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A study of cracks in dry cereal products

Chloé Bailhache^{a,b,c,e}, Bruno Pontoire^{b,c}, Lucie Ribourg^{b,c}, Camille Jonchère^{b,c}, Delphine Queveau^{a,c}, Mark Irle^d,
Ellen Thieffry^e, Alain Le-Bail^{a,c}, Patricia Le-Bail^{b,c} *

^a ONIRIS, UMR 6144 GEPEA CNRS, F44322 Nantes, France

^b INRA, UR1268 Biopolymers Interactions Assemblies, BP 71627, F44316 Nantes, France

^c SFR IBSM 4202 INRA CNRS BP 71627, F44316 Nantes, France

^d ECOLE SUPERIEURE DU BOIS, F44306 Nantes, France

^e FRANDEX, Z.I. Saint Denis les Lucs B.P. 18 85170 Saint Denis la Chevasse

* Corresponding author.

Present address: INRA BP 71627, F-44316 Nantes, France

E-mail address: patricia.le-bail@inra.fr

Abstract

This paper is a study of checking and breakage of dry cereal products like crackers. The products studied were produced on an industrial line; almost no cracks were observed for Plain crackers (PCs), whereas 100% of the crackers with topping (CTs) exhibited cracks. Environmental SEM images suggested that miniature cracks initiated around the piercing holes of the crackers and then extended during storage.

A study of the impact of each ingredient and of their interaction on the degree of starch gelatinization was carried out using a simplified model system (wheat flour, water and gradual enrichment until a model cracker dough was obtained). The addition of salt or sugar to flour at 40% water content shifted the starch gelatinization temperature slightly higher in comparison to a control mixture (only flour and 40% water content). A comparison of the residual gelatinization enthalpy between the PCs and the CTs made during storage (up to 3 weeks) showed that the degree of gelatinization of the CTs was more significant than the PCs (especially in the center) because of the presence of water in the topping in the center of the cracker. X-ray diffraction confirmed that the center of the CTs was indeed very different from the PCs.

Keywords: crackers, breakage, gelatinization, starch, structure

30

31 **Highlights:**

- 32 • Checking and breakage of cracker with and without topping has been investigated
- 33 • The strong heterogeneity of water distribution contributes to a higher checking risk
- 34 • Checking starts from the piercing done in the crackers as observed by SEM
- 35 • Crackers with topping have a higher amount of gelatinized starch under the topping
- 36 • A higher amount of amylose lipid complex was present in crackers with topping

37

38 **1. Introduction**

39 Dry cereal products (DCP) such as crackers, biscuits and cookies undergo a very specific baking
40 process combining a baking followed by a drying until reaching a final water content in the range of
41 3-5 % on a dry basis (DB). DCP are generally classified by the consistency of the dough (Whiteley,
42 1971); hard or semi-hard doughs are usually related to salted, unsweetened and semi-sweet biscuits.
43 This includes all types of crackers, puff pastries and semi-sweet biscuit varieties. In addition to having
44 low sugar, or even no sugar, the fat content rarely exceeds 22% of the quantity of flour, except in the
45 case of puff pastry (Whiteley, 1971). This category of DCP differs from bread and cakes in terms of
46 crispiness and a water content usually below 5%, providing a fairly long shelf life (Wade, 1988). The
47 type of cracker considered for this study are "hard dough" type crackers and more precisely in the
48 group "savory or snack crackers" (Manley, 2011).

49 In the cracker industry, certain groups of products are renowned for breakage at variable times after
50 baking as a result of a hairline cracking phenomenon known as "checking". Cracker checking is
51 usually observed as cracks which extend partway across a central portion of the biscuit rendering it
52 very prone to complete breakage on subsequent handling (Dunn & Bailey, 1928; Saleem, Wildman,
53 Huntley, & Whitworth, 2005). The mechanisms of the crack phenomenon seem to find their
54 explanation during the cooling phase of crackers. Indeed, once the crackers exit the oven, a water
55 gradient is present within the product with higher water content at the center than at the periphery.
56 This moisture gradient can be attributed to baking but also to the evolution of the distribution of
57 water during baking among the various constituents (starch, proteins etc). This gradient will drive
58 water transfer within the cracker in order to reach equilibrium. The sections of the crackers that will
59 uptake water will expand whereas the sections that will lose water will shrink, resulting in thermo

and/or hydro mechanical stress that may cause cracks and eventually breakage, particularly if the product is in a glassy state (Manley, 1983).

The use of topping, usually rich in water, increases the risk of breakage due to the setting of higher moisture content in the surface onto which the topping has been added. In addition, the presence of a higher amount of water is supposed to modify the starch gelatinization process, which is strongly dependent on the availability of water.

This work aims at elucidating the precise impact of an added topping on the risk of cracker breakage. To address this objective, a comprehensive study based on a multi-scale approach has been considered covering microscopic and molecular scales by focusing on the interactions between the different constituents of the dough but also by relying on the role and distribution of the water during baking, post baking cooling and storage.

2. Materials and methods

2.1. Cracker making

The crackers considered in this study were produced in an industrial baking line. For the crackers with topping (CT), a specific topping was used as shown in Figure 1. The precise recipe of the topping cannot be revealed for confidentiality reasons. The water content of the topping added on the dough cracker top is $61.4 \pm 0.6\%$ in dry basis before baking. The addition of the topping before baking can therefore have a significant impact during baking since it causes a very substantial water intake in the center of the cracker. For this reason, analyzes were done on CTs and on PCs, in order to observe the impact of the topping on the final structure of the products.

The cracker dough consists mainly of flour, fat, sugars and salt in the proportions shown in Figure 1a. The dough contains 38% water in dry basis. The composition of dough pieces with addition of topping was presented in Figure 1b.

The cracker with topping (CT) before baking is composed of dough and topping; representing respectively 79% and 21% of the final dough. As the topping has a water content of $61.4 \pm 0.6\%$ dry basis, the 21% of topping are decomposed into 8.1% dry topping and 12.9% water. CTs therefore contain 43% water compared to 38% for PCs, ie a 5% increase in water by adding the topping to the surface of the product.

The dough was laminated very finely and was baked in a conveyor oven. The set of steps in the preparation of crackers is very close to the classic biscuit production scheme presented by Manley

(1998) with preparation of puff pastry, rolling using three sets of sizing rollers to reduce the thickness, the relaxation of the dough, the imprint to give the shape of the biscuit, the piercing, and the removal of a possible topping. The industrial oven used on the line of crackers is divided into 5 zones. The average baking temperature is from 200°C and the average baking time is from 4 minutes. At the exit of the oven, the crackers were sprayed with oil, packaged and stored.

The experiments were carried out on 3 different productions and on 3-5 samples per experiment, for PCs and CTs.

2.2. Cracker storage conditions

The PC and CT crackers studied had followed the industry partner's normal post cooking procedure, i.e. they were stored in a plastic pouch within a large storage bin for 4 weeks at around 20 °C. The crackers were analyzed at the end of baking and before storage (week 0) and after storage in bins for 1, 2 and 3 weeks in order to follow the evolution of any cracks and to assess the degree of staling.

