Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Polymers 64 (2006) 197–204

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Characterization of water mobility in biscuit dough using a low-field ^{1}H NMR technique

A. Assifaoui [a,*], D. Champion [a], E. Chiotelli [b], A. Verel [b]

[a] ENSBANA—IMSAPS, 1 Esplanade Erasme, F 21000 Dijon, France

[b] Danone Vitapole—Centre de Recherche Daniel Carasso, RD 128, F 91767 Palaiseau, France

Received 12 May 2005; received in revised form 23 September 2005; accepted 9 November 2005

Available online 19 January 2006

Abstract

Biscuit dough is a complex system containing numerous components in different states, such as starch, gluten, lipids (flour constituents), sugars, fats and water. Proton mobility in these dough systems was studied using low field ^{1}H nuclear magnetic resonance (NMR). Transverse relaxation times (T_2) were obtained from single pulse (FID) and Carr-Purcell-Meiboom-Gill (CPMG) experiments. Four populations can be distinguished: the first population observed with FID sequence at $T_{2s}^* \sim 11$ μs, corresponds to flexible protons associated with the crystalline phase of palm oil, starch and gluten; the other three populations which are measured with CPMG sequence are observed at $T_2(1) \sim 2$ ms, $T_2(2) \sim 12$ ms and $T_2(3) \sim 105$ ms. The population (1) corresponds to intra-granular protons while the population (2) which is more sensitive to moisture and sucrose content, is attributed to protons in interaction with sucrose and starch. The protons of water are assumed to be distributed between these two populations. The population (3) is associated with apolar protons corresponding to the fat fraction present in the biscuit dough formula.

Keywords: Biscuit dough; Sucrose content; Water mobility; Spin–spin relaxation

1. Introduction

In order to optimise processing operations and obtain a given quality of biscuit dough, a particular understanding of water distribution is required. Many authors (Ruan et al., 1999; Sai Manohar & Haridas Rao, 2002) showed that the distribution of water could affect the rheology and then the machinability of dough. Therefore, dough, which is too hard or too soft, too brittle or too sticky, will not process in satisfactory conditions on the appropriate dough forming equipment and will not yield a satisfactory product. A considerable number of papers are devoted to the study of water distribution in systems such as starch, gluten, and flour doughs. However, only limited works have pointed out the mobility of water in complex systems such as bread dough (Chen, Long, Ruan, & Labuza, 1997; Engelsen, Jensen, Pedersen, Norgaard, & Munck, 2001; Wang, Choi, & Kerr, 2004). Water in biscuit dough can be associated with flour constituents (starch, gluten, pentosans) on one hand, and with added ingredients such as sugars in their different states (amorphous and/or crystalline) on the other hand. Therefore, the study of water in biscuit dough is a very complex subject, which necessitates a preliminary characterisation of water mobility in flour and its constituents (gluten and starch). The insight of this paper is to characterize water distribution in a multicomponent mixture (biscuit dough) and to correlate it with what was observed in more simple systems such as flour–water and starch–water mixtures. We showed also that a low field ^{1}H nuclear magnetic resonance (^{1}H NMR) could be used to determine water distribution between components in a real food products and to characterize dough during its process.

Many researchers (Kou, Dickinson, & Chinachoti, 2000; Le Botlan, Rugraff, Martin, & Colonna, 1998; Le Meste, 1995; Ruan et al., 1999) have reported that the mobility of water in food systems can be studied by measuring the protons spin–spin relaxation time (T_2). In general, T_2 relaxation of complex food exhibits multi-component behaviour, in which the individual components can be interpreted as representing different water regions, and diffusive exchange between separate regions in the system.

In starch–water mixtures (waxy corn, potato and wheat starch), many authors (Chatakanonda et al., 2003; Choi & Kerr, 2003a,b; Tananuwong & Reid, 2004; Tang, Brun, & Hills, 2001; Tang, Godward, & Hills, 2000) have found two distinct

* Corresponding author. Tel.: +33 3 8039 3663; fax: +33 3 8039 6647.
E-mail address: ali_assifaoui@hotmail.com (A. Assifaoui).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.11.020

regions of T_2 distributions at $T_2(1)\sim 2$–5 ms and at $T_2(2)\sim 10$–40 ms corresponding to intra and extra granular water, respectively. Tananuwong and Reid (Tananuwong & Reid, 2004) have shown that an increase in the total water content of the system does not produce a significant effect on the less mobile intra-granular water, though it strongly influences the relaxation behaviour of the more mobile extra-granular water. Other studies (Kim & Cornillon, 2001; Ruan et al., 1999) have shown that the more mobile population is very sensitive to temperature variations and that the gelatinisation phenomenon of starch in presence of sufficient water content modifies this population mobility. Furthermore, studies (Li, Dickinson, & Chinachoti, 1996; Umbach, Davis, Gordon, & Callaghan, 1992) have showed that the more mobile population ($T_2(2)$) can be also affected by gluten content. Li, Dickinson and Chinachoti (Li et al., 1996) have found that wheat gluten has a stronger affinity for water molecules as the water in gluten remained immobile while water in starch was more mobile. Thus, the water self-diffusion, measured by pulsed gradient spin echo NMR, decreased when the amount of gluten added to starch–water mixture increased (Umbach et al., 1992). This indicated that gluten binds or entraps water more effectively than starch.

