Relationship Between Firming and Water Mobility in Starch-Based Food Systems During Storage[1]

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ABSTRACT

Magnetic resonance imaging (MRI) and pulsed nuclear magnetic resonance techniques were used to study the water mobility in sweet rolls during storage. Different fractions of water with distinguishable molecular mobility were identified. MRI provided information on the spatial distribution of water content and of water mobility. During storage, moisture migrated from the crumb to the crust, which was associated with the firming of the crumb. A spatial redistribution of water mobility within the sample was also observed. As storage time increased, the mobility of the less mobile water fraction decreased; whereas the mobility of the more mobile water fraction increased upon staling, suggesting a redistribution of water mobility within the water molecules in the samples. A relationship between water mobility and staling was discussed.

Firming of starch-based products has been studied for many years. However, the mechanism of firming has not been well established. At present, it is commonly believed that the states of water (i.e., characteristics of molecular motion of water or water mobility) play an important role in the firming process (Martin et al 1991), and considerable interest has been focused on the dynamic states of water in starch-based products (Kulp and Ponte 1981, Martin et al 1991).

A number of reports have discussed the use of nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) to study the states of water in starch-based products (Leung et al 1979, 1983; Leung 1981; Wynne-Jones and Blanshard 1986; Kim-Shin et al 1991; Slade and Levine 1991; Lim et al 1992; Teo and Seow 1992). A number of controversial hypotheses on the migration of water molecules from starch to gluten or vice versa during staling of baked products have been proposed. Leung et al (1983) proposed that as starch changes from the amorphous state to the more stable crystalline state, water molecules become immobilized as they are incorporated into the crystalline structure, resulting in a decrease in mobility of water during the firming process. Whistler and Daniel (1985) suggested that water was expelled from the starch matrix because of retrogradation. This has been supported by polymer theory and DSC results, which indicate that freezable water in the amorphous matrix migrates to crystalline hydrate of B-type wheat starch, where the water becomes unfreezable (Slade and Levine 1989). Willhoft (1971) and Breaden and Willhoft (1971) reported that gluten underwent a transformation resulting in the release of water, which became absorbed by retrograding starch. This leads to many questions about the role of starch retrogradation in the firming process of starch-based products during storage.

The techniques used in these experiments were sensitive only to certain states of water, and thus they are insufficient to provide complete details of the staling process. It would be advantageous to develop techniques that can be used to study water in its different states or with different molecular mobility. It is particularly desirable that the techniques be nondestructive and noninvasive, so that a system can be studied using a single sample during shelf life storage. Pulsed NMR and magnetic resonance imaging (MRI) techniques are ideal for such a study (Schmidt and Lai 1991).

Pulsed NMR and MRI are nondestructive techniques that enable detection of changes in the distribution and mobility of water and in the structure of the food matrix during storage. This is a major benefit, because using the same sample for observation during the entire storage period will certainly avoid the experimental errors caused by sample variations when multiple samples are used. Both NMR and MRI are capable of measuring the relaxation rates of protons within the sample, which can be represented by a spin-lattice or a spin-spin relaxation time constant T_1 or T_2. If the water molecule protons relax faster (if the proton signal decays faster), it generally indicates a shorter T_2 and less mobility of the water molecules. MRI can also provide information on the spatial distribution of water content and T_1 and T_2 values through mapping techniques (Ruan and Litchfield 1992).

The objective of this research was to explore the relationship between firming and water mobility in starch-based food products through the observation of changes in water content, water mobility, and starch recrystallization in the staling samples, using MRI, NMR, and DSC.

