxation time associated with the mobility of water was calculated as well. However, as the decay in this region is more affected by field inhomogeneity, a CPMG pulse sequence was subsequently used to study this component (*22*). **Figure 4** shows the T_2 relaxation time from a CPMG experiment for the different samples. The protons of the water molecules with a higher mobility will have longer magnetic relaxation times. The T_2 value is a result of a

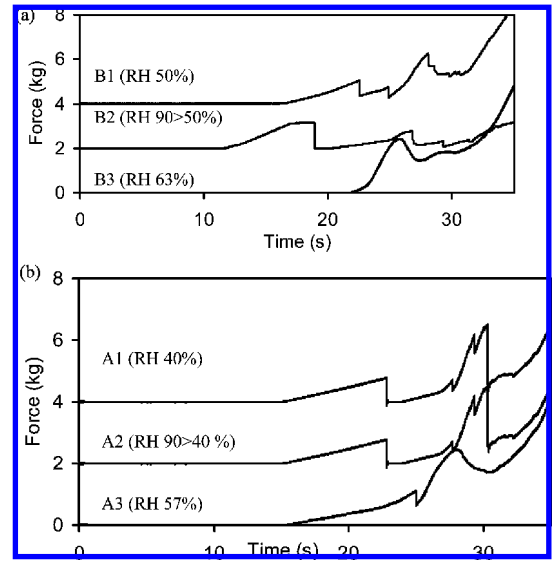

Figure 5. Force−time curves as measured with a puncture test with a needle by a texture analyzer. Results for samples A1, A2, and A3 (**a**) and B1, B2, and B3 (**b**). For clarity reasons, the upper lines are shifted along the *y*-axis.

double exponential fit. The shown value for T_2 corresponds to around 90% of the total amplitude. T_2 (mobility of protons and therefore mobility of water) increases with increasing water activity. At lower water activity (up to a water activity of around 0.58), the T_2 value for this fraction of water protons increases very slowly with increasing water activity. This probably means that at a molecular level not all water-binding sites have been hydrated at a water activity below ∼0.58. At higher water activities, the T_2 value starts to increase more rapidly. Likely, then only part of the water molecules present will be directly bound to the polymer matrix; therefore, the mobility will be higher on average. **Figure 4a**,**b** shows that at a fixed water content, this relaxation time is unaffected by a variation in water activity.

Texture Analyzer. To evaluate the effect of water content and water activity on the mechanical properties and acoustic emission during breaking of the model crusts, a puncture test was performed. Several pieces of model bread crust were punctured, and the sound and force signal were recorded. Results of the force−time signal during puncturing of a model crust with a needle are shown in **Figure 5a** for the set of samples stored at 40 and 57% RH and in **Figure 5b** for the set of samples stored at 50 and 63% RH. As can be seen, the three different samples all show different behaviors, especially the samples stored at 57 and 63% RH, which show more bending than breaking behavior. To evaluate the results in more detail, the linear distance and the number of force and sound peaks were counted for all samples, and the results are displayed for the series with samples A in **Figure 6a**−**c**, respectively. For the series with the B samples, the trend was the same (results not shown). The linear distance is a measure to evaluate the jaggedness of the curve. It is defined as the length of an imaginary line joining all points on the graph between in this case the point at which the force curve starts to increase (when the needle hits the sample, generally after around 15 s) until 38 s, which is about the end of the experiment. A highly jagged line will have a longer linear distance and is expected to correspond to a more crispy product than a smooth line (*23*). **Figure 6a** showed no significant difference between the linear distances of the samples, but the average linear distance was shorter for samples A3 and B3, which had a high water content

