

Low moisture cereal products: texture changes versus hydration¹⁾

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1. Introduction

The research team constitutes part of the Food Technology School within the University of Burgundy right in the middle of the Burgundy region which interests for food and wine are famous throughout the world. The research goals are summarised in Fig. 1.

The general objective of the research activities is to understand both the mechanisms and parameters, related to the structure and physical state of a multiphase matrix (model for foods or pharmaceuticals), and controlling the dynamical properties of the molecules of this matrix.

Water is a crucial parameter controlling structure, physical state, and molecular mobility of matrices. Therefore, we focus part of our work on the investigations of its role in the quality and stability of products.

Generally, the multiphase matrices considered are concentrated suspensions of dense or porous biopolymers such as polysaccharides and/or proteins; particular materials, gels or films.

The approach chosen comprises:

1. physical characterisation of the matrix through:

- analysis of the structure at the molecular, mesoscopic and finally macroscopic scale,

¹⁾ Part of this work was presented at various conferences: *ISOPOW 7* (Helsinki, June 1998), *Biopolymer Science: Food and Non food Applications* (Montpellier, September 1998), *IFT 2001* (New Orleans, June 2001), and *ACS Symposium* (Chicago, August 2001).

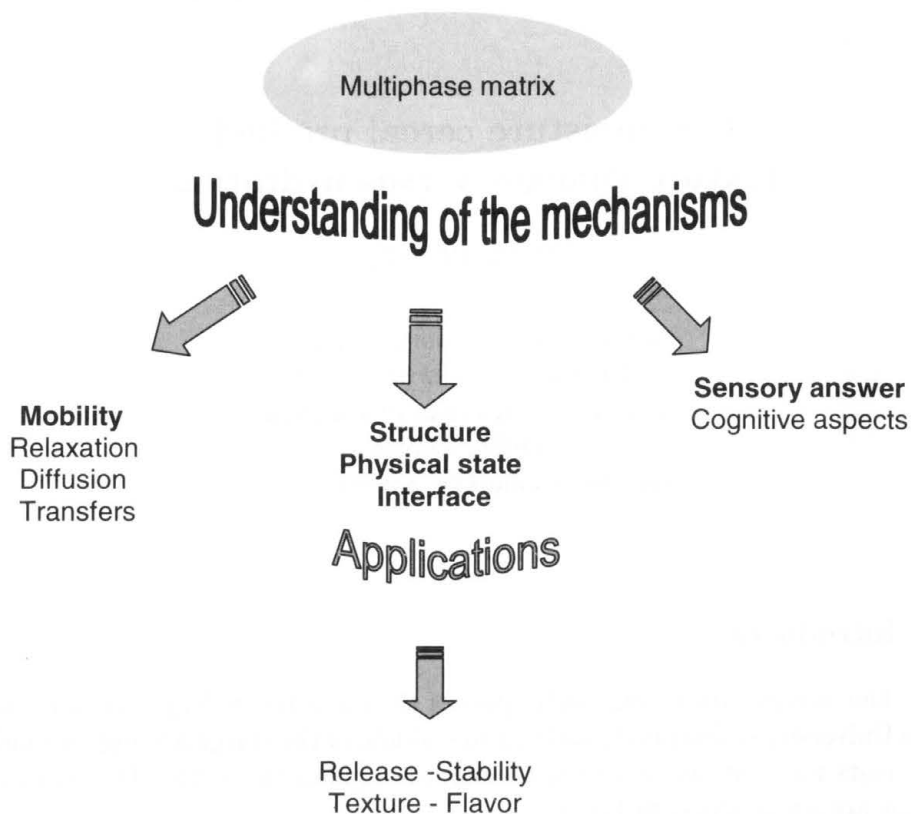


FIGURE 1. Thematic organisation of the research activity of the Molecular and Sensory Engineering of Foods and Pharmaceuticals team.

- study of the physical state, the phase transitions occurring in the sample being important for the stability and texture of the products,
 - study of the structural and thermodynamic properties,
2. study of the dynamic properties through mobility measurements, and diffusion and transfers studies,
 3. validation when necessary of the instrumental data with sensory data.