MATERIALS AND METHODS

Preparation of Samples

Native wheat starch was obtained from Ogilvie Mills Inc. (Minnetonka, MN); flour was obtained from ADM Milling Co. (Shawnee Mission, KS); shortening was obtained from Van den Bergh Foods Co. (Lisle, IL); and yeast was obtained from Universal Foods Corp. (Milwaukee, WI). The starch gels (20 g of starch and 80 g of water), flour batters (30 g of flour and 70 g of water), and sweet roll dough (54 g of flour, 10.5 g of sugar, 1.05 g of salt, 0.3 g of shortening, 1.4 g of yeast, and 32.75 g of water) were baked in a reel oven (Cutler National Manufacturing Co., Niles, IL) at 177°C for 20 min, cooled to room temperature, and then sealed in polyethylene bags and stored in a refrigerator (4°C) before and after each measurement. Finished samples were ≈7 cm in diameter. Tests were performed on the samples obtained immediately after baking and on Day 1, 3, and 5 of storage. Three replicates of samples were used for all the tests.

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Firmness Measurement

A universal testing machine (UTM) (model 1011, Instron Corporation, Canton, MA) was used to measure the firmness of the samples. A 1-in.^{3} sample taken from the crumb was compressed between two plates, and a force-distance curve was obtained. Crosshead speed was set at 10 cm/min, and the data were recorded digitally. Duplicate samples from the same batch were used in all tests. From the curve, the highest peak was taken as the firmness and load at 25% compression was also calculated.

MRI

A 4.7 tesla/330 MRI system (200 MHz, 33-cm bore diameter, housed at the Center for Magnetic Resonance, University of Minnesota) was used for mapping the moisture content and T_2 of the samples. An 8.5-cm i.d., high-sensitivity, and high-efficiency RF probe that could accommodate a full-size sweet roll was developed and used in this study. The fast, three-dimensional spin-echo technique (Zeng et al, in press) was used for the acquisition of the T_2-weighted images. Five T_2-weighted images with echo-delay times of 4, 9, 14, 24, and 39 μsec, were acquired. A fitting software developed by Ruan (1991) was used to obtain images of T_2.

A temperature-control system was also employed to maintain the environmental temperature of samples. This system used fiber-optic probes (Luxtron Corp., Mountain View, CA) to measure temperature, thus avoiding interference from thermocouple wires. The sample temperature was maintained at 4°C ± 0.5°C.

To acquire MRI, a whole sample of sweet roll, starch gel, or flour batter was placed into the RF probe, and three-dimensional images were taken from several slices of the sample. However, only the center horizontal slice was presented in this study.

NMR

A PCT-20/30 NMR analyzer (20 MHz, 3-cm bore diameter, housed in the Department of Biosystems and Agricultural Engineering, University of Minnesota) was used to acquire the free induction decay (FID) curves that indicate the rate of signal decay. Faster signal decay is associated with a shorter T_2, or lower water mobility, and vice versa. For the acquisition of the μsec range FID, a simple one-pulse sequence was used; whereas for the acquisition of the msec range, a CPMG pulse sequence (Carr-Purcell-Meiboom-Gill) was used, because with this sequence, the signal decay is less affected by the field heterogeneity (Carver and Richard 1972).

Measuring Gelatinization with DSC

Starch gelatinization was examined using a DSC7 differential scanning calorimeter (Perkin-Elmer Corp., Norwalk, CT) at a heating rate of 5°C/min over a temperature range of – 40 to 90°C. Specimens of ≈15 mg were taken from the crumb of the baked samples, weighed into aluminum pans, and sealed. Temperature and heat flow were recorded. The areas under the melting peaks were determined from the temperature-heat flow curves and were regarded as degree of gelatinization of starch.

RESULTS AND DISCUSSION

Firming

The relationship between firmness and storage time in the sweet rolls, as measured by the UTM, is illustrated in Figure 1. As expected, firmness increased considerably during the five-day experimental period. This was in agreement with results reported for other baked products (Willhoft 1973).

Spatial Distribution of Moisture

The moisture distribution in the sweet roll is shown in Figure 2, The intensity of each pixel is an approximate moisture content. Initially, the moisture content in the crust was lower than that in the crumb, apparently because of the baking process. As the product aged, the inner crumb lost moisture; whereas the crust gained moisture over time, which may have partially contributed to the firming of the crumb.