2.3. Visual observation of cracks

PC and CT were observed by environmental scanning electron microscopy (ESEM Quanta 250, FEI, Holland) used in "Lo Vac" mode. This mode is recommended for "dry" samples. The maximum chamber pressure was 130 Pa and, consequently, the samples dried slightly whilst being observed.

2.4. Sorption isotherm

The PC and CT samples were ground and placed in sorption flasks containing the following saturated saline solutions LiCl, MgCl₂, Mg(NO₃)₂, NaCl, KCl, BaCl₂ with relative humidities of 11.1%, 32.7%, 54.4%, 75.3%, 84.3%, 90.2% respectively. The flasks were set under vacuum and after a sufficient storage time (2 weeks), the water content was measured by Thermo Gravimetric Analysis. The water content of the sample was determined using the equation (1) below with S: water content, m_w: wet mass and m_d: dry mass (Table 1).

$$S = \frac{(m_w - m_d)}{m_w} * 100 \quad (1)$$

2.5. Freezable water content

DSC thermograms were recorded with a micro differential scanning calorimeter MicroDSC7 evo (SETARAM instrumentation, Caluire, France). The equipment was calibrated with indium. Stainless steel pans were used and an empty pan was taken as a reference.

PCs and CTs were studied before and after equilibration in the flasks containing saturated saline solutions. Samples were collected and placed on the pan and the pan was hermetically closed. The

DSC scans were performed from 20 to -20 °C ; -20 to -30°C and from -30 °C to 20 °C at a scanning rate of 0.3 °C/min. A 10 minutes plateau was imposed between each temperature ramp.

2.6. Measurement of lipid content in a cracker

Lipid content in PCs and CTs was measured with the Bligh and Dyer method, which is a cold lipid extraction method. The proportions of chloroform / methanol / aqueous phase were 2/2/1.8 v/v/v. A biphasic system was obtained: methanol and water constitute the upper phase and the chloroform phase, which contains lipids, corresponds to the lower phase. 50 mL capped glass tubes were used, in which about 1 g of sample, 10 mL of methanol, 10 mL of chloroform and 5 mL of 150 mM NaCl were placed. Tubes are vortexed for one minute, decanted for 30 s, and then centrifuged for 15 min at 2000 rpm at 15°C (JOUAN GR2022 rotor 99mm centrifuge). The lower lipid-containing phase was recovered, filtered through a funnel containing glass wool and anhydrous sodium sulfate and collected in a previously weighed glass flask (m_1). The upper phase was washed twice more with 10 mL of chloroform, vortexed again, centrifuged and the lower phase recovered. Then the solvents were evaporated with a rotary evaporator (Büchi Rotavapor R-200) with a water bath at 30°C (Büchi Heating Bath B-490). The last traces of solvent were removed under a stream of nitrogen (N-EVAP 111 Nitrogen evaporator). The balloon was again weighed (m_2). The mass remaining in the flask determines the amount of lipids extracted $m = m_2 - m_1$. Lipid content in crackers was expressed in g / g dry crackers, then in g / g dry flour. The same method was used for the dough which was first freeze dried to reduce its water content (Lyolab 3000 freeze-dryer).

2.7. Glass temperature determination

DSC thermograms were recorded with a differential scanning calorimeter DSC Q100 (TA Instruments, Guyancourt, France). For the analysis of the glass transition temperature (T_g), CTs and PCs were taken directly from the factory after their manufacture. Five crackers of each type are recovered after 7 hours of storage and crushed. 50mg of ground material is introduced into the cell, the reference cell is empty. The kinetics chosen for this study is as follows: a first temperature decrease from 20 to -80 °C to 10 °C / min ; a temperature rise from -80 to 180 °C to 10 °C / min and a second temperature drop from 180 to 20 °C to 10 °C / min. The determination of the glass transition temperature is made during the rise in temperature.

2.8. Assessment of starch gelatinization by thermal analysis

DSC thermograms were recorded with a differential scanning calorimeter DSC Q100 (TA Instruments, Guyancourt, France). The assessment of non-gelatinized starch was determined as follows: 20 mg of sample were placed on to the DSC pan and 30 mg of water were added in order to run a temperature scan in excess of water to ensure a full gelatinization. Water was previously stirred for 10 min with

nitrogen bubbling to prevent oxidation. Each run was made of a temperature scan at 3 °C/min from 10 to 160 °C. A final temperature of 120 °C was in fact sufficient to detect the gelatinization peak. DSC tests were done in triplicate and the thermograms were analyzed (gelatinization peak) to determine the gelatinization enthalpy in Joule/g of dry flour.

2.9. Assessment of starch retrogradation and starch complexation by X ray diffraction

The edge and center of the crackers are separated using a cookie cutter after a specific storage time. About 50 mg of each sample was sealed in a copper ring between two adhesive tape sheets to prevent any change in water content and examined by Wide Angle X-ray Scattering. Measurements were performed using a D8 Discover spectrometer from Bruker-AXS. Cu K_{α1} radiation (Cu K_{α1} = 1.5405 Å), produced in a sealed tube at 40 kV and 40 mA, was selected and parallelized using a double Göbel mirror parallel optics system and collimated to produce a 500-μm beam diameter with sample alignment by microscopic video and laser. Data were monitored by a GADDS 2D detector for 10 minutes and normalized.

2.10. Model systems preparation

Model systems were prepared by hand mixing with a spatula for 5 min. The four principal ingredients (flour, salt, sugar and fat) were always in the same proportions which were similar to those of the real dough. The model dough was built and evaluated progressively. The impact of each ingredient and the interactions between ingredients were studied by making doughs with either two, three or four ingredients; the last one represents a complete model system with all ingredients (final model system). The different model systems were prepared with 40% water content (dry basis) and represented by the following formula (2) where F, S, Su, FA and W refer to flour, salt, sugar, fat and water respectively with a,b,c,d representing mass ratio that were calculated on a dry matter basis (a+b+c+d=100). The y mass ratio represents the total water content, which was always measured on a humid basis). The ingredients were added while respecting the recipe of the reference crackers.

$$(F_a S_b S_u c F_a d)_x W_y \quad (1)$$

2.11. Statistical analysis

Statistical analysis was performed on the basis of results obtained at least in triplicate and on three different productions. The average and standard deviation were calculated for each experiment.

3. Results and discussion

The fragility of dry products like crackers causes the appearance of cracks (rift) that may result in cracker breakage (dislocation of the cracker in 2 or several parts). A test has been established to count and locate the cracked or broken crackers.

3.1. Counting cracks on PCs and CTs during storage

The counting of cracks was performed on 100 PCs and 100 CTs at T_{0+8H} (8 hours in storage bin) by visual observation. No crack was detected on all the examined PCs (Figure 2a). On the other hand, the observation of CTs reveals a crack rate of 67% with cracks mostly visible on the bottom surface (Figure 2b), but also present on the top of the crackers, that is to say on the topping. Then, for the 33% showing no crack, a second analysis was performed which consisted of carefully scratching the topping with a scalpel to look at the top surface of the crackers under the topping. These observations revealed that all the remaining crackers had cracks under the topping, which were not visible to the naked eye before removing the topping. Thus all the samples observed with topping already all have cracks eight hours after their production. These products (CTs) are therefore likely to be much more fragile and sensitive to manipulation, unlike PCs that had no cracks.