In wheat flour, at 38% w.b. of water, Kim and Cornillon (Kim & Cornillon, 2001) have found three water populations: $T_2(1)=1.5$ ms, $T_2(2)=6$–7 ms and $T_2(3)=40$–60 ms representing 30, 60 and 10% of the total mobile population, respectively. Engelsen et al. (Engelsen et al., 2001) have also found three water populations in bread (45.3% w.b. of water) at $T_2(1)=4$ ms, $T_2(2)=20$ ms and $T_2(3)=185$ ms (34, 64 and 2% of the total mobile population, respectively). These populations have been attributed to water in association with gluten (population 1) and starch (population 2). The third population may be due to a diffusive exchange of water between starch and protein fractions. The effect of water and gluten content on the water mobility in white bread has been studied by Wang et al. (Wang et al., 2004). They observed that, before heating, the bread dough with low gluten content did not absorb as much water as the dough with high gluten content, and appeared more sticky and wet. Therefore, they suggested that a redistribution of water occurred from gluten to starch.

In biscuit dough, the presence of numerous components in different states, and their competitions in respect of water make the study of the water mobility particularly complex. Moreover, data on these types of mixes are scarce in literature (Chevallier, Colonna, Della Valle, & Lourdin, 2000) and only few papers reported information on water distribution between components. In this work, we studied proton mobility in biscuit dough using a low-field pulsed ^{1}H NMR. Free induction decay (FID) measurements were used to evaluate the less mobile protons ranged between 10 and 1000 μs; while a Carr-Purcell-Meiboom-Gill (CPMG) spin echo sequence was used to study the mobile and more mobile protons in dough (0.1–1000 ms). The effect of moisture, sucrose content and temperature was also examined in order to understand interactions and competition between the different components and water.

2. Experimental section

2.1. Preparation of dough samples

All ingredients (wheat flour, sucrose, palm oil) used for the preparation of biscuit dough samples were provided by Danone Vitapole (Palaiseau, France). Wheat flour contains 15.0% wet basis (w.b.) of moisture, 11.1% w.b. of proteins and 4.2% w.b. of damaged starch. Sucrose was used in two physical states: crystalline and amorphous (dissolved in water before use). The palm oil was melted at 55 °C and stored under agitation at 35 °C for at least 24 h before use.

The biscuit dough (49.7% w.b. of flour, 21.4% w.b. of total sugars, 9.6% w.b. of palm oil and 19.4% w.b. of water) was prepared by mixing for 8 min in a Consistograph CHOPIN mixer (at 24 °C). The relative humidity and the temperature of the room were recorded for every batch. Before NMR measurements, biscuit dough was allowed to rest (in a closed environment) for 30 min at 24 °C in a water-bath. Biscuit doughs with 16.3, 17.5, 19.4, 21.0 and 23.0% w.b. of moisture were prepared to study the effect of water. If we calculate the moisture content of the 19.4% (w.b.) water biscuit dough sample on the polar phase basis, then water content of 22% (22 g water for 100 g of dough without palm oil) is obtained.

A set of flour–water samples was prepared as well at 22% water (w.b.), by equilibrating under known relative humidity, and at 30, 35 and 40% water (w.b.), by manual blending. Two levels of sucrose content (3.5 and 7.0% w.b.) were also manually blended. The moisture concentration of flour–sucrose–water preparations were kept constant (40% w.b.)

2.2. NMR measurement

The proton relaxation studies were carried out on a low-resolution MARAN Ultra NMR spectrometer (Resonance Instruments, Oxford, UK) operating at a ^{1}H resonance frequency of 23 MHz. The NMR system was equipped with a temperature control device allowing temperature regulation at ±0.5 °C. In this study, Free Induction Decay (FID) and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences with the settings shown in Table 1 were used.

Samples (∼0.3 g) were weighted in 8-mm diameter NMR tubes and then sealed with parafilm. In order to avoid evaporation during heating of the sample, a glass rod was introduced into the tube before sealing to reduce the free volume for water vapour inside the tube. Temperature was increased from 25 to 80 °C with a step of 5 °C. At every point, the sample temperature was maintained for 2 min before measurement.

Spin–spin relaxation times (T_2^*) in the 11.5–1000 μs range were determined by a single-pulse experiment (FID). The FID data ($I_{FID}(t)$) were fitted using a discrete method based on a Gaussian function for the less mobile phase (T_2^*), and on a multi-exponential function for the mobile phase (T_{2i}^*) (Le Botlan & Ouguerram, 1997; Ruan, Long, Song, & Chen, 1998)

Table 1
NMR sequence parameters

FID	DT = 9.0 μs	P90 = 2.5 μs	RD = 4.0 s	DW = 0.1 μs	SI = 12500	NS = 4
CPMG	DT = 9.0 μs	P90 = 2.5 μs P180 = 5.0 μs	RD = 5.0 s	Tau = 75 μs	Necho = 12500	NS = 16

RD is the recycle decay between scans (s), P90 and P180 are the pulse width (μs), DT is the dead time before and after applying the pulse (μs), DW is the dwell time or Tau delay (μs), which is the interval between two neighbouring data points, SI and Necho are the number of data points to be acquired and the number of echoes for CPMG sequence and NS is the number of scans.

according to the Eq. (1):

$$I_{\mathrm{FID}}(t) = I_0 \exp\left[-\left(\frac{t}{T_2^*}\right)^2\right] + \sum_i I_i \exp\left(-\frac{t}{T_{2i}^*}\right) \tag{1}$$

where T_2^* and T_{2i}^* are the relaxation times of the less mobile (s) and mobile (m) phases, respectively. I_0 and I_i correspond to the intensity, which is proportional to the amount of protons in the less mobile and mobile phases, respectively.

Transverse relaxation curves obtained from a CPMG sequence (Fig. 1a) were fitted as a continuous distribution of exponentials with WinDxp software from Resonance Instruments (Oxford, UK). This routine is based on the 'CONTIN' program of Provencher (Provencher, 1982) (Eq. (2)).

$$I_{\mathrm{CPMG}}(t) = \sum_i I_i \exp\left(-\frac{t}{T_{2i}}\right) \tag{2}$$

where T_{2i}, I_i are, respectively, the relaxation time and the intensity of different populations. The curves obtained from the WinDxp software were then deconvoluated to three Gaussian functions in order to estimate the number of protons associated with each population (Fig. 1b) and to understand the evolution of each population during heating or when water content is changed.