Spatial Distribution of Water Mobility

Nevertheless, changes in the distribution of water mobility followed a different pattern, as illustrated in Figure 3. In these MRIs, the intensity of each pixel is directly related to the T_2 and, hence, to the mobility of the water. It can be seen that the crust, although its moisture content was lower than the crumb, had higher initial T_2 values (in the msec range) and that the T_2 values in the crumb increased over the five-day storage period. The images (Fig. 3) also show that initially the crumb had a uniform distribution of T_2 values, whereas the T_2 values in the crust were unevenly distributed. By calculating the average of all T_2 readings within each of the annuli of a sweet roll sample, quantitative profiles of the mean T_2 values along the radial direction were established (Fig. 4). These profiles clearly demonstrate an increase in the mean T_2 in the crumb over the storage period. This resulted in a decrease in the gradient of water mobility between the crust and the crumb.

As the roll aged, the water mobility in the crumb became progressively less uniform. The distribution of T_2 values broadened markedly over the storage period, as illustrated by the frequency histogram of T_2 values (Fig. 5). The frequency histogram was obtained by counting the number of pixels with the same T_2 within the discretized images of a sweet roll sample. In general, the T_2 values ranged from 5 to 60 msec. At Day 0, T_2 values were more narrowly distributed, indicating that the distribution of water mobility was more uniform. At Day 5, the frequency distribution became broader, indicating that the distribution of water mobility became less uniform. Furthermore, during the firming process, the mean T_2 of the crumb, as measured by MRI, increased ≈10% (Fig. 4), clearly demonstrating the difference in water mobility between Day 0 and Day 5.

These results suggest that some water molecules became more mobile as a result of the firming of the matrix structure of the sweet rolls. The change in T_2 values was highly correlated with the firmness (r = 0.91). Thus, the T_2 images (Fig. 3) may be viewed as a progressive firming front moving from the crust toward the crumb. Note that, despite the loss of moisture from the crumb to the crust, the T_2 values in the crumb still increased upon staling, suggesting that such a change in the mobility of the water is not a simple function of moisture content, but may be a result of physiochemical processes taking place during the staling. One possibility is that water molecules were expelled from the starch matrix as a result of retrogradation (Whistler and Daniel 1985). However, starch retrogradation is characterized by recrystallization

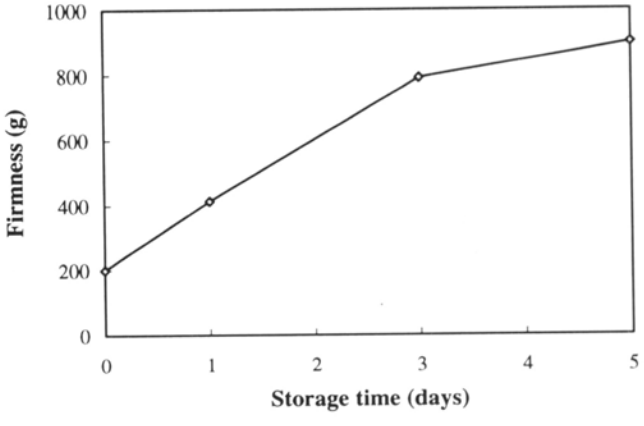

Fig. 1. Change in firmness of a sweet roll during storage.