3.2. SEM Observation

PCs and CTs were observed in an environmental scanning electron microscopy (ESEM). Many blisters were visible on the surface of the PCs but no cracks were observed on either side of the PCs. Whereas for the CTs, cracks were visible on both sides of the crackers. A zoom of the termination of the crack was made with x600 magnification (Figure 2c). This refined observation showed that the cracks started from the piercings of the dough before baking. The image reveals a sort of extension of the crack, and these “ways” containing fewer starch granules on the bottom surface of several CTs continue for a long distance, sometimes even to the edge of the cracker. These seem to be at the origin of crack extension and finally of cracker breakage. A mechanical shock may also contribute to provoke breakage but it clearly appears that these weaker domains (path containing less starch granules) were more often observed in CTs (Figure 2c).

Indeed, most of the cracks observed on the CTs were passing through one or several piercings. The weaker domains observed on the CTs may be responsible for the fragility of the cracker during cooling (Figure 2d). However, these cracks as well as these crack paths were not present on the PCs. Connection between the piercing points did not seem to be the only explanation of cracks in CTs.

3.3. Calculation of the amount of freezable water

The total water content was evaluated by Thermo Gravimetric Analysis 24 hours after the cooking. The values for PCs and CTs were respectively 2.7 ± 0.2 ; and 4.5 ± 0.5 ($\text{g}_{\text{water}}/\text{g}_{\text{sample}}$) corresponding to 0.042 ± 0.003 and 0.084 ± 0.009 ($\text{g}_{\text{water}}/\text{g}_{\text{dry flour}}$). This shows that the topping significantly increases the water content for the CTs.

The amounts of free or bound water were expressed in grams per gram of dry flour. Indeed, the mass of dry flour used is identical in a cracker before and after baking and with or without topping. This makes it possible to compare the values obtained between the two types of crackers.

After the sorption equilibria in the different saturated saline solutions, the total water content of PCs and CTs ($\text{g}_{\text{water}}/\text{g}_{\text{dry flour}}$) was obtained and presented by the sorption isotherms in Figure 3.

Although the general appearance of the sorption curves is identical for both types of crackers, there is a clear difference between PCs and CTs; the presence of topping seems to lead to greater water absorption. This phenomenon seems to increase with increasing water activity.

The amount of freezable water was determined by calorimeter (Le-Bail, Chapleau, Anton-De Lamballerie, & Vignolle, 2008). Figure 4 shows DSC heating curves of PCs and CTs after sorption equilibria and cooling from 20 to -30°C at a scanning rate of $0.3^{\circ}\text{C}/\text{min}$. On the heating thermogram, a double endothermic transition was observed between -20°C and -4°C ; it was attributed not only to the ice melting (Pradipasena, Tattiakul, Nakamura, & Miyawaki, 2007; Tran, Thitipraphunkul, Piyachomkwan, & Sriroth, 2008) but also to the lipid phase and to the topping for the CTs (verified by DSC of the lipids - not shown).

The integration of the double peak indicates the amount of heat Q_1 ($\text{J}/\text{g}_{\text{sample}}$) needed to melt the ice contained in the product. By dividing this amount by the latent heat of pure water (333.3 J/g) one can obtain the amount of water frozen per gram of sample. The unfreezable water can be calculated from the difference between the total water of the sample and the freezable water. However, in this particular case, it is necessary to determine the amount of lipids present in the crackers at the end of the process in order to subtract the thermal effect of the lipid during the DSC runs. Lipid content in crackers and in the dough was measured with Bligh and Dyer method and the amount of the freezable lipid phase of the both crackers was defined by calorimeter.

The quantities of lipids and water in the free and bound states were expressed as before in grams per gram of dry flour. Figure 5 shows the amount of bound water in grams of water per gram of dry meal in the PCs and CTs on the day of production and after equilibration over saturated salt solutions.

At D_0 , the PCs have 100% bound water ($0.042 \text{ g}_{\text{bound water}} / \text{g}_{\text{dry flour}}$) whereas the CTs have more ($0.075 \text{ g}_{\text{bound water}} / \text{g}_{\text{dry flour}}$) and possess a small quantity of free water ($0.01 \text{ g}_{\text{free water}} / \text{g}_{\text{dry flour}}$), which can be attributed to the topping. During conditioning in relative humidities created by the saturated salt solutions the crackers absorbed water. The evolution of the bound water for the different salt solutions is identical for both types of crackers but the amount of bound water was always greater for crackers with topping and increases with the ERH% (Water activity). The detection of the amount of free water was observed starting at different level of water activity for the CTs and the PCs. In the case of CTs, 2% of the water was observed as being free at a relative humidity of 75.3%. At 90.2% relative humidity, 18% of the water was present as free water for CTs, while the PCs only had 5% free water present. The free water detected in the CTs corresponds to the water absorbed in a big part by the topping.

3.4. Interactions between dough ingredients in the presence of water

This part of the study aims to understand the effect of the interactions between the ingredients on the phase changes occurring in the cracker dough (38% water content dry basis) during baking. To do this, hydrothermal transitions were studied using a simplified model dough made of wheat flour, water and of other ingredients whose proportions were progressively increased until reaching the reference "model dough" recipe. This reference model dough was then compared to the "real" cracker dough.

A preliminary investigation was done to determine the impact of the ingredients on the hydrothermal transitions of starch. The impact of the water content on the evolution of the gelatinization profile of the flour was carried out at different water contents (30%, 40%, 50%, 60%, and 80% on dry basis) by DSC.

In the literature, many authors have shown that the starch gelatinization temperature in wheat flour dough is influenced by the water content as well as by the other wheat flour constituents, such as proteins (Ghiasi, Hosney, & Varriano-Marston, 1982; Zobel, Young, & Rocca, 1988; Rolée, Chiotelli, & Le Meste, 2002; Liu, Charlet, Yelle, & Arul, 2002; Mohamed & Rayas-duarte, 2003). The comparison of thermograms of F as a function of the water content (Figure 6a) shows that in excess of water, the sample $(F_{100}S_0Su_0Fa_0)_{17}W_{83}$ had a single endotherm " G_e ". This endotherm corresponds to the phenomenon of gelatinization of the starch (Donovan, 1979). The gelatinization temperature corresponding to the bottom of the endotherm (T_{Ge}) observed for these samples was $60.5^\circ\text{C} \pm 0.5$. The lipid fraction of the flour F being about 1%, the second endotherm M_2 characteristic of the fusion of complexes formed by amylose during gelatinization with the endogenous lipids of flour is clearly visible $T_{M2} = 92^\circ\text{C} \pm 0.4$ (Biliaderis, Page, Slade, & Sirett, 1985). As the amount of water decreases, the

first endotherm G_e has a shoulder for the higher temperatures. This endotherm then transforms into an endotherm M_1 corresponding to the fusion of the starch, which will move towards higher temperatures with decreasing water content. In parallel, the endotherm G_e decreases and eventually disappears. The M_2 fusion endotherm of complexes was also shifted to higher temperatures, but in a more progressive way; for the lowest levels of water content, the M_2 endotherm tended to merge with the M_1 endotherm.