As an invited lecture for the Workshop on Nondestructive Testing of Materials, Structures and Textures, the following pages will be an overview of our work on low moisture cereal products, with a particular focus on texture changes versus hydration.

Living in a society of large choice of quality foods, the consumers' appreciation has become one of the main criteria in their food choice, as well as

nutrition and safety. The contribution of texture to the consumers' appreciation of a food product has been studied for nearly 40 years. In the early studies on the awareness of food texture, the importance of crispness was highlighted. For instance, word association tests, in which consumers were asked to generate attributes related to a list of specific foods, showed that the term "crisp" was mentioned more often than any other attribute [1, 2], many studies also mentioned that in ranking tests, crispness order often corresponds to consumer preference order. Thus, the food industry has considered the necessity to control this characteristic both during production and storage. To achieve such an objective requires the knowledge of intrinsic parameters (physical, chemical, product-related) responsible for crispness. But crispness, like any other textural attribute, depends not only on the sensations perceived upon eating, as relevant to crispness but also on ad hoc rheological/mechanical characteristics exhibited by a product. Although sensory analysis gives a more complete description of the texture of tested products, there has been a great interest in developing instrumental techniques to assess crispness. Instrumental techniques present some advantages, especially in industrial environments where quick and easy-to-use methods are in great demand and economically more profitable. Crispness is described as a concept with kinesthetic and auditory components. The instrumental methods developed to evaluate it (compression tests, acoustic measurement have focused on the measurements of these properties singularly or in combination [3, 4]).

Moreover, with a view to understanding the physical basis for the textural properties, techniques originally used in material science are employed:

- dynamic rheology,
- thermal analysis,
- Nuclear Magnetic Resonance (low resolution H-NMR),
- Raman spectroscopy.

Most low moisture baked or extruded products such as breakfast cereals, wafers, biscuits, and snacks have a crispy texture. If the moisture content of these products increases, due to water sorption from the atmosphere or by mass transport from neighbouring components, it results in a soggy, soft texture: i.e. crispness is lost. Since crispness is associated with pleasing textural contrasts and with freshness and quality [5], its loss is a major cause of consumer rejection. In spite of the economical impact of this loss, and although many works have been dedicated to it, there has been yet no agreement on the molecular basis of these textural changes.

In order to lead a broad study of the origin of the textural changes from "the molecules to the mouth", cereal-based samples (commercial extruded

flat bread) were equilibrated at different water activities, corresponding to a range of water content between 3 and 13% of water (wet basis), and analysed with a multi-technique approach.

A trained panel was asked to evaluate both the crispness and the hardness intensities of the different samples.

The effect of water content increase on crispness and hardness (defined as the force required to break the sample between the teeth) is presented in Fig. 2.