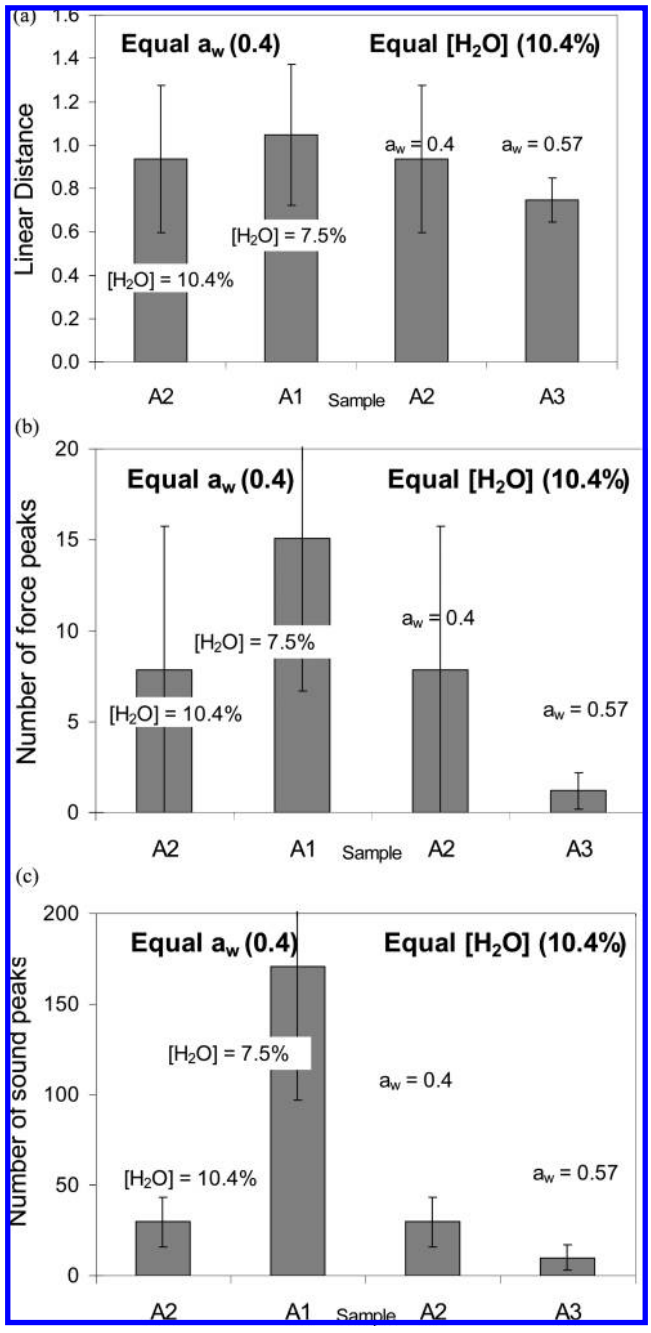

Figure 6. Effect of water content and a_w on the linear distance (LD) and number of force and sound peaks in a puncture test. Results for LD (**a**), number of force peaks (**b**), and number of sound peaks (**c**) for reference model crusts (A1 and A3) and model crusts with a history of high a_w (A2) as measured with a needle by a texture analyzer. On the left, a comparison at equal a_w; on the right, a comparison at equal water content.

and a high a_w. However, the results for the number of sound peaks (above a noise threshold of 6×10^{-5} Pa) and force peaks did show significant differences. The samples stored at 40 and 50% RH (A1 and B1) showed the most force and sound events, whereas the sample stored at 57 and 63% RH (A3 and B3) showed the lowest number of force and sound events. For the latter samples, the fracture was actually more bending rather than breaking as can be seen by the rounding (lack of sharp peaks) in the force vs time curve for these samples (**Figure 5**). The behavior of samples stored at 90% RH and later dried back to 40 or 50% RH (A2 and B2) was intermediate.

Sensorial Test. The two sets of samples were tested by a panel with respect to their difference in sensorial crispness.

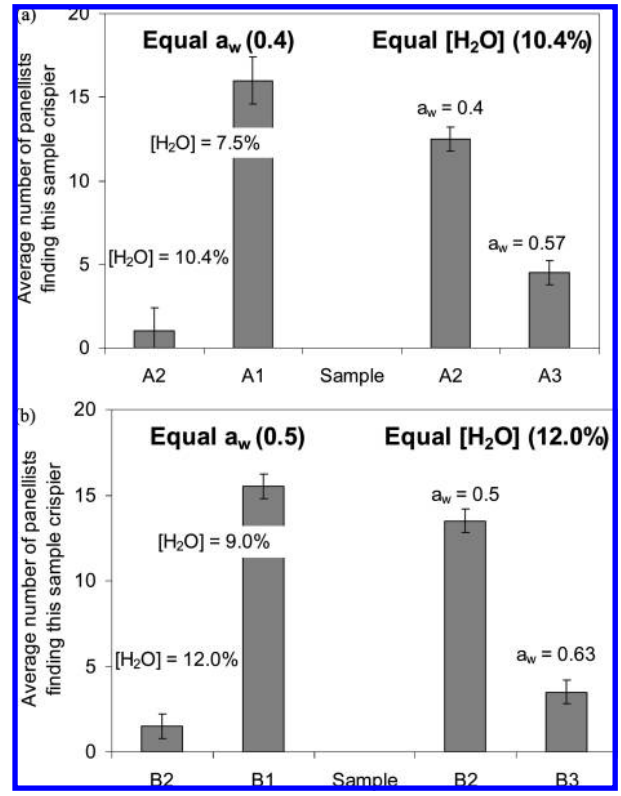

Figure 7. Contribution of water content and a_w to crispness perception as measured in a "two alternatives first choice test". The average number of panelists finding the specified Soissons model crust sample the crispier one of the two for series A (**a**) and B (**b**). Comparison for equal a_w on the left and for equal water content on the right.