The interactions between the different ingredients of the dough were first studied in model systems composed of two ingredients. These model systems provided an indication of the effects of fat, salt and of sugar on starch gelatinization. The recipes of these systems were calculated from the final batter model systems respecting the mass ratio between the ingredients.

In general, the binary systems thermograms (Figure 6b) appear similar to flour system $(F_{100}S_0Su_0Fa_0)_{60}W_{40}$. The fat did not affect starch gelatinization at a 40% water content, in agreement with previous studies such as Eliasson (1994) and Chiotelli & Le Meste (2003). On the other hand, the addition of salt or sugar to flour at 40% water content ($(F_{99}S_1Su_0Fa_0)_{60}W_{40}$, $(F_{92}S_0Su_8Fa_0)_{59.5}W_{40.5}$ systems) tends to shift the starch gelatinization temperature towards a higher temperature (69°C and 70°C respectively) in comparison with the mixture $(F_{100}S_0Su_0Fa_0)_{59}W_{41}$ (61°C) (Table 2). This shift in the gelatinization endotherm is related to the presence of salt or sugar, which competes with starch for water; in turn, less water is available for the gelatinization of the starch. Indeed, the increase in the gelatinization temperature has been attributed to the solute's ability to limit the availability of water for starch, i.e., to reduce the chemical potential of water (D'Appolonia, 1972; Spies & Hosene, 1982). However, the effect of sucrose and salt on starch gelatinization was not solely due to the decreased availability of water, because the gelatinization energy did not decrease progressively and at the same rate as the amount of sucrose or salt in aqueous phase (Wootton & Bamunuarachchi, 1979).

Consequently, more complex systems (Figure 6c) (ternary and final model system) were prepared, to understand the behavior of the real system. The different endotherms that were obtained can be explained in the same way as the final model system (Figure 6d). A difference between the two systems was found; it could be explained by the difference in the preparation and mixing method between the model system and the real batter. In model systems, the mixing was done manually while in the real batter (real cracker recipe) was mixed in an industrial way. In addition, it can be also attributed to the decrease in the water content, which was 41% and 38% (dry basis) for the final model system and the real batter, respectively.

Nevertheless, this approach explains that the interactions between the dough ingredients, the water limitation and probably the mode of preparation of the dough are the major factors responsible for the shift and combination of the different phase transitions observed during baking.

This study allowed us to locate on the phase diagram the melting temperatures $T_m = (T_{Ge} + T_{M1}) / 2$ of the biscuit flour used in this study compared to the T_m of wheat starch (Figure 7). It is known in the literature that the thermograms obtained by DSC for wheat flour are identical in appearance to those obtained for wheat starch with the same water content. Indeed, Hoseney, Zeleznak and Lai in 1986 showed that wheat gluten hydrated at 60% did not show a peak of protein denaturation or other; which testifies to the lack of long-distance order in the gluten molecule. Eliasson and Hegg (1980) were able to identify transitions that could be attributed to gluten proteins, but the enthalpies were less than 0.1 cal / g gluten. It can therefore be considered that the thermal denaturation of gluten is not detectable in DSC. The thermograms of wheat flour can therefore be interpreted as representing the thermal behavior of starch alone. The gelatinization temperature is slightly higher for flour which may be due to competition for water between starch and gluten. Eliasson in 1983 assumes that the diffusion of water into the starch granules can be delayed by the presence of gluten on their surface.

This study has shown that the model systems composed of four ingredients (F, S, Su, Fa) make it possible to explain the different phase transitions in the real system but the temperatures obtained are strongly shifted. The model systems approach explained that the interactions between dough ingredients, water limitation and probably the dough preparation mode are the main factors responsible for the shift and the combination of the different phase transitions observed during baking.

3.5. Assessment of starch gelatinization in the crackers

A sample was taken from a crushed cracker; A DSC run was then carried out with this sample in excess of water (60% according to the protocol previously described in materials and methods). The thermograms obtained for the CTs and PCs are presented in Figure 8. They show the presence of a gelatinization endotherm (G), which indicates that the starch present in the sample had been only partially gelatinized during the baking process. In addition, a second endotherm was observed around 100 °C; such endotherm is characteristic of the fusion of amylose/lipid complexes (M_2). The residual gelatinization temperature was 66 °C \pm 0.3 °C and was the same for both PCs and CTs samples.

The residual gelatinization enthalpies were $\Delta H_R = 3.2 \pm 0.1$ (J/g of dry flour) and 5.1 ± 0.5 (J/g of dry flour) for CTs and PCs samples respectively. The enthalpy of the cracker dough in excess of water was

also determined by DSC as being $\Delta H_T = 8.2 \pm 0.5$ (J/g of dry flour). ΔH_T represents the total gelatinization enthalpy; in excess water conditions the starch has sufficient water to swell and undergo a complete leaching of the amylose and amylopectin macromolecules out of the granule.

The enthalpy of partial gelatinization ΔH_P is therefore $\Delta H_T - \Delta H_R$ J/g of dry flour: Values of $\Delta H_P = 5.0 \pm 0.5$ (J/g of dry flour) and $\Delta H_P = 3.1 \pm 0.5$ (J/g of dry flour) were observed for the CTs and the PCs respectively corresponding to 61% and 38% of gelatinized starch for CTs and PCs respectively. The presence of the topping in CTs provides extra water to the cracker during baking and allows a higher ratio of gelatinization in the center of the cracker. A new study was then conducted by taking a sample at the center of the cracker and another at the edge to determine the partial enthalpies in the periphery and in the center of the CTs. For CTs, the partial gelatinization enthalpies in the periphery and in the center were respectively $\Delta H_{PP} = 4.4 \pm 0.3$ (J/g of dry flour); $\Delta H_{PC} = 5.5 \pm 0.5$ (J/g of dry flour).

The gelatinization of CTs was therefore more significant than for PTs; this is attributed to the presence of water provided by the addition of topping in the center of the cracker. In fact, the gelatinization of the starch during the baking of CTs is not done in a homogeneous way in the cracker, the water brought by the topping benefits essentially to the dough located directly underneath.

3.6. Assessment of starch retrogradation and starch complexation

PCs and CTs were stored in closed bins at room temperature. Samples were taken from both types of crackers at their edges and the centers after 7 h, 24 h, 48 h and 1 week of storage, and studied by X-ray diffraction as described above. The X-ray diffraction spectra of PCs (center and edge) and CTs (center and edge) are shown in Figure 9a and Figure 9b ; and Figure 9c and Figure 9d respectively as well as the spectrum of the cracker dough.

The cracker dough displayed the typical A-type crystallinity patterns ($2\Theta = 9.7^\circ, 11.1^\circ, 15^\circ, 14.9^\circ, 17^\circ, 18^\circ, 19.5^\circ, 23^\circ, \lambda_{CuK\alpha} = 0.15405\text{nm}$), very frequently encountered in cereals (Katz & Derksen, 1933). The spectra of the PC center and edge were identical and did not vary during the storage. They showed amorphization of the type A structure after the cracker baking, with the appearance of a diffusion bump centered on 19° in 2Θ . The gelatinization of the wheat starch, responsible for the A-polymorphic structure, is incomplete, leading to a partial destructure of the starch granules. The spectra of the edge of the CTs were identical to those obtained from the PCs, however, those from the center of the cracker were different. The CT center is unstructured, however, by comparing the spectra of samples PC center to the CT center, an onset of crystallization was observed with the appearance of a peak around 20° (2Θ). A V-type polymorphic structure seems to appear, masked by

the large diffusion bump. This suggests that amylose reacts with endogenous lipids or exogenous fats during baking and the crystallization of amylose lipids complexes increases during the cooling and the storage period, despite the presence of all the cracker components.