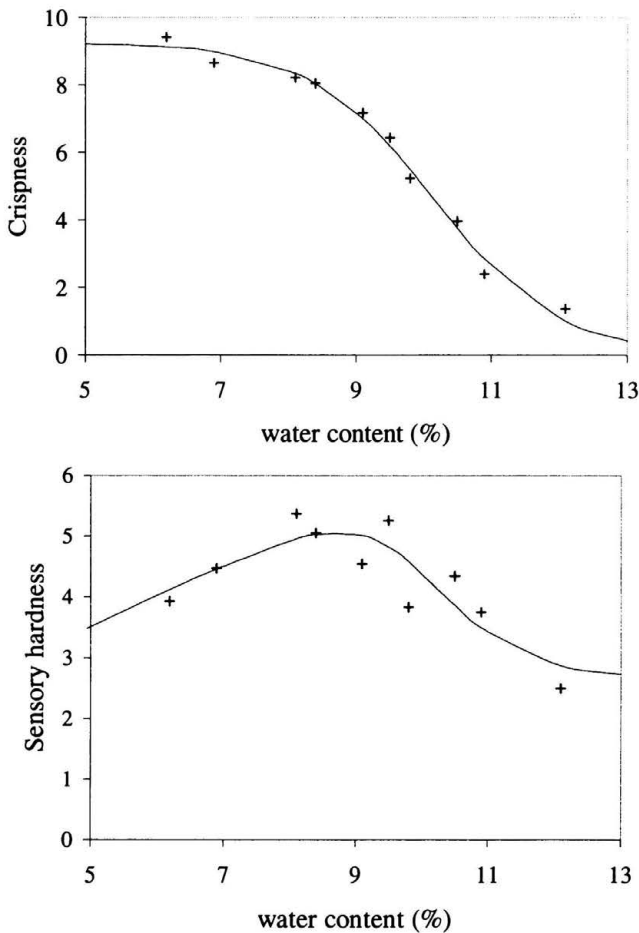


FIGURE 2. Influence of water content on “sensory” crispness (left) and hardness (right) for extruded flat bread. The line corresponds to a prediction of crispness by the Fermi equation [6].

In order to describe a mathematical model, the relationships between the textural properties and the water content of the samples studied, we

applied the empirical model classically used: depending on the behaviour of the relationships, we used the form:

$$P(w) = \frac{P_0}{1 + \exp[(w - w_c)/b]} \quad (1.1)$$

or

$$P(w) = \frac{P_0 - P_r + k w}{1 + \exp[(w - w_c)/b]} + P_r, \quad (1.2)$$

where $P(w)$ is the magnitude of the property, w the water content of the sample, P_0 its magnitude in the dry state, w_c is the characteristic water content where $P(w_c) = P_0/2$, and b is a constant describing the steepness of the transition in the property magnitude. The form described in Eq. (1.2) is used when the property exhibits an increase prior to the transition and has a residual value after the transition. k is a constant roughly corresponding to the slope of the increasing region and P_r is the residual magnitude of the property after the transition [7]. The critical values for both attributes fall around 9% of water.

Similar features were obtained with instrumental measurements.

2. Acoustic measurements

The extruded samples were subjected to compression tests, and the sounds produced during the tests were recorded on a digital recorder.

Power spectrum density of each recorded sound was calculated over the first 3.2 s of the record with a signal analyser over the frequency range 16 to 16 000 Hz. Power spectra density are given in third octave intervals which is convenient to study such sounds [6, 8]. For each water content, spectra are averaged over the 10 replications and corrected for the background noise.

The evolution of each third octave frequency band, as a function of water content, showed a similar pattern, indicating that the modifications of frequency composition of fracture sounds is negligible. Thus, only the sound intensity is of interest. The intensities of the 3rd octave bands were averaged over the whole spectrum, using the A weighing in order to account for the sensitivity of the human ear [9]. The resulting values expressed in logarithmic scale give a measurement of the overall intensity of the fracture sounds.

The evolution of the intensity of the sound generated during the fracture is presented in Fig. 3. Up to 9% moisture, the sound intensity is slightly increasing, between 9 and 11% of water the sound intensity falls rapidly, becoming negligible above 11.5% water. The frequencies most represented in the spectrum are the high frequencies (2000-8000 Hz), it is in agreement with previously published data on similar products [9, 10].