Alphabetic (A, B, C) and numerical (1, 2, 3) characters are used to distinguish different populations in wheat flour preparation and biscuit dough, respectively. All measurements in this study were performed at least in triplicate; the means and standard deviations were calculated. The variation coefficient is around 10% for T_2 determination.

3. Results

3.1. Characterization of protons mobility in biscuit dough

T_2 relaxation time distribution obtained from a single pulse (FID) for a biscuit dough at 19.4% (w.b.) of water (at 25 °C) showed two proton populations: the first one is given at $T_{2s}^* \sim 11$ μs representing 65% of total protons; the second population appeared at $T_{2m}^* \sim 2.4$ ms with 35% of total protons. The population associated with the less mobile region, T_{2s}^*, may correspond to protons in solid-like components, such as starch, proteins and water molecules tightly associated with those of solids (Kim & Cornillon, 2001; Ruan et al., 1999). The second population, T_{2m}^*, may correspond to all more mobile protons in the biscuit dough. It is known that FID signal is limited for measuring high mobility. In fact, the FID signal contains not only the spin–spin relaxation but also the lost signal due to inhomogeneous local magnetic field (Hore, 1995). So high time constant values T_2^* measured using FID are not true spin–spin relaxation times (T_2), and caution must be taken when comparing and using T_2^* data. High spin–spin relaxation times can be better determined using a spin-echo sequence (CPMG). Thus, distribution of relaxation times in biscuit dough at 19.4% (w.b.) water showed three populations (Fig. 1) observed at $T_2(1) = 1.9$, $T_2(2) = 12.4$ and $T_2(3) = 104.7$ ms. The relative numbers of mobile protons associated to these CPMG populations are, respectively, 9.8, 19.2 and 6.0% of the total protons (the sum of these populations being equal to the % total protons of the second FID population, T_{2m}^*).

In order to understand the contribution of the different ingredients of biscuit dough on the NMR CPMG signal, T_2

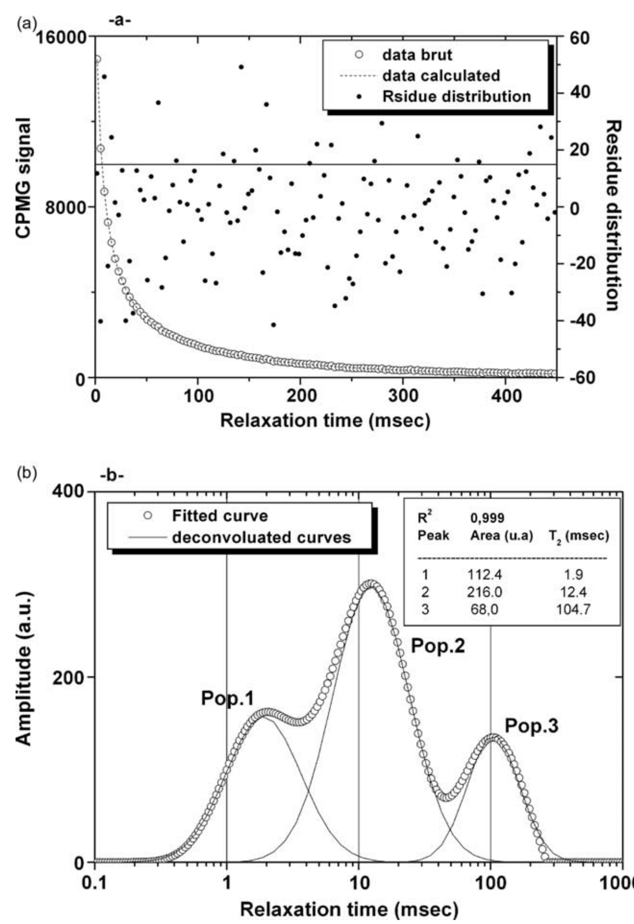

Fig. 1. (a) NMR CPMG signal for biscuit dough at 19.4% of moisture and residue distribution obtained from WinDxp software, (b) $T2$ distribution from the fit; lines represent the deconvolution by three-Gaussian functions. Values on the table present the deconvolution results.

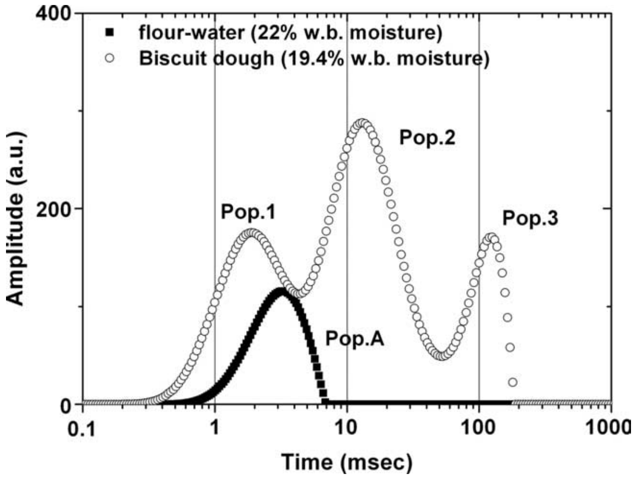

Fig. 2. Distribution of relaxation time (T_2) obtained by CPMG sequence for wheat flour at 22.0% w.b. of water (■) and biscuit dough at 19.4% w.b. of water (○) at $T=25$ °C.