The X-ray diagrams of the PCs and the CTs samples did not display the typical peaks of B-type crystallinity patterns due to the presence of amylose and/or amylopectin having retrograded during storage (Putaux, Buléon, & Chanzy, 2000).

A sufficient amount of water seems to be present in the dough for CT resulting in a higher rate of gelatinization of the starch in the heart of the cracker with topping and also allow the complexation of the fat with the amylose outside of the granule. On the other hand, the mobility of amylopectin and / or amylose macromolecules does not seem sufficient to allow their reorganization into double helices and to form a B type structure during storage for the two types of crackers studied.

4. Conclusion

This study investigated the origin of cracker breakage in the case of crackers with and without topping. As a result, it clearly appears that the topping, which is rich in water, has an impact on the degree of starch gelatinization of the dough located underneath the topping. In the case of the control cracker without topping, no major difference was observed between the center and the edge of the cracker.

A comprehensive study done on a model recipe showed that the main ingredients that were restricting the gelatinization of starch were the salt and the sugar, plus of course the water content. The water provided by the topping resulted in a cracker with a highly heterogeneous structure, with a matrix poorly gelatinized on edge and highly gelatinized on center. Additional observation of the crackers under SEM showed that crackers with topping contained crack primers starting from the piercing done on the cracker dough before baking. Counting of crackers stored in realistic conditions showed that 100% of crackers with topping were either exhibiting cracks or were broken, whereas crackers without topping did not exhibit any cracks or crack primers. Solutions to mitigate breakage of crackers with topping could be to reduce the water content of the topping and to apply an additional thermal treatment after baking in order to reduce the water gradient inside the crackers with topping.

5. Acknowledgements

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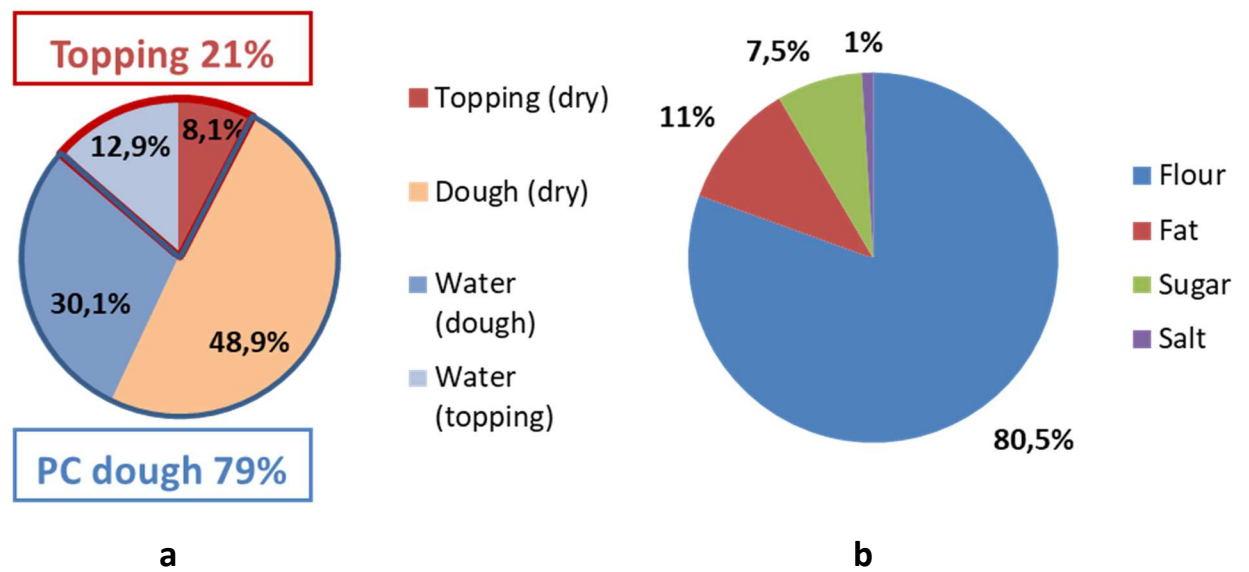


Figure 1 : CTs (a) and PCs (b) composition in dry mass

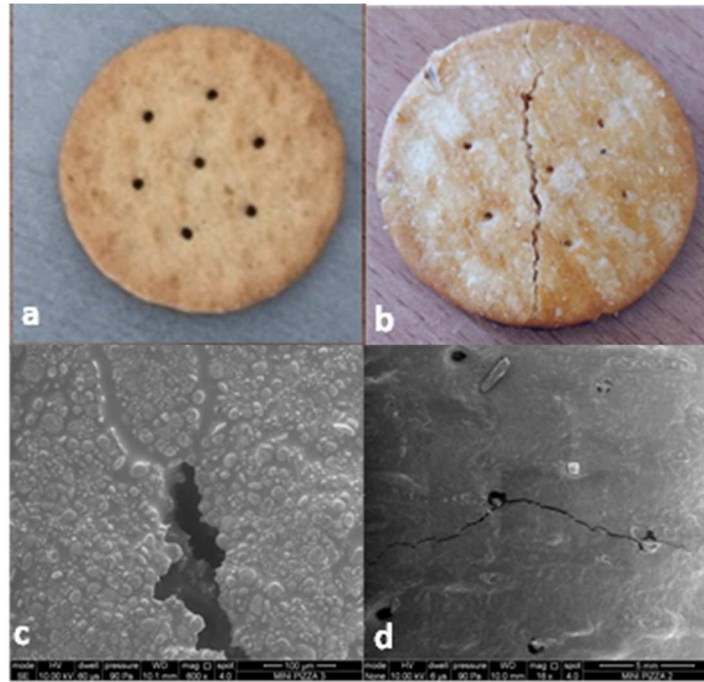


Figure 2 : The PC on the bottom side (a) and crack of the CT on the bottom side(b); Image of the end of a crack zoomed with a magnification of x600 on a PT after one week of storage (c); Observation of the underside of a CT by environmental scanning electron microscopy after one week of storage. A crack joining two piercings of the cracker. Image obtained by stitching several scans together in order to obtain an image at low magnification (x16) (d)