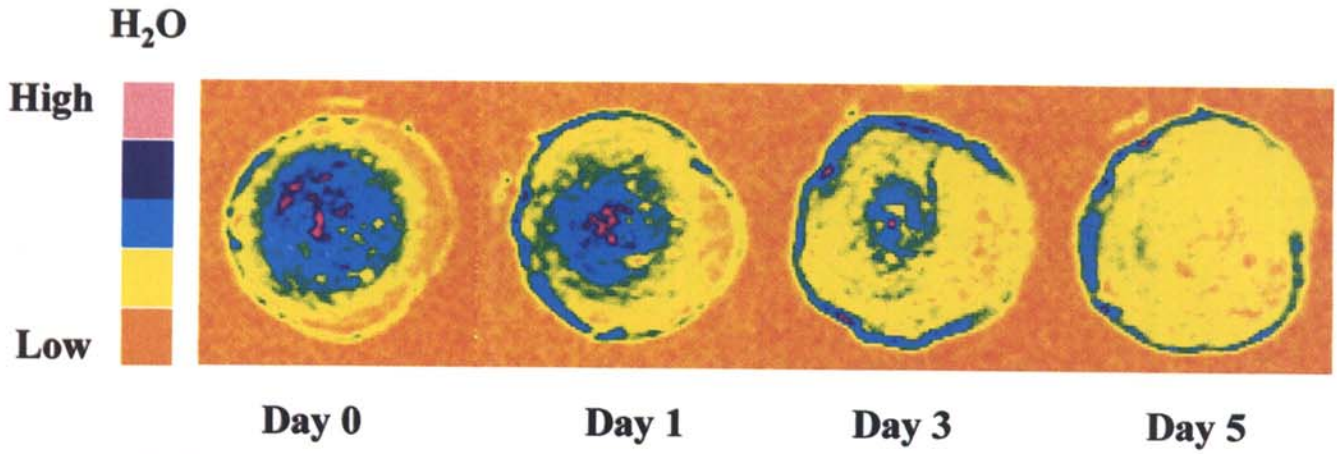

Fig. 2. Magnetic resonance images of moisture distribution in a sweet roll over a five-day storage period.

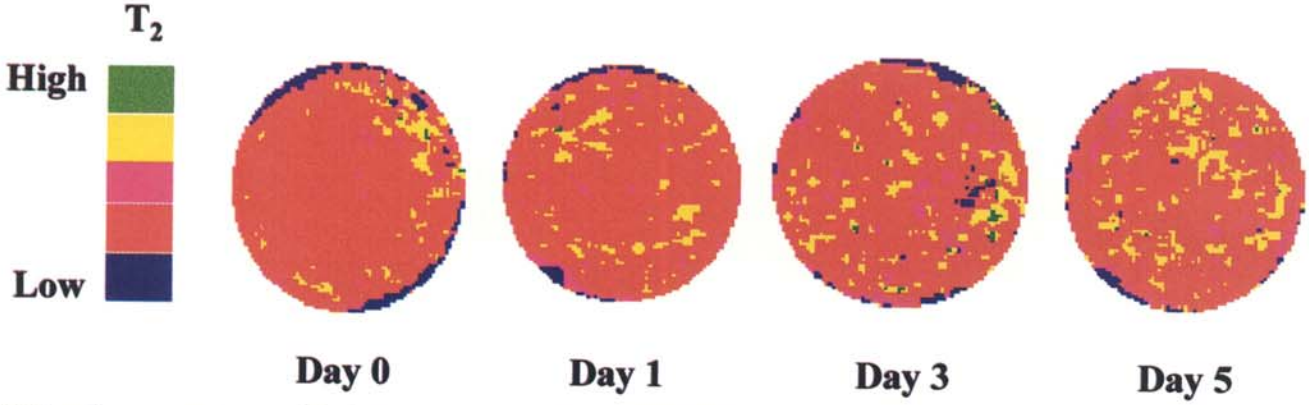

Fig. 3. Magnetic resonance images of T_2 of a sweet roll over a five-day storage period.

of starch molecules, which may cause entrapment of water molecules within the crystalline structure of the starch molecules, resulting in a decrease in the water mobility (Leung et al 1983). It would be appropriate to hypothesize that water molecules with different mobilities, because of their different interactions with the surrounding macromolecules, may behave differently during the staling process.

Fractions of Water with Distinguishable Mobility

The pulsed NMR used in this study was capable of identifying water molecules that relax at different rates. In the current study, a two-component model, consisting of a T_2 in the msec range and a T_2 in the μsec range, was employed to represent two fractions of water, each with a distinguishable molecular mobility. Figure 6 illustrates that the FID signal decay with a T_2 in the μsec range is faster in the aged rolls than that in the fresh rolls, whereas Figure 7 shows that the FID signal decay with a T_2 in the msec range is faster in the fresh rolls than in the aged rolls. This confirmed our earlier hypothesis that water molecules with different mobilities may respond to the firming process in different ways, depending upon their interactions with the macromolecules. In our case, the mobility of the less mobile water fraction decreased during staling, whereas the mobility of the more mobile water fraction increased during staling.