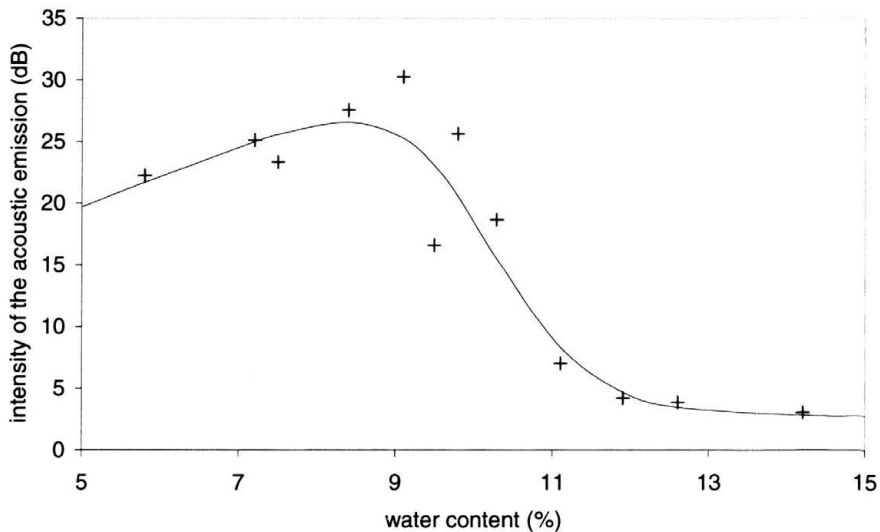


FIGURE 3. Influence of moisture content on the intensity (dB) of the acoustic emission at fracture of extruded bread. The line represents the predicted value of the intensity using Fermi's equation.

3. Mechanical measurements

The fracture properties of the material were also assessed with uniaxial compression tests (using an INSTRON 1122 machine, or a TAX-T2, Stable Microsystems). The tests were based on large deformations with a pin probe penetrating through the cellular extruded sample. The force-deformation plots obtained are typical and similar to those described in the literature for solid foams. Each force peak present on the force-deformation curve represents the rupture of cell wall [6].

As previously observed with sensory analysis, the fracture properties exhibit versus hydration important changes, characterised by an attenuation of the jaggedness of the force-deformation curves (Fig. 4). These patterns can be analysed throughout the determination of the number of spatial ruptures (peak number per puncture distance). The logarithm of the latter was observed to be correlated to crispness [11]: the higher the number of peaks (corresponding to fracture of individual cells) the greater the crispness. It suggests that the panel evaluates crispness on the basis of the number of ruptures detected at first bite.

Further study aiming at the understanding of the molecular basis of texture changes requires the use of a physico-chemical approach based on tech-

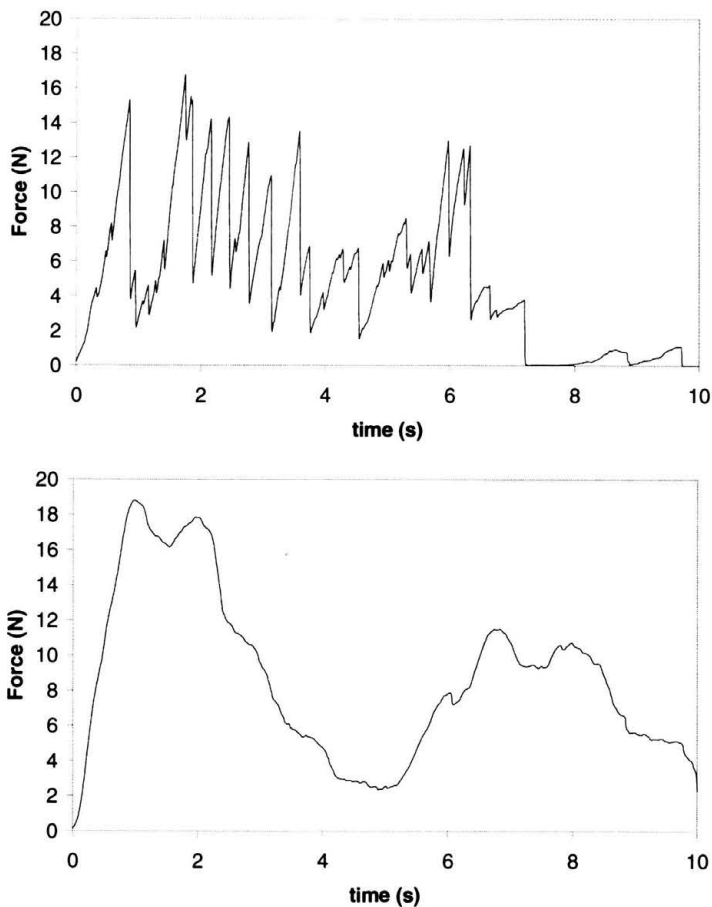


FIGURE 4. Typical force-deformation curves obtained for cereal product at 6.8% (top) and 13.8% moisture (bottom).

niques and concepts developed in material science. In material science, the loss of crispness upon rehydration could be described in terms of change in fracture mechanisms. Extensive studies performed on synthetic polymers have demonstrated that mechanical behavior is highly dependent on the physical state and organization of the polymer network [12]. Thus for further study, the dynamic properties and the physical state of the cereal products have to be considered.