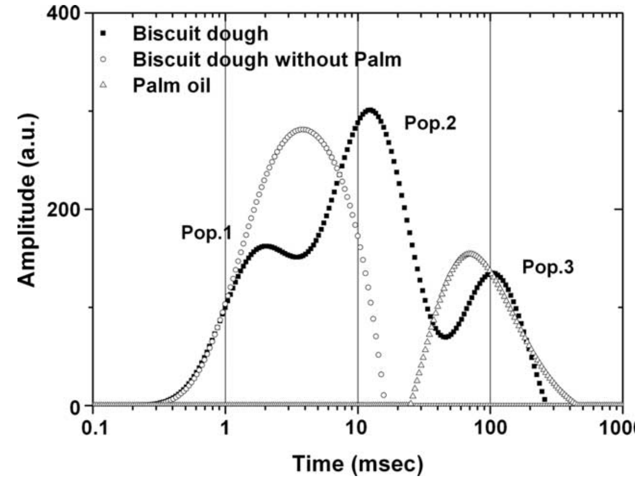

Fig. 4. Relaxation time distribution (T_2) for palm (△), biscuit dough prepared with palm (■) and without palm (○) at 22 g of water per 100 g of polar phase in the dough ($T=25$ °C).

relaxations of flour–water blends at 22% water and palm oil were analysed separately. Variable water contents of the flour–water preparations and the biscuit dough were also studied.

3.1.1. Characterisation of proton mobility in flour–water preparations

Only one broad population at $T_{2A}=3.2$ ms was observed in flour–water preparations at 22% (w.b.) water; this population appeared between $T_2(1)$ and $T_2(2)$ determined on the biscuit dough spectrum (Fig. 2). The relaxation time for this mobile population increased with the moisture indicating increased mobility of protons as shown in Fig. 3. This can be related to an increase of free volume, in which starch granules are free to move and to the proton population likely associated with water (Fullerton & Cameron, 1988; Ruan et al., 1999; Tang et al., 2000). This population has been found at 20 ms by Engelsen et al. (Engelsen et al., 2001) in bread dough at 45% w.b. of moisture and was attributed to water in association with starch and pentosans. In this study, the two populations (Pop.1 and Pop.2) observed in biscuit dough (Fig. 2) at $T_2(1)=1.9$ ms and $T_2(2)=12.4$ ms, respectively, may be attributed to water protons in association with gluten, starch and sucrose.

3.1.2. Characterisation of proton mobility in apolar phase in biscuit dough

The T_2 relaxation times of the palm oil were studied with a CPMG sequence at $T=25$ °C (Fig. 4). Results showed only one proton population with high mobility ($T_2=60$ ms). Then, the T_2 relaxation times from CPMG sequence for biscuit dough prepared with and without palm oil at the same water content (22 g of water per 100 g of polar phase) were compared (Fig. 5). In the biscuit dough without palm, only one broad peak has been observed at $T_2=4.0$ ms corresponding probably to mobile protons of starch, gluten and sucrose and of water associated to these molecules. Moreover, the $T_2(3)$ observed at 104 ms in the biscuit dough with palm, disappeared in the biscuit dough without palm. Thus, this population should correspond to protons of the apolar phase (palm oil). However, the relaxation time obtained at $T_2=60$ ms for the palm oil at

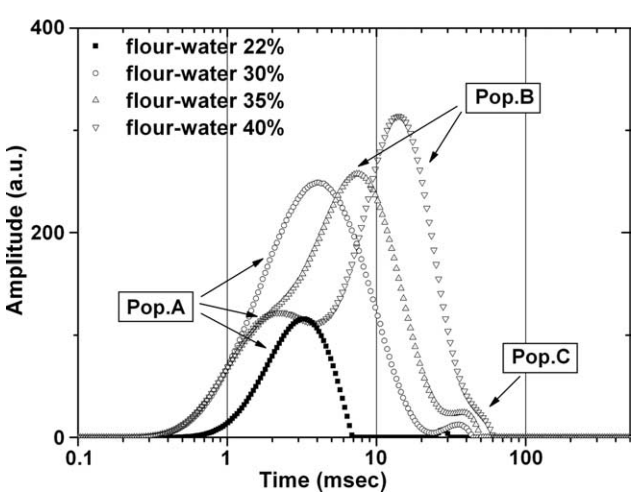

Fig. 3. Distribution of relaxation times (T_2) for flour preparations at different water contents ($T=25$ °C).

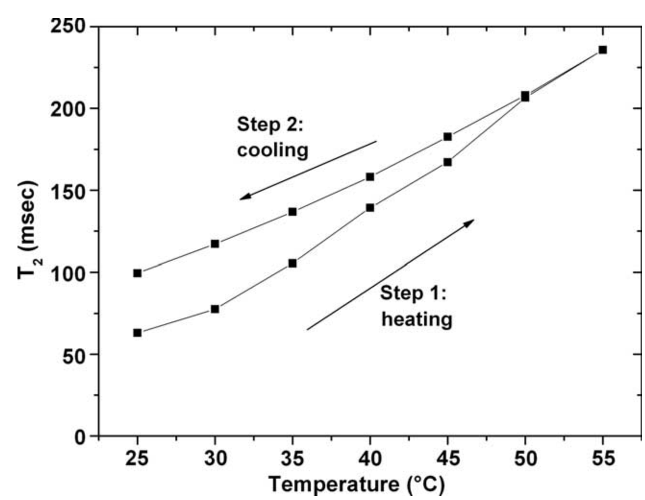

Fig. 5. Variation of the relaxation time T_2 with temperature for palm oil used in biscuit dough. (Arrows indicate the temperature changes).

25 °C is lower than the relaxation time $T_2(3)=104$ ms observed in the biscuit dough. This difference can be due to the thermal history and liquid crystal evolution of palm oil during dough preparation. Indeed, the palm has been melted at 55 °C and stored under agitation at 35 °C, for at least 24 h, before its use in biscuit dough recipe. In order to take into account the effect of thermal treatment, the relaxation time of palm oil was studied as a function of temperature during heating and subsequent cooling (Fig. 5). The relaxation time increased with temperature, indicating increased mobility of palm protons during heating due to thermal agitation and melting of fat crystals. On decreasing temperature, the relaxation time (T_2) values decreased but remained higher than the T_2 obtained during heating. This is probably due to the rate of cooling (1.5 °C per minute), which did not allow the achievement of fatty acid re-crystallisation. Indeed, the T_2 relaxation value obtained after cooling of palm oil at 25 °C ($T_2=100$ ms) was not significantly different from the relaxation time of the third population ($T_2(3)=104$ ms) observed in the biscuit dough.