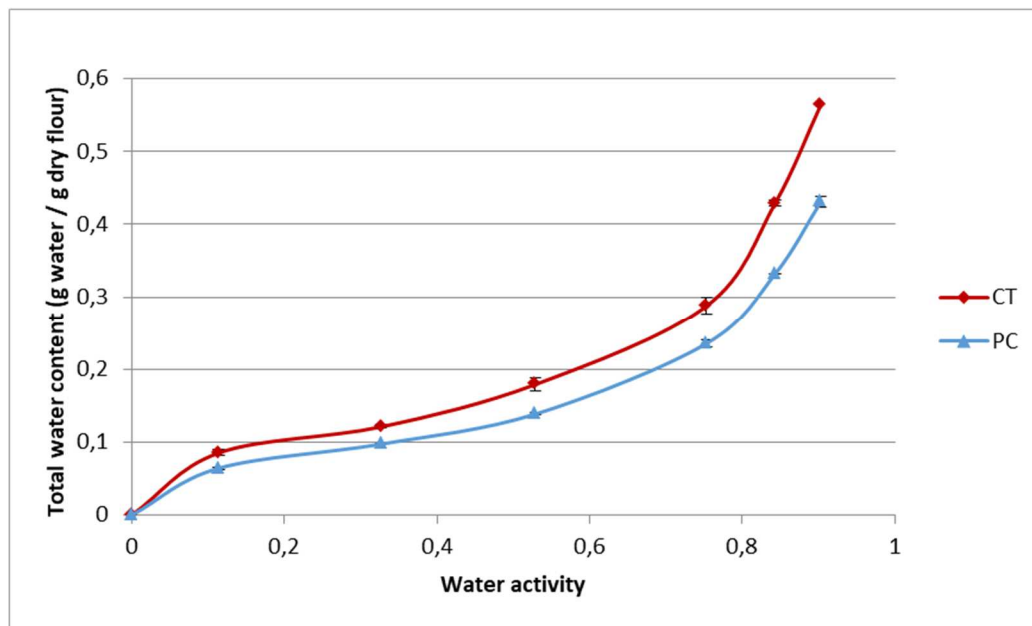


Figure 3 : Sorption isotherms at the beginning of storage for CTs and PCs at 20°C

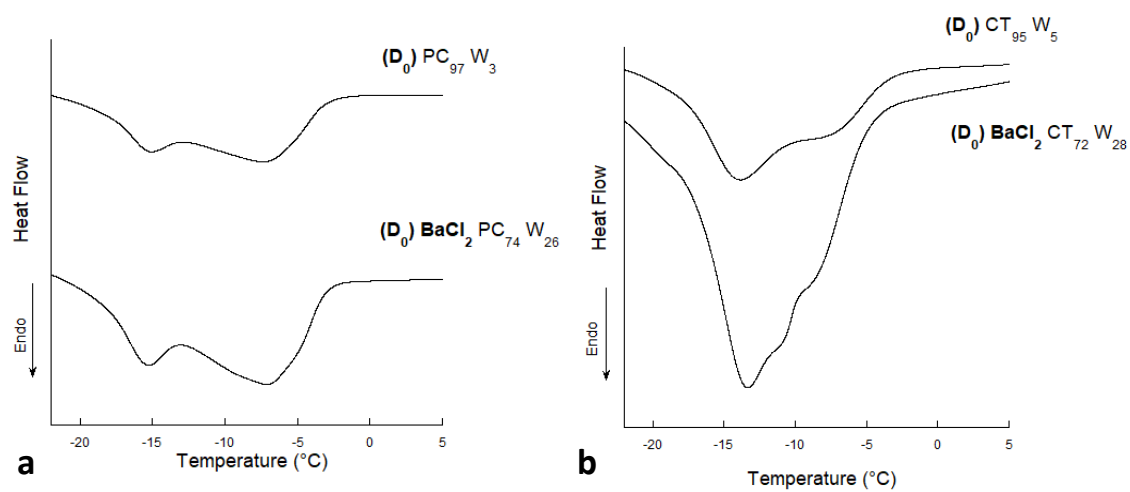


Figure 4 : Endothermic transitions before storage (Day 0) for PCs (a) and CTs (b)

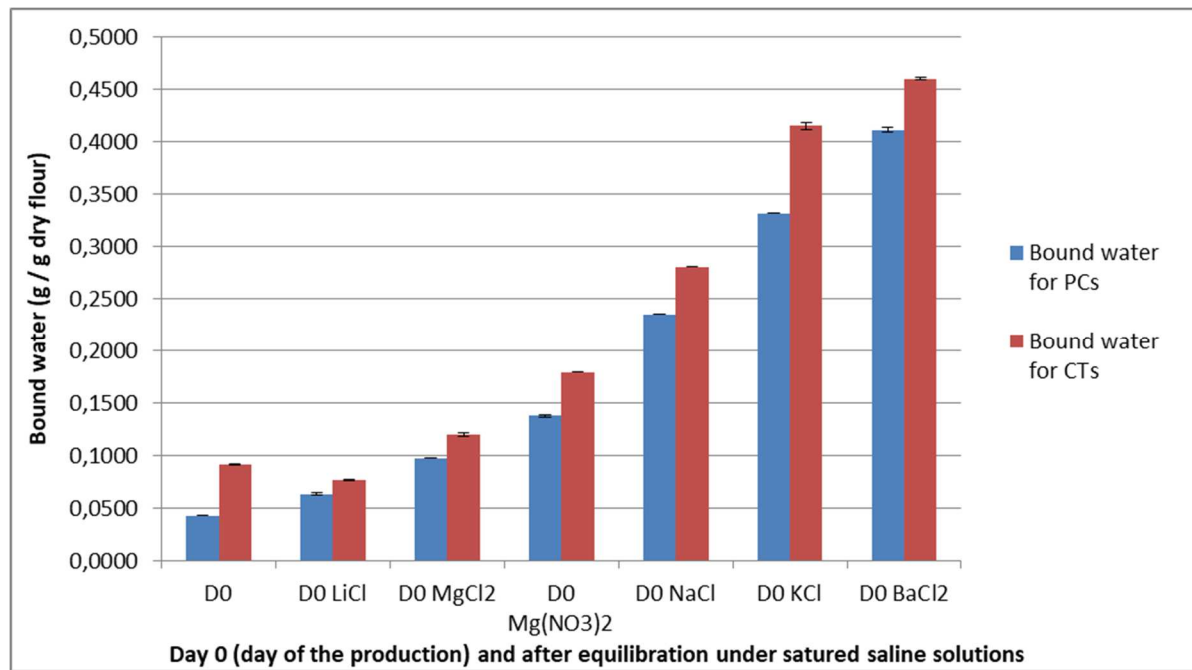


Figure 5 : Quantity of bound water for PCs and CTs according to the saturated salt solutions used