The experimental results indicated that there was not only a spatial redistribution of water content and water mobility but also a redistribution of magnitude and mobility of water between two distinguishable fractions of water, one of which is less mobile and the other more mobile. Figure 8 depicts a qualitative concept of water mobility redistribution in a sample, demonstrating that some of water molecules become less mobile upon staling, whereas others become more mobile upon staling. Macromolecules may expel some water molecules as a result of molecular structural changes (Whistler and Daniel 1985), causing an increase in the water fraction with higher water mobility. At the same time, macromolecules may incorporate some water molecules into the crystalline structure because of crystallization (Leung et al 1981), resulting in a decrease in the water fraction with lower water mobility.

Relationships Between T_2 and Starch Recrystallization

It appears from these results that, during the firming process, there was an exchange of T_2 values or water mobility between the less mobile and more mobile water fractions in the sweet roll samples, which may be associated with changes in macromolecular structures (starch recrystallization or gluten-gluten entanglement). Examination of the starch gel and flour batter model systems, showed that firmness, load at 25% compression, and starch crystallization peak correlated well with T_2 in both the starch gel and the flour batter systems (Table I). However, differences did exist between the two systems. Firmness, load at 25% compression, and starch recrystallization peak correlated with T_2 values better in the starch gel system than in the flour batter system. This fact indicates that, although starch retrogradation was the major factor affecting the changes in water mobility associated with the firming process, gluten and other components in the flour system also influenced the interactions between water and the environment within the system. This is in agreement with other research findings (Whistler and Daniel 1985, Martin et al 1991).

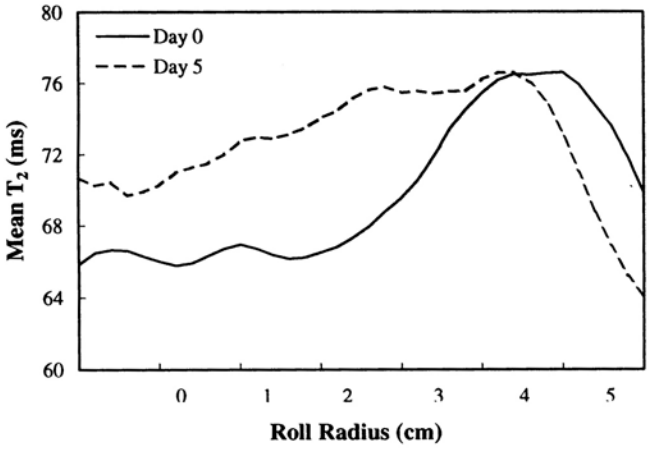

Fig. 4. T_2 as a radial function in sweet roll crumb.

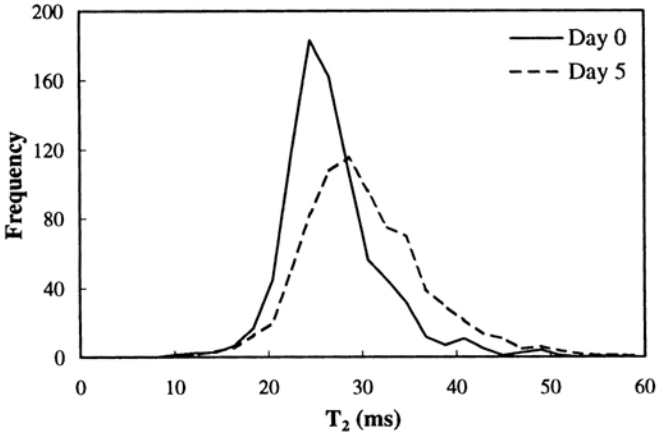

Fig. 5. Frequency spectrum of T_2 in a sweet roll during shelf-life storage.