3.1.3. *Effect of water content on proton mobility of biscuit dough*

The distribution of the relaxation times determined by CPMG sequence was studied on biscuit dough at different levels of water content (16.3, 17.5, 19.4, 21.0 and 23.0% w.b.). The evolution of the three populations deconvoluated by three Gaussian functions is presented in Fig. 6a.

Moisture variation had no significant effect on populations (Pop.1) and (Pop.3). However, a significant effect of water content on the relaxation time values and T_2 distribution was observed for the population (Pop.2) (Fig. 6a). In fact, the relaxation times and the amount of protons increased linearly as a function of water content for this intermediate population (Pop.2) (Fig. 6b). Therefore, the second population (Pop.2) observed in biscuit dough is not only the most marked one, but also the most sensitive to water content.

4. Discussion

In flour–water preparations (Fig. 3), at 22% (w.b.) water, only one proton population was observed. The mobility of this population increased from $T_2=3.0$ ms at 22% (w.b.) of moisture to $T_2=3.8$ ms at 30% (w.b.) of moisture. This population may be due to protons of starch, gluten and water in association with starch and gluten. The increase in T_2 relaxation times when the water content is increased (Fig. 3) was also noticed in previous studies. Indeed, Choi and Kerr (Choi & Kerr, 2003a) have found one large population in native wheat starch system (which is the major component of wheat flour), and proton mobility increased with moisture, ranging from $T_2=0.14$ ms at $a_w=0.11$ (5.4% w.b. of water) to $T_2=20$ ms at $a_w=0.93$ (28.8% w.b. of water).

Above 35% (w.b.) of water content, the broad population in flour–water preparations is divided into two populations at $T_2(a)\sim2$ ms and $T_2(b)=7$–14 ms, respectively (Table 2). The less mobile population could be assigned to water inside starch granules (Tananuwong & Reid, 2004; Tang, Godward et al., 2000) and to water in association with gluten (Wang et al., 2004). Indeed, in bread dough Wang (Wang et al., 2004) showed that this population was affected neither by the gluten content (11.2–14.2 g/100 g of flour) nor by water content (34–43% w.b. of water content); while the number of protons increased with moisture content in the more mobile population. These results are in agreement with ours, so the more mobile population observed at $T_2(2)$ is more sensitive to water content variations and may correspond to inter-granular water.

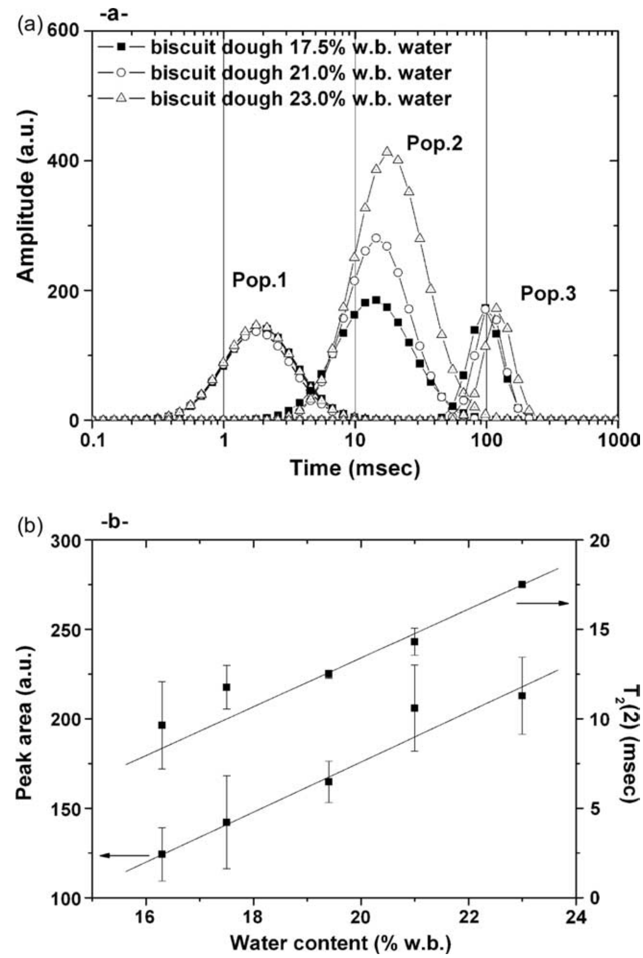

Fig. 6. (a) Relaxation time distribution (T_2) for biscuit dough prepared with different water contents ($T=25$ °C). (b) Effect of water content on T_2 relaxation time and the associated peak area for the population (Pop.2) in biscuit doughs ($T=25$ °C).

Table 2
T_2 relaxation time and peak area in wheat flour preparations at different levels of moisture (standard deviation is below 4%)

Water content (%w.b.)	Population A	Population B
22	$T_2(A)=3.0$ ms	–
	$I=60.6$ (a.u.)	–
30	$T_2(A)=3.8$ ms	–
	$I=216.8$ (a.u.)	–
35	$T_2(A)=1.9$ ms	$T_2(B)=7.8$ ms
	$I=73.5$ (a.u.)	$I=164.0$ (a.u.)
40	$T_2(A)=2.3$ ms	$T_2(B)=14.0$ ms
	$I=100.0$ (a.u.)	$I=178.0$ (a.u.)