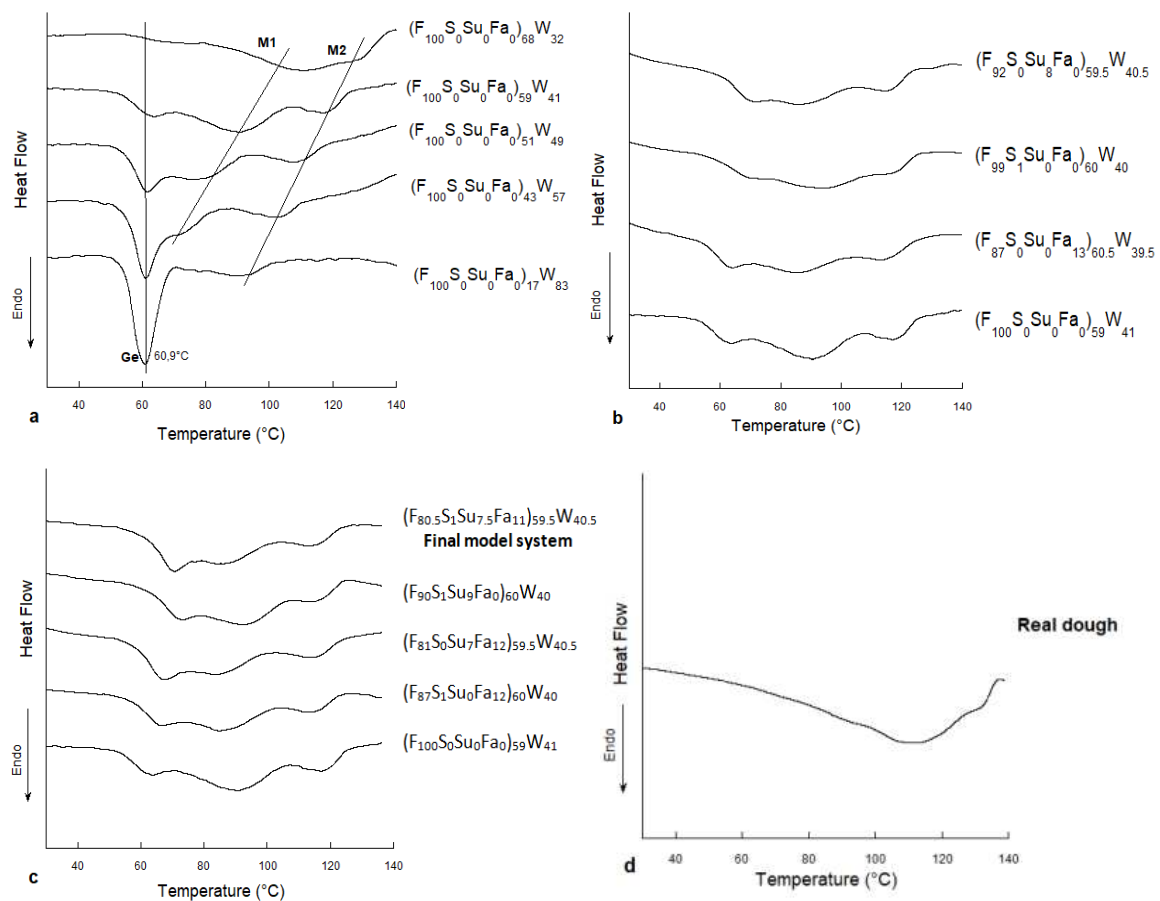


Figure 6 : Thermograms of flour (F) with different water content (a) ; Binary systems thermograms with 40% water content (b) ; Ternary and final model systems thermograms with 40% water content (c) ; Real cracker dough (d)

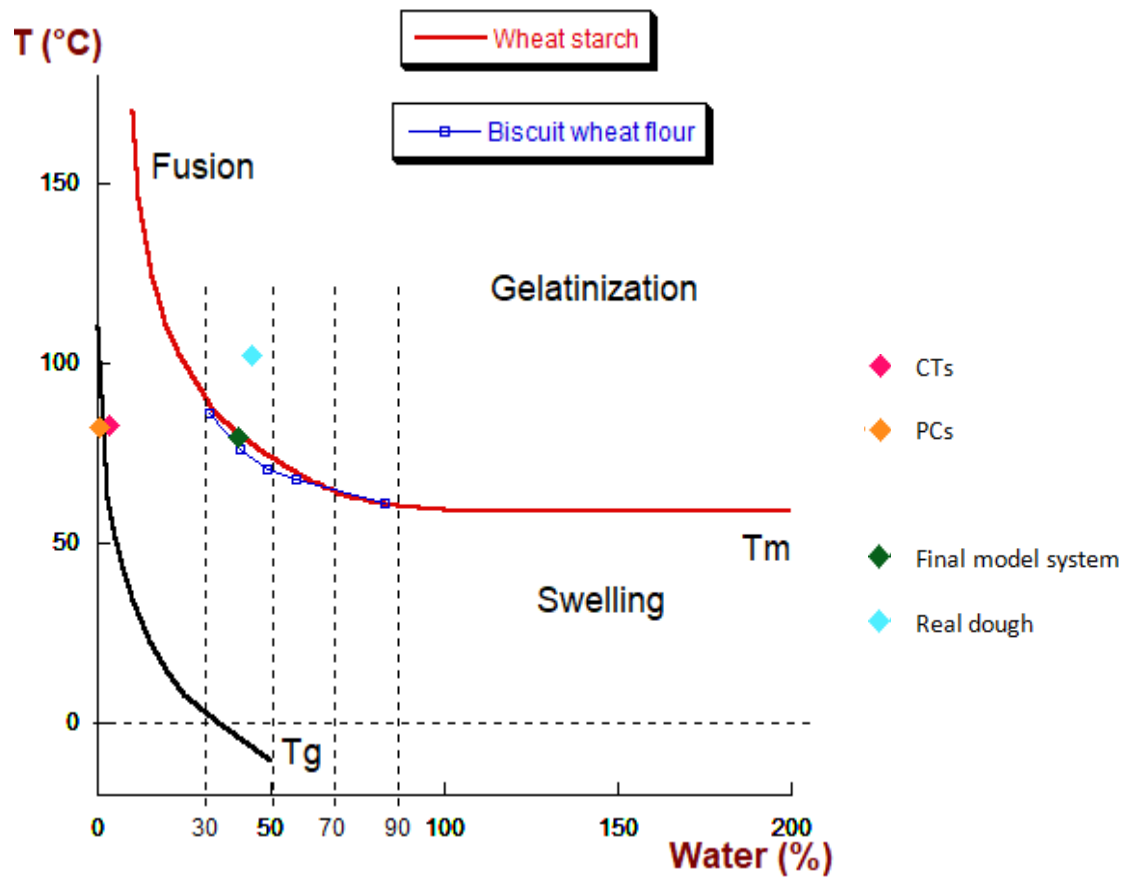


Figure 7 : Phase diagram of biscuit wheat flour (blue), wheat starch (red) and model systems (points) depending on the water content (Biliaderis, Page, & Maurice, 1986)

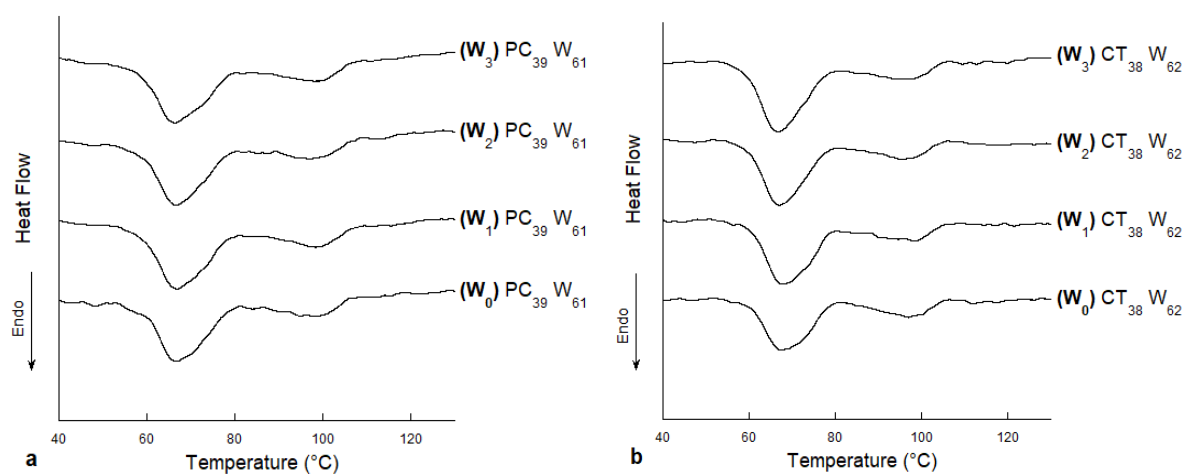


Figure 8 : Thermograms of residual gelatinization during storage (from 0 to 3 weeks) with the PCs (a) and the CTs (b)