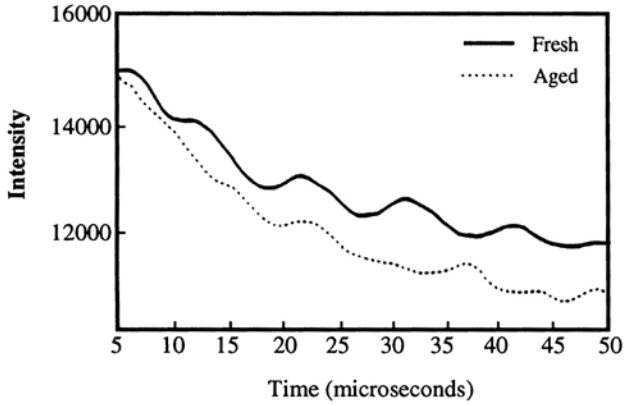

Fig. 6. Free induction decay curves having T_2 values in the microsecond range for a sweet roll.

CONCLUSIONS

Water mobility was highly correlated with the firming process in the starch-based systems used in this study. The most important finding of this study was a spatial redistribution of water content and water mobility, as well as a redistribution between distinguishable fractions of water that have different levels of water mobility within the systems. As storage time increased, the mobility of the less mobile water fraction decreased, whereas the

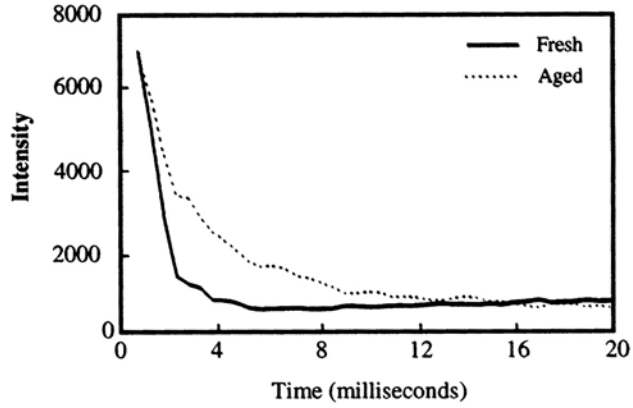

Fig. 7. Free induction decay curves having T_2 values in the millisecond range for a sweet roll.

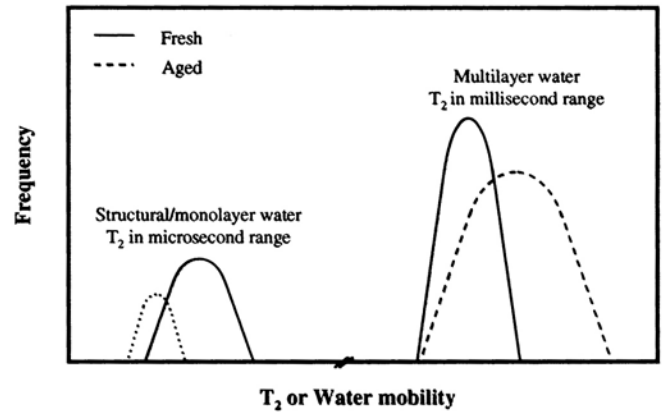

Fig. 8. Schematic diagram showing the concept of water-mobility redistribution in baked products during staling.

TABLE I
Correlation Analyses *r* Values Between T_2 and Firmness, Load at 25% Compression, and Starch Crystallization Peak Measured by Differential Scanning Calorimetry

Model System	Firmness	Load	Starch Crystallization Peak
Starch gel	0.87	0.98	0.92
Flour batter	0.82	0.72	0.76

mobility of the more mobile water fraction increased, which may have corresponded to the starch retrogradation and gluten entanglement in the samples during storage. Further study on the effect of initial states of water on the physical and chemical processes in food systems during processing and storage may lead to optimization of formulations and prediction of product shelf life based on the characteristics of initial water-holding capacity.

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