Small and Large Deformation Rheology for Hard Wheat Flour Dough as Influenced by Mixing and Resting


ABSTRACT: The effects of mixing and resting on the physicochemical properties of doughs prepared with strong and weak hard wheat flours were investigated, specifically concerning aspects related to their rheological behavior and molecular mobility. Small deformation dynamic tests showed that, during the initial resting period, the complex modulus $G'$ decreased and phase angle decreased for undermixed dough, whereas overmixed dough showed opposite trends. $G'$ values for optimally mixed dough did not vary during the resting period investigated. This was more obvious for the strong dough. Large deformation tests more clearly showed differences among optimal, under-, and overmixed dough, and also between doughs prepared with strong and weak flour. Optimally mixed dough exhibited the highest peak stress and strain for both samples. In addition, the peak stress of dough prepared with the strong flour was higher than that of dough prepared with weak flour. Inconsistent results between small and large deformation tests implied that small and large deformation tests reflected different structural aspects of dough. NMR measurements were performed to estimate the relaxation properties of the sample upon resting. Decreased water mobility during resting, indicated by decreasing $T_1$, relaxation time, was possibly attributed to increasing molecular interactions caused by continued hydration. Evidence of additional molecular interactions created by mixing was also observed.

Keywords: hard wheat flour dough, mixing time, NMR, resting time, rheological properties

Introduction

From the 1st step in the breadmaking process (blending of flour and water with other ingredients) to the final step (baking), the ingredients undergo a number of physical and chemical changes. In fact, upon mixing, dough properties continuously change simply due to the passage of time (Faubion and Faridi 1986). The type and extent of physicochemical changes that wheat flour dough experiences during each step profoundly influence finished baked products (Ramkumar and others 1996). Each step in breadmaking has optimum processing parameters, that is, an optimum water absorption, an optimum mixing time, and an optimum resting time, to name a few of the numerous processing parameters used during breadmaking. Exceeding or undercutting these values can significantly affect the properties of the resulting dough, and, most important, the quality of the final product (Faubion and Faridi 1986). Therefore, optimum conditions must be properly determined, and understanding of how they can be achieved is essential to control the breadmaking process. During breadmaking, dough undergoes different degrees of stress and deformation, which range from severe stretching and molecular reorganization during mixing to mild expansion during fermentation. The rheological responses of dough to these actions govern its breadmaking properties (Abdelrahman and Spies 1986).

To overcome the limitations of empirical measurements, such as mixograph, farinograph, alveograph, and extensograph (Bloksma 1978), many researchers have looked at fundamental rheological properties. However, it is fair to say that still there is not a unique fundamental rheological technique that could completely replace empirical methods mainly due to the fact that dough systems are far more complex than synthetic polymers for which fundamental methods are routinely utilized. Nevertheless, the results from fundamental measurements have provided valuable information on the relationship between chemical and rheological properties of complex dough systems and how they are affected by processing conditions, for example, mixing (Zheng and others 2000).

There are still conflicting results regarding relationships between fundamental rheological properties and processing variables. For instance, in the case of mixing, some researchers (Dreese and others 1988; Mani and others 1992) reported a decrease in storage modulus with increasing mixing time, whereas others (Bohlin and Carlson 1980; Navickis 1989; Zheng and others 2000) found an increase with increasing mixing time. The literature on the effects of resting time on fundamental rheological properties also shows conflicting results. A limited number of studies have examined this effect in combination with mixing time (Abdelrahman and Spies 1986; Mani and others 1992; Lindborg and others 1997). However, only 2 or 3 different resting times were used, making it difficult to observe clear trends that enable the understanding of the physicochemical changes occurring during resting. More intensive and systematic monitoring of this process is needed, and experiments should also be designed to study the combined effect of resting and mixing.
The important roles of water during dough processing (Hoseney 1994; Cherian and Chinachoti 1997; Piazza and Schiraldi 1997) have prompted researchers to investigate the relationship between water mobility and functionality of dough using qualitative and quantitative NMR analyses (Leung and others 1979, 1983; Richardson and others 1988; Belton and others 1995; Cherian and Chinachoti 1997; Grant and others 1999; Kim and Cornillon 2001). Results have provided useful information about physicochemical changes occurring in wheat flour dough during processing. It is expected that this and future research will provide new insights to aid dough processing and to improve the quality of the final products derived from dough.

The overall goal of this research was to study the physicochemical changes occurring in dough samples prepared with hard wheat flour of different strengths. Specifically changes occurring during mixing and resting were studied. It is expected that this study will provide a clearer understanding of structural changes during dough processing, which still remain uncertain. It should provide a knowledge base necessary to determine the influence of important processing parameters such as mixing time and resting time on different flours.

Materials and Methods

Materials

Two flour samples were produced in the Hard Winter Wheat (HWW) Quality Laboratory at Kansas State Univ. using wheat from 9 experimental hard winter wheat lines. The samples came from Kansas, Colorado, Oklahoma, and Nebraska. The flours from these wheats were individually evaluated for milling, rheological, and baking quality, and then especially blended to produce 2 flours with different strengths for the purposes of this research. Mixing properties for the 2 samples are given in Table 1. Sample number 401 had weak mixing properties and sample number 402 had strong mixing. The blending was carefully conducted to produce 2 flour samples having as little difference as possible in protein content (11.6% compared with 12.0%) and water absorption requirements (62.3% compared with 62.9%) but considerable differences in optimum mixing time (2.88 min compared with 5.75 min) and mixing tolerance (1 compared with 5).