4. Physical state of cereal-based products

Baked or extruded cereal products are generally in the glassy state since cooking is accompanied by the disappearance of most crystalline structures

of native starch. The sensitivity of cereal products to the water content contributed to the proposal of T_g as a predictive parameter for the stability of low moisture products [13, 14, 15]. Indeed, stored above their glass transition temperature, amorphous samples exhibit mechanical changes; moreover due to collapse phenomena, cellular (a common feature to crispy foods) products could show densification which is also known to control mechanical/ texture properties [16]. Finally, above their glass transition temperature starch-based products are known to be subjected to retrogradation, this crystallization being able to affect the texture of the products [17].

Differential Scanning Calorimetry (DSC) is classically used for the determination of the glass transition of simple systems (e.g. sugars). However, no event assignable to a glass transition was detected for the extruded bread described above; this is probably due to the heterogeneity of the system which causes a spreading of the transition over a very broad temperature range and thus an undetectable progressive increase of heat capacity.

For complex systems, thermo-mechanical methods are more sensitive, they have been applied successfully to cereal-based products Thermo-Mechanical Analysis (TMA), or Dynamic Mechanical Thermal Analysis (DMTA) [18, 19] are more accurate/more sensitive for T_g measurement.

A viscoanalyser (Metravib RDS; Ecully, France), was used to apply a sinusoidal tension-compression test to each sample, with a constant deformation rate ($1.7 \cdot 10^{-2}\%$) at 5 Hz. The samples were glued onto the sample holders. Previous studies have shown that, in these conditions (frequency and deformation rate) the samples were in the linear viscoelastic region. The measurement of stiffness K and loss angle δ permitted the calculation of dynamic parameters: the storage (or elastic) component E' and dissipative (viscous) component E'' of the dynamic Young's modulus, the ratio E''/E' ($\tan \delta$) corresponds to the damping factor.

The glass transition temperature of extruded bread was determined by DMTA at several frequencies (from 5 to 40 Hz) from the drop of the storage modulus E' , this feature was characterized by a frequency shift towards higher temperature with increasing frequency.

It is important to notice that according to these data, the glass transition takes place at room temperature when extruded bread contains a minimum of 15% of moisture. Therefore, the texture changes observed around 9% could not be attributed to the glass transition of the samples, but possibly to more localized motions occurring in the glassy state [6, 20-22].

These localised motions were further investigated with impedance spectroscopy, and secondary relaxations (attributed to localised motions of lateral groups or of the main chain).