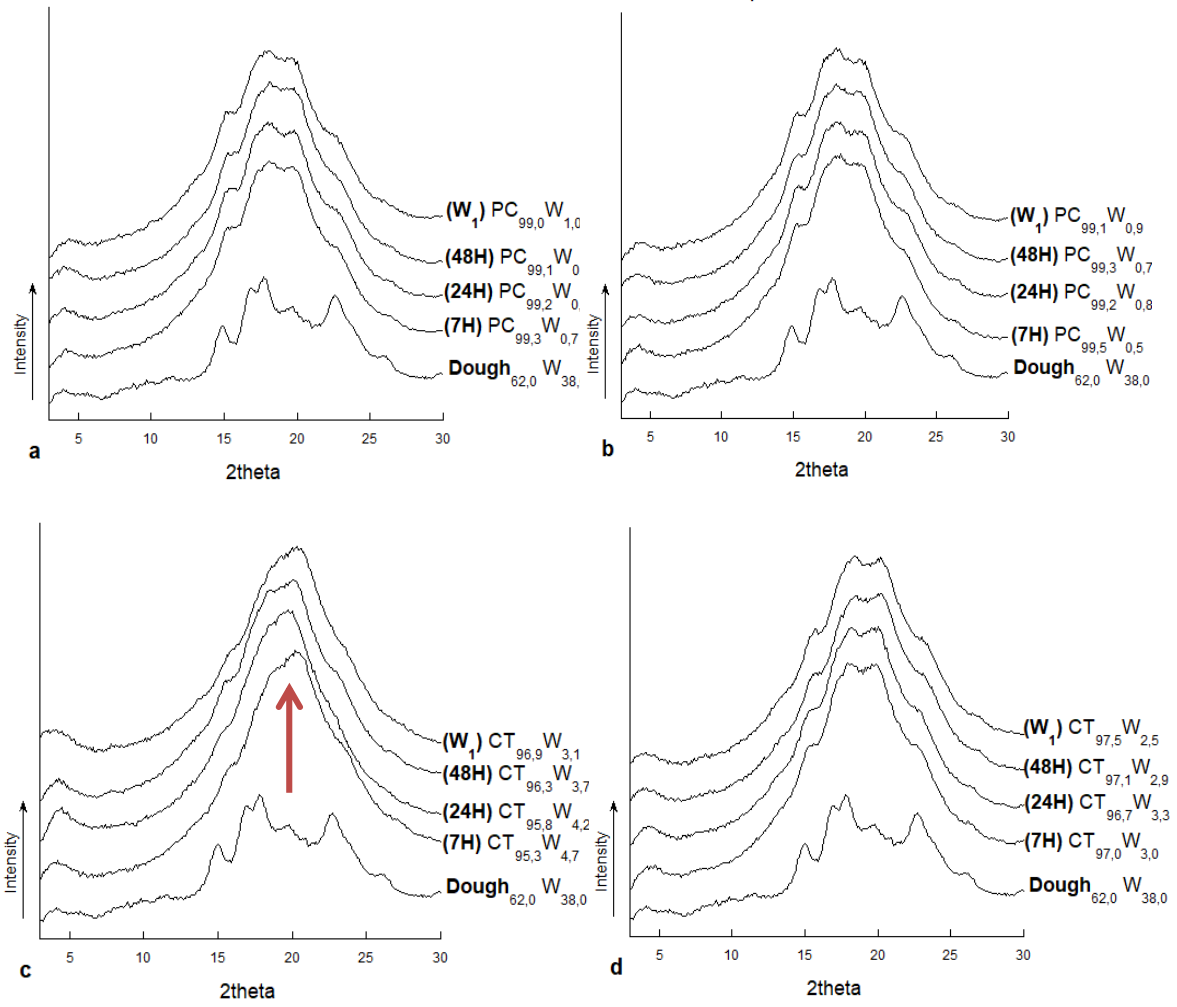


Figure 9 : The X-ray diffraction spectra of PCs center (a) and edge (b); The X-ray diffraction spectra of CTs center (c) and edge (d)

Table 1 : The water contents ($\text{g}_{\text{water}}/\text{g}_{\text{dry flour}}$) of the PC and CT samples after equilibration in the flasks

Saturated saline solutions (20°C)		PCs	CTs
LiCl	(aw = 0.114)	0.064 ± 0.001	0.085 ± 0.004
MgCl ₂	(aw = 0.313)	0.0973 ± 0.0002	0.121 ± 0.002
Mg(NO ₃) ₂	(aw = 0.545)	0.138 ± 0.002	0.179 ± 0.008
NaCl	(aw = 0.754)	0.235 ± 0.005	0.29 ± 0.01
KCl	(aw = 0.851)	0.3319 ± 0.0006	0.429 ± 0.004
BaCl ₂	(aw = 0.907)	0.431 ± 0.007	0.564 ± 0.005

Table 2 : Gelatinization (G_e) and fusion of the starch (M_1) temperatures

Systems	T°(C) G_e	T°(C) M_1
(F ₁₀₀ S ₀ Su ₀ Fa ₀) ₁₇ W ₈₃	60.9	
(F ₁₀₀ S ₀ Su ₀ Fa ₀) ₄₃ W ₅₇	61.0	74.3
(F ₁₀₀ S ₀ Su ₀ Fa ₀) ₅₁ W ₄₉	61.0	79.8
(F ₁₀₀ S ₀ Su ₀ Fa ₀) ₅₉ W ₄₁	60.8	91.1
(F ₁₀₀ S ₀ Su ₀ Fa ₀) ₆₈ W ₃₂	60.9	110.7
Final model system	70.6	88.7
Real dough	92.7	111.7

Plain cracker



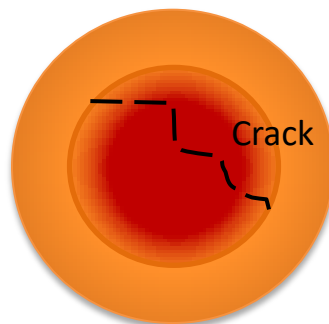
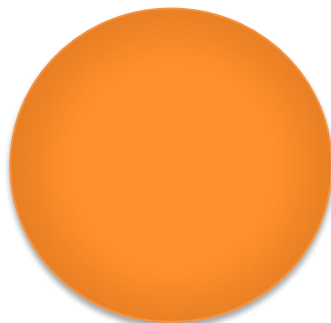
Cracker with topping



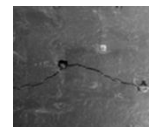
Before baking



During baking



During storage



Water and structure repartitions