Dough preparation

To rule out the effects of other ingredients, only flour and distilled water were used to prepare dough samples. Optimum miexograph water absorption (14% moisture basis) was used for dough formulation throughout the experiment. A 100 g miexograph mixer (National MFG. Co., Lincoln, Nebr., U.S.A.) was used for dough mixing. The optimum mixing times for both flour samples were determined from the obtained mixograms. These optimum times were 2 min 53 s for the weak flour (sample 401) and 5 min 45 s for the strong flour (sample 402). Under- and overmixing times were determined from these optimum mixing times, and a ratio to their optimum mixing time was maintained the same for both samples. Accordingly, mixing times for under- and overmixed dough were determined as 1 and 5 min for sample 401, and 2 and 10 min for sample 402. Mixing was conducted at room temperature.

Rheological measurements

A ViscoTech® mechanical spectrometer (ReoLogica Instruments, Lund, Sweden) with a plate–plate system was used for measuring the rheological properties of the dough samples. Operation, including temperature control and data handling, was conducted using a PC-based software provided by the spectrometer manufacturer. Serrated plates of 25-mm dia were used to prevent slippage during measurement. Before dough samples were loaded into the rheometer, approximately 2 g of each sample was placed between 2 parallel aluminum plates and slowly pressed, minimizing normal stress built up while pressing, to make the sample thickness uniform (2.5 mm) as fully described in Kim (2001). To prevent dough samples from sticking to the aluminum plates, a thin layer of mineral oil was applied to the contact area of the plates. The prepressed dough samples were loaded between the serrated plates in the instrument, and after the desired gap (2 mm) was achieved the samples were trimmed to get approximately the same diameter (25 mm) as the upper plate. To prevent moisture loss during measurements, mineral oil was applied around the open edge of the sample. The gap between the 2 plates was maintained at 2 mm during the measurement. All the measurements were performed at a constant bottom plate temperature of 25 °C, which was controlled using an electrical heater and an air cooler connected to the bottom plate. Dynamic oscillatory tests were performed at a strain of 0.5% and a constant frequency of 1 Hz. The complex modulus (G*) and the phase angle (δ) as well as storage (G') and loss (G'') moduli were obtained from these experiments. For the large deformation test, stress growth was monitored over time at a constant shear rate of 0.1/s (the maximum shear rate at the rim of the plate). The strain (the maximum strain at the rim of the plate) was calculated by multiplying the shear rate by time. From the stress growth curves, the peak stress and the strain at the peak were determined (Figure 1).

Immediately after mixing, the samples were covered with plastic wrap to prevent moisture loss. During the 3 h of resting, small pieces of dough were sampled, and small (dynamic oscillatory tests) and large (stress growth curve) deformation tests were performed on each sample. A resting period much longer than the actual resting time used in bakeries (approximately 30 min) was selected for scientific purposes. The 1st measurements were conducted 5 min after mixing. After the 1st and 2nd (15 min after mixing) measurements, sampling was conducted every 15 min. The whole procedure was repeated for duplicated experiments.

<table>
<thead>
<tr>
<th>Sample nr</th>
<th>MC (%)</th>
<th>PC (%)</th>
<th>MIXO WA (%)</th>
<th>MIXO MT (min)</th>
<th>MIXO TOL Scale (0 to 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>401</td>
<td>13.3</td>
<td>11.6</td>
<td>62.3</td>
<td>2.88</td>
<td>1</td>
</tr>
<tr>
<td>402</td>
<td>13.5</td>
<td>12.0</td>
<td>62.9</td>
<td>5.75</td>
<td>5</td>
</tr>
</tbody>
</table>

MC = moisture content; PC = protein content; MIXO WA = miexograph water absorption; MIXO MT = miexograph mixing time; MIXO TOL = miexograph mixing tolerance.

Figure 1 — Typical stress growth curve for large deformation test.
Dough influenced by mixing and resting . . .

NMR measurements

NMR relaxation times were measured using a Maran benchtop NMR spectrometer (Resonance Instruments Ltd., Witney, U.K.) running at 15 MHz having a variable temperature control system. PC-based NMR software, provided by the instrument manufacturer, was used for pulse sequencing and data acquisition. For every set of experiments, about 3 g of dough sample was used. Freshly mixed dough samples were placed into 18 mm (O.D.) glass NMR tubes, which were then placed into the NMR probe inside the magnet module. The spin-lattice ($T_1$) relaxation time was continuously measured at every 4 to 5 min during the 3 h of resting period using the inversion recovery pulse sequence (180°-r-90°). The relaxation delay was 1 s. The signal acquisition was averaged over only 4 scans due to the long acquisition time required to measure $T_1$. A set of 20 logarithmic scale time spacings between the 180° and 90° pulses was selected. The intervals between the 180° and 90° pulses varied between 100 μs and 2 s. The obtained $T_1$ curves were fitted to exponential decay equations using data fitting software (WinFit, Resonance Instruments Ltd.) to calculate corresponding relaxation time, $T_1$. Three independent resting experiments were performed for each sample and the obtained data were averaged. To prevent moisture loss during measurements, the top surface of the sample was covered with a circular piece of plastic wrap and the NMR tube was sealed with a rubber stopper.

Results and Discussion

Small deformation test

Figure 2 shows the complex modulus ($G'$) and the phase angle of samples 401 (Figure 2A) and 402 (Figure 2B) mixed for different periods during 3 h of resting period. The strong flour 402 showed higher $G'$ and lower phase angle than the weak flour 401, as expected. The rheological changes occurring during resting could be divided into 2 periods: (1) before 30 to 45 min; (2) after 30 to 45 min. After 30 to 45 min of resting, the trends of $G'$ and phase angle changes were similar regardless of