Choi and Kerr (Choi & Kerr, 2003b) have found two distinct water fractions in partially gelatinized wheat starch solutions at 2–6 ms and at 10–300 ms the latter being dependant on gel concentration. They associated the longer T_2 region with the continuous amylose-rich gel and intragranular amylopectin-rich, while the shorter T_2 region was associated only with granule remnants.

Our results on biscuit dough (Fig. 6), also showed that the intermediate population (Pop.2) is the most sensitive to water content. It seems that additional water mainly stays outside starch granules, (Tananuwong & Reid, 2004) interacting preferentially with sucrose present in the biscuit dough. This can be due to competition of sucrose with starch for water (Hoseney & Rogers, 1994). In order to verify this hypothesis, the effect of sucrose content on T_2 relaxation time in flour preparations (40% w.b. of moisture) was studied (Fig. 7).

Three distinguishable populations were observed in flour preparations (40% w.b. of moisture) in presence of sucrose. The first two populations (noted Pop.A and Pop.B) were observed at $T_2(A)=2$ ms and $T_2(B)$ ranging from 13 to 16 ms (Table 3). These populations can be correlated to the Pop.1 and Pop.2 observed in biscuit dough. Moreover, a new population (noted Pop. C) appeared more clearly at $T_2(C)=50$–60 ms with added sucrose (Table 3).

At constant water content (40% w.b.), the population (Pop. B) was sensitive to sucrose content. In presence of sucrose, water may interact preferentially with sucrose than with starch, which increased the relaxation time $T_2(B)$ (Table 3). Thus, the amount of water retained by starch granules is decreased corresponding to a decrease in $T_2(A)$ (Table 3). The relaxation time $T_2(C)$ increased with increasing sucrose content. This population may be related to water in weaker interactions with matrix molecules or to the presence of molecules of low molecular weight (such as mono, or di-carbohydrate molecules), which can relax quickly explaining the high mobility, observed.

In order to further confirm previous hypotheses on different proton populations attribution, the wheat flour (40% w.b. of moisture) preparations varying on sucrose contents were then heated from 25 to 80 °C with a heating rate of 1.5 °C/min. Relaxation times ($T_2(A)$, $T_2(B)$ and $T_2(C)$) were collected from the fitted CPMG data and plotted versus temperature (Fig. 8).

Results showed that $T_2(A)$ slightly increased with temperature, which may be due to additional absorption of water by starch granules. Indeed, native wheat starch granules are highly hydrophobic, and as the mass is heated, it expands and absorbs more water (Grant, Belton, Colquhoun, & Parker, 1999) explaining the increase of $T_2(A)$. The higher the sucrose content, the more the population A disappeared at higher temperature: from 60 °C for the flour preparations without sucrose to 80 °C for the flour preparations with 7% sucrose (Fig. 8). This temperature can be correlated to the onset of starch gelatinisation of wheat flour preparations corresponding to the swelling of granules. Grant and Belton (Grant et al., 1999) have found similar results on wheat flour preparations at 38% (w.b.) of moisture. Furthermore, the shifting of the temperature of the Pop.A disappearance with sucrose content corresponds to shifting of the gelatinisation temperature observed with increasing sucrose content in wheat flour preparations at 40% (w.b.) of water. Chiotelli et al. (Chiotelli, Rolée, & Le Meste, 2000) have studied using DSC measurements the effect of sucrose (0–20% w.b.) and water contents (30–60% w.b.) on the gelatinisation temperature of wheat and waxy starch–sucrose–water mixtures. They found that when sucrose was added to the starch–water system, the melting of amylopectin crystals shifted to higher temperatures

Table 3
T_2 relaxation time and peak area in wheat flour preparations at 40% w.b. of moisture and different sucrose contents

Sucrose content (%w.b.)	Population A	Population B	Population C
0.0	$T_2(A)=2.3$ ms	$T_2(B)=14.0$ ms	–
	$I=100$ (a.u.)	$I=178.0$ (a.u.)	–
3.5	$T_2(A)=2.0$ ms	$T_2(B)=13.6$ ms	$T_2(C)=50.3$ ms
	$I=92.4$ (a.u.)	$I=169.3$ (a.u.)	$I=20.3$ (a.u.)
7.0	$T_2(A)=2.0$ ms	$T_2(B)=16.4$ ms	$T_2(C)=62.1$ ms
	$I=93.5$ (a.u.)	$I=176.0$ (a.u.)	$I=21.1$ (a.u.)

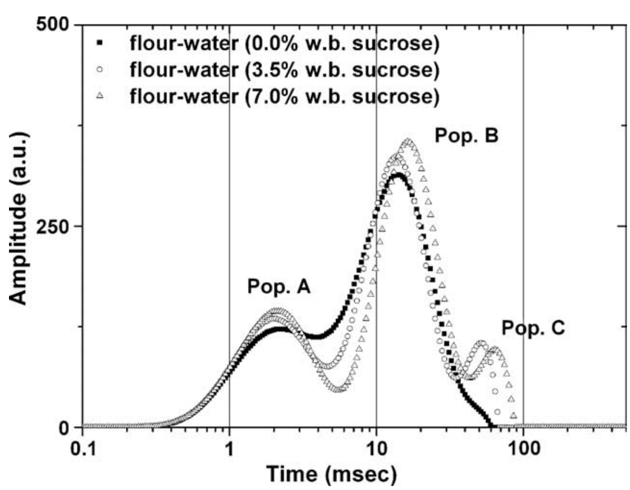

Fig. 7. Relaxation time distribution (T_2) for flour dough (40% w.b. of moisture) prepared with different amount of sucrose ($T=25$ °C).