During each test, two samples of Soissons model crust were compared. In the first set, we compared samples with equal a_w but different water contents. For this purpose, one sample was stored at 90% RH and dried back to a certain a_w (A2 or B2), and the other sample was brought immediately at this set a_w from a dry state ($a_w \sim 0.2$) (A1 or B1). In a second test, we compared samples with equal water content but different a_w. For this purpose, the samples stored at 90% RH and dried back to 40 or 50% RH (A2 or B2) were compared with samples that were brought at a similar water content but higher a_w from a dry state (A3 or B3). The results of the sensory test are presented in **Figure 7**. Subjects selected samples with low water content as more crispy for samples with equal a_w [$n = 34$, x (number of subjects choosing higher water content as less crispy) $= 32$ and 31, $p \leq 0.00000033$, for A1 and B1 as compared to A2 and B2, respectively]. Subjects selected samples with low a_w as more crispy for samples with equal water content ($n = 34$, $x = 25$, and 27 $p \leq 0.0018$, for the samples A2 and B2 as compared to A3 and B3, respectively). The first results indicate that the water content determines crispness. On the other hand, the second result suggests that crispness depends on the water activity. These results followed the same trend as the results from the puncture test in the sense that both water content and water activity seem to play a role in determining crispness.

DISCUSSION

Effect of Water Content and Relation with RH. A dry crust starts losing its crispness when water migrates into the crust. It is not clear if it is the amount of water absorbed or the water activity that is the most important factor in the process leading to loss of crispness.

The hysteresis effect observed when recording a water sorption isotherm allowed us to study effects of a_w and moisture content separately. Information on the mobility of water and the macromolecules was obtained, as well as information on the sensorial and textural properties of the model crusts. The results show that the sensorial crispness and instrumentally determined fracture behavior may depend on both the water content and the water activity or, in other words, on the history of the sample. According to the NMR results, the water in the samples with a history of high a_w is still in a "more free" state than the sample with the same a_w but a lower water content. Because NMR is a technique that measures an average mobility of the water in the complete sample, this technique says nothing about where the water exactly is. The water in the samples with a history of high a_w could be more inhomogeneously distributed than in the samples with equal water content but higher a_w. This also means that the regions where cracks can be stopped are more inhomogeneously distributed. As a consequence, regions with different crispness might be present in the sample resulting in an apparently overall more crispy product.

For starch type products, the hysteresis effect is often explained as the creation of more water binding places due to the history of the sample that has been at RH 90% and dried back. This would explain the lower measured water activity. If there are more binding places for water, the water will on average be more tightly bound, resulting in a lower water activity. The fact that a history of high a_w has no effect on the mobility of the water protons at equal water content suggests that hysteresis in bread crust may not be caused by an increased number of binding places for water in the sample. Possibly, the a_w is, as well as the water, not homogeneously distributed in the sample with a history of high a_w. More research has to be done before a more definitive conclusion can be drawn.

Labat (*24*) investigated the effect of starch crystallinity on the number of force peaks as measured with a puncture test. She concluded that the retrograded samples were characterized by a higher number of peaks than the reference samples. The former are therefore likely to be more crispy. In bread crust, only part of the starch is gelatinized; therefore, only part of the starch can retrogradate (*25*). DSC results (**Table 2**) show that only the samples that were stored at higher RH (57 and 63%) showed a significantly higher amount of retrograded starch (expressed as ΔH_r) than the other samples. However, these samples were rated as the least crispy. Therefore, we do not expect that retrogradation of the starch has had a clear effect on the outcome of our experiments. Why there is no difference in retrogradation between the samples with a history of 1 day of storage at 90% and the samples stored at 40 and 50% RH from a dry state is not clear.

The different water activities of samples with equal water content had no influence on the glass transition temperature as measured with the PTA. This may be expected because the transition temperatures are quite elevated and some transfer of the water possibly already took place due to the high pressure put on the sample and the increase in temperature.

Results from sensory and texture analyses in which the effect of water content and water activity on the crispness of model crusts is evaluated show that the history of the sample plays a role in sensory perception of crispness. The glass/rubbery transition temperatures as measured by PTA and the mobility of the protons as measured by NMR are directly related to the water content. Samples with a different a_w but equal water content give equal results. Possibly an inhomogeneous distribution of water and consequently crispy and less-crispy regions exist in the samples with a history of high a_w, thus making them overall more crispy than samples with the same water content but higher a_w.

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