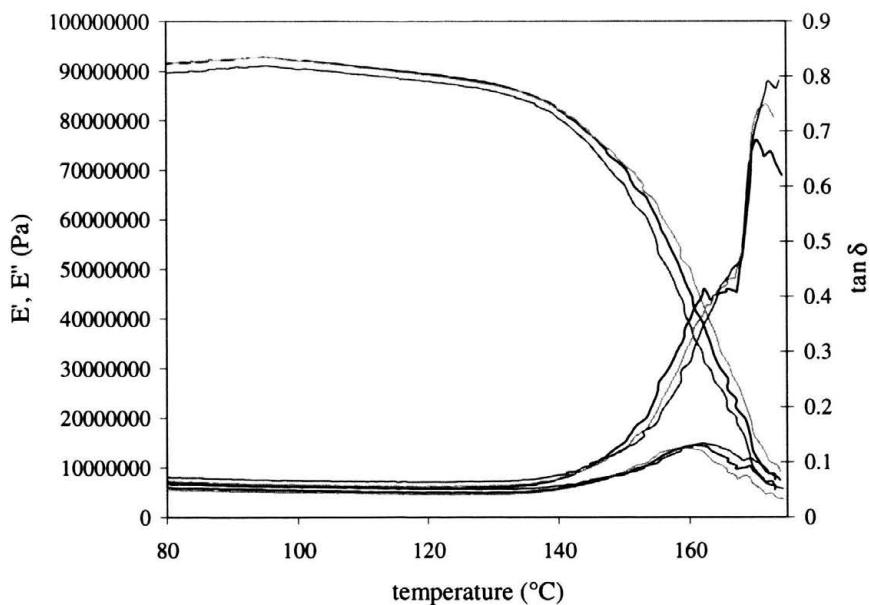


FIGURE 5. Viscoelastic behavior of extruded bread with 5% moisture at 10, 20 and 40 Hz [20].

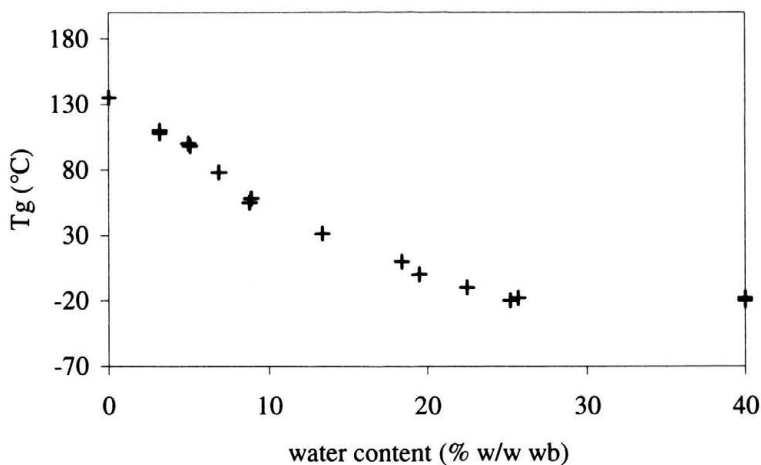


FIGURE 6. Influence of water on the glass transition temperature (T_g) of extruded bread (determined at the onset) of E' drop of DMTA at 5 Hz [20].

Moreover, viscoelastic data were also compared at 25°C. Indeed, the loss tangent is known to be a measurement of the damping following the deformation cycle, thus reflecting energy dissipation from molecular motions.

The effect of water on $\tan \delta$, measured at 5 Hz and 25°C is given in Fig. 7. The loss tangent is rather constant up to 9%, starts to increase up to a maximum value at 24% of water. The maximum was attributed to the water content corresponding to a glass transition temperature of 25°C [20].

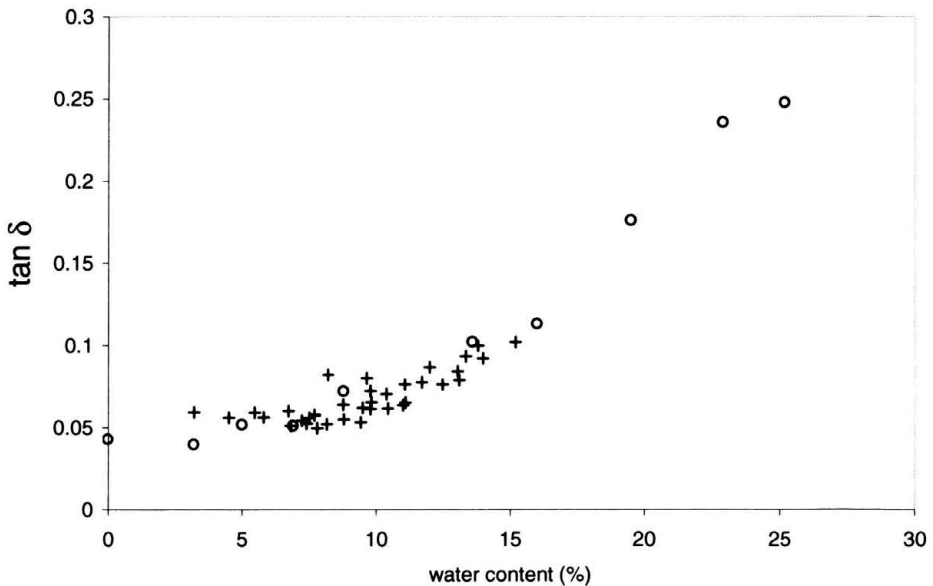


FIGURE 7. Effect of water content on the loss factor measured at 5 Hz and 25°C for cereal products (extruded bread or white bread) [6].