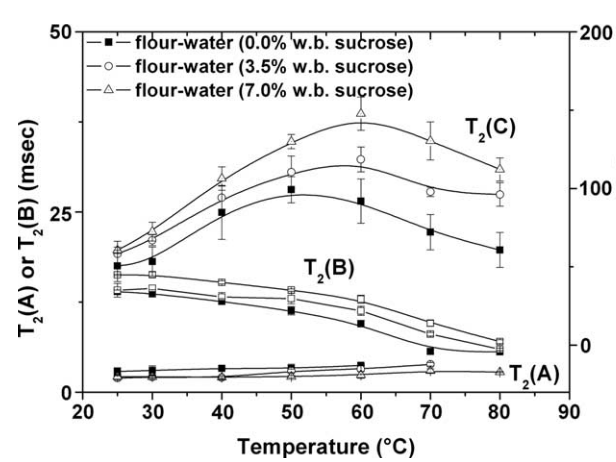

Fig. 8. T_2 relaxation time values versus temperature for flour dough at 40% w.b. of moisture.

and the total enthalpy of gelatinisation increased. The increase in the gelatinisation temperature has been often attributed to the sugar's ability to limit the availability of water for starch i.e. to reduce the chemical potential of water (Spies & Hoseney, 1982). However, water activity (Aw) does not appear to be the only factor delaying starch gelatinisation in sucrose solution. Moreover, at the same Aw but with different sucrose contents, Chiotelli et al. (Chiotelli et al., 2000) have observed an increase of gelatinisation temperature in wheat starch–sucrose mixture when sucrose content increased. The delaying in gelatinisation temperature in starch–sucrose–water preparations can be also explained by the antiplasticizing effect of sucrose (reduction in the flexibility of the amorphous regions of starch and then increases in Tg) (Slade & Levine, 1989). The effect of sucrose on the gelatinisation temperature of starch may also depend in sucrose–starch interactions. Indeed, the formation of 'sucrose bridges' would decrease starch chain flexibility and granular swelling, and then reduce gelatinisation temperature (Acquarone & Rao, 2003; Hoover & Senanayake, 1996). Moreover, Sobcyzynska et al. (Sobczynska, Setser, Hansen, & Paukstelis, 1990) concluded from ^{17}O and ^{13}C NMR data that the sucrose should interact with glucose residues of starch to increase the chain rigidity, so more energy is needed to break the starch–sucrose–water bonds, which increase the gelatinisation temperature. In wheat flour–water preparation, the absorption of water by starch granules occurs in the detriment of sucrose–water interactions inducing a decrease in the mobility of protons associated to sucrose (decrease of T_2(B)). Moreover, T_2(C) increased up to a temperature corresponding to starch gelatinisation (shifted to higher temperatures with sucrose content), then a decrease was observed (Fig. 8). Considering that population C corresponds to protons of small sugar molecules, the increase of T_2(C) with temperature may be due to the effect of thermal agitation. Our results suggested that when gelatinisation occurs, the small sucrose molecules are surrounded by swollen and distorted starch granules (environment of reduced mobility), which could explain the decrease in the mobility of protons associated to these molecules and then the decrease in T_2(C) relaxation.

5. Conclusion

The study of water mobility in biscuit dough is a very challenging subject. Indeed, the presence of numerous components such as starch, gluten, lipids as flour constituents, sucrose at different physical states and added fat can affect the distribution of water within the dough and thus makes the study very complex. However, using a low field ^{1}H NMR technique on the complex dough system and on more simple flour preparations and palm alone allowed us to characterise the water mobility in the biscuit dough. Accordingly, we have distinguished protons associated with different phases. Protons in apolar phase (palm oil) correspond to the more mobile population in the studied range of water content. Protons in polar phase have been observed at three different levels of mobility. The less mobile population is observed at very low relaxation time ($\sim$11 μs) and corresponds to flexible protons associated with the crystalline phase of palm oil, starch, gluten and perhaps of crystalline sucrose if present. The mobile population observed around 1 ms can be attributed to internal water in starch granules and to water in association with gluten. The third population, which appeared around 10 ms, is due to inter-granular water. This population is very sensitive to water and sucrose contents and to the temperature variations. Indeed, an increase in this population has been observed when water and sucrose content was increased. In presence of sucrose, water interacts preferentially with sucrose inducing a decrease in amount of intra-granular water in starch. We have also demonstrated that this population is correlated to gelatinisation phenomena of native starch present in the wheat flour. These results may provide information about the homogeneity and physical state of biscuit dough systems, and thus help understanding the mechanisms of dough formation and rheological properties. The correlation between rheological behaviour and water distribution determined by NMR is the subject of our next paper. However, more investigations are still needed to understand and evaluate sucrose–starch interactions in biscuit dough; i.e. in changing the nature of the sugar in order to modify these interactions.

References

Acquarone, V. M., & Rao, M. A. (2003). Influence of sucrose on the rheology and granule size of cross-linked waxy maize starch dispersions heated at two temperatures. *Carbohydrate Polymers*, *51*(4), 451–458.

Chatakanonda, P., Chinachoti, P., Sriroth, K., Piyachomkwan, K., Chotineeranat, S., Tang, H.-R., et al. (2003). The influence of time and conditions of harvest on the functional behaviour of cassava starch—a proton NMR relaxation study. *Carbohydrate Polymers*, *53*(3), 233–240.

Chen, P. L., Long, Z., Ruan, R., & Labuza, T. P. (1997). Nuclear magnetic resonance studies of water mobility in bread during storage. *Lebensmittel-Wissenschaft und-Technologie*, *30*(2), 178–183.

Chevallier, S., Colonna, P., Della Valle, G., & Lourdin, D. (2000). Contribution of major ingredients during baking of biscuit dough systems. *Journal of Cereal Science*, *31*(3), 241–252.

Chiotelli, E., Rolée, A., & Le Meste, M. (2000). Effect of sucrose on the thermomechanical behavior of concentrated wheat and waxy corn starch–water preparations. *Journal of Agricultural and Food Chemistry*, *48*(4), 1327–1339.

Choi, S. G., & Kerr, W. L. (2003a). ^{1}H NMR studies of molecular mobility in wheat starch. *Food Research International*, *36*(4), 341–348.

Choi, S. G., & Kerr, W. L. (2003b). Water mobility and textural properties of native and hydroxypropylated wheat starch gels. *Carbohydrate Polymers*, *51*(1), 1–8.

Engelsen, S. B., Jensen, M. K., Pedersen, H. T., Norgaard, L., & Munck, L. (2001). NMR-baking and multivariate prediction of instrumental texture parameters in bread. *Journal of Cereal Science*, *33*(1), 59–69.

Fullerton, G. D., & Cameron, I. L. (1988). Relaxation of biological tissue. In F. W. Wehrli, D. Shaw, & J. B. Kneeland (Eds.), *Biomedical magnetic resonance imaging*. New York: VCH Publishers.

Grant, A., Belton, P. S., Colquhoun, I. J., & Parker, M. L. (1999). Effect of temperature on sorption of water by wheat gluten determined using deuterium nuclear magnetic resonance. *Cereal Chemistry*, *76*(2), 219–226.

Hoover, R., & Senanayake, N. (1996). Effect of sugars on the thermal and retrogradation properties of oat starches. *Journal of Food Biochemistry*, *20*, 65–83.

Hore, P. J. (1995). *Nuclear magnetic resonance*. New York: Oxford University Press.

Hoseney, R. C., & Rogers, D. E. (1994). Mechanism of sugar functionality in cookies. In H. Faridi (Ed.), *The science of cookie and cracker production*. New York: Chapman & Hall.

Kim, Y.-R., & Cornillon, P. (2001). Effects of temperature and mixing time on molecular mobility in wheat dough. *Lebensmittel-Wissenschaft und-Technologie*, *34*(7), 417–423.

Kou, Y., Dickinson, L. C., & Chinachoti, P. (2000). Mobility characterization of waxy corn starch using wide-line ^{1}H nuclear magnetic resonance. *Journal of Agricultural and Food Chemistry*, *48*(11), 5489–5495.

Le Botlan, D., Rugraff, Y., Martin, C., & Colonna, P. (1998). Quantitative determination of bound water in wheat starch by time domain NMR spectroscopy. *Carbohydrate Research*, *308*(1–2), 29–36.

Le Botlan, D. J., & Ouguerram, L. (1997). Spin–spin relaxation time determination of intermediate states in heterogeneous products from free induction decay NMR signals. *Analytica Chimica Acta*, *349*, 339–347.

Le Meste, M. (1995). Mobility of small molecules in low and intermediate moisture foods. In G. V. Barbosa Canovas, & J. Welti-Chanes (Eds.), *Food preservation by moisture control fundamentals and applications* (pp. 209–225). Lancaster, PA: Technomic.

Li, S., Dickinson, E., & Chinachoti, P. (1996). Proton relaxation of starch and gluten by solid state nuclear magnetic resonance spectroscopy. *Cereal Chemistry*, *73*(6), 736–743.

Provencher, S. W. (1982). A constrained regularization method for inverting data represented by linear algebraic or integral equations. *Computer Physics Communications*, *27*(3), 213–227.

Ruan, R. R., Long, Z., Song, A., & Chen, P. L. (1998). Determination of the glass transition temperature of food polymers using low field NMR. *Lebensmittel-Wissenschaft und-Technologie*, *31*(6), 516–521.

Ruan, R. R., Wang, X., Chen, P. L., Fulcher, R. G., Pesheck, P., & Chakrabati, S. (1999). Study of water in dough using nuclear magnetic resonance. *Cereal Chemistry*, *76*(2), 231–235.

Sai Manohar, R., & Haridas Rao, P. (2002). Interrelationship between rheological characteristics of dough and quality of biscuits; use of elastic recovery of dough to predict biscuit quality. *Food Research International*, *35*(9), 807–813.

Slade, L., & Levine, H. (1989). A food polymer science approach to selected aspects of starch gelatinization and retrogradation. In R. P. Millone, J. N. BeMiller, & R. Chandrasekaran (Eds.), *Frontiers in carbohydrate research 1. Food applications*. London: Elsevier.

Sobczynska, D., Setser, C. S., Hansen, L. M., & Paukstelis, J. V. (1990). Use of ^{13}C and ^{17}O NMR to study wheat starch–water–sugar interactions with increasing temperatures. In J. W. Finley, S. J. Schmidt, & A. S. Serianni (Eds.), *NMR applications in biopolymers*. New York: Plenum Press.

Spies, R. D., & Hoseney, R. C. (1982). Effect of sugars on starch gelatinization. *Cereal Chemistry*, *59*(2), 128–131.

Tananuwong, K., & Reid, D. S. (2004). DSC and NMR relaxation studies of starch–water interactions during gelatinization. *Carbohydrate Polymers*, *58*(3), 345–358.

Tang, H.-R., Brun, A., & Hills, B. (2001). A proton NMR relaxation study of the gelatinisation and acid hydrolysis of native potato starch. *Carbohydrate Polymers*, *46*(1), 7–18.

Tang, H.-R., Godward, J., & Hills, B. (2000). The distribution of water in native starch granules—a multinuclear NMR study. *Carbohydrate Polymers*, *43*(4), 375–387.

Umbach, S. L., Davis, E. A., Gordon, J., & Callaghan, P. T. (1992). Water self-coefficients and dielectric properties determined for starch–gluten–water mixtures heated by microwave and by conventional methods. *Cereal Chemistry*, *69*(6), 637–642.

Wang, X., Choi, S.-G., & Kerr, W. L. (2004). Water dynamics in white bread and starch gels as affected by water and gluten content. *Lebensmittel-Wissenschaft und-Technologie*, *37*(3), 377–384.