The increase in $\tan \delta$ values coincides noticeably with the decrease of the acoustic emission (9% water).

Although the acoustic data were acquired at fracture, whereas the dynamic data originate from small strain tests, it seems possible to correlate the two different sets of results. If there is an energy dissipation occurring prior to the fracture, there should be less elastic energy released at rupture, and thus the intensity of the emission would be lower. The increasing values of $\tan \delta$ with increasing water content reflect a greater energy dissipation, thus resulting from a greater molecular mobility (appearing above 9%) within the system. This mobility could possibly be associated with the previously mentioned secondary relaxations or could be associated with motions just preceding or accompanying the onset of the glass transition (α relaxation).

5. Origin of the hardening of the material with increasing moisture

No marked macroscopic density changes were detected in this hydration range. No crystallinity could be detected with either DSC nor DMTA or X-rays diffraction, and therefore the hardening observed in the samples could not be attributed to retrogradation or to crystals remaining from the baking process.

The hardening observed upon hydration has been described as an “antiplasticizing” effect. Indeed, although the increasing water content still decreases the glass transition temperature, the effect observed for limited hydration (< 9%) is opposite to the usual consequences of plasticization on mechanical properties, whereas the softening one only becomes dominant for higher hydration values. This antiplasticizing process has been observed in several systems but its molecular origin has not yet been clearly identified. It has been attributed to a densification at a molecular level through a decreasing amount of defects (lower density regions) present in the glass [23-24] or to a strengthening of the interactions with the polymeric matrix or to a structural relaxation [25-26]. Finally, Le Meste et al. (1996) [20] suggest that the stiffening of the samples could result from a short range reorganization throughout H-bonding (at such a limited scale that undetected by DSC or X-rays) allowed by a greater mobility induced by the dilution.

Recently, the study has been completed by the analysis of starch+sucrose mixtures equilibrated at different hydrations. The crispness appeared to be “protected” by sucrose versus hydration, samples with 20% sucrose being crispy up to 12% of water when pure starch ones lost their crispness above 7%. Similarly, the hardening was mainly observed with the pure starch samples.

6. Hydration of glassy material: suggested mechanism

The results obtained with the starch-sucrose mixtures strengthen some of the hypothesis previously brought up. Glassy systems consist of both dense regions and lower density ones. The latter are characterized by the presence of voids (also called defects or free volume) which are sometimes referred to as “mobility islands” [27] for the possible greater mobility they offer throughout the greater space. When considering hydration, the water molecules “first” added to the systems (below 9% for extruded bread) would localize in the low density regions, filling the voids and therefore causing an increased density (at a molecular level) and thus an increased hardness of the glasses. Further hydration will see water interacting with polymers through hydrogen bonding in competition with the interpolymer H-bonding. When this level of

hydration has been reached, the dominant effect of the water uptake will be a "softening" of the matrix by replacement of the interpolymer network by water-polymer interactions. When the matrix contains a mixture of starch and sucrose, the hydrogen-bonding could be first established between the water molecules and the solutes before affecting the biopolymer. Therefore crispness would be maintained up to a greater hydration level in presence of sucrose.

At present, the role of polar solutes (such as sugars) is under investigation based on mixtures with solutes of different polarities. Preliminary studies showed that low resolution proton NMR was able to detect differences in the dipolar interactions between the samples at different sugar and water contents. Moreover, techniques such as RAMAN spectroscopy could be suitable to further investigate and test the hypothesis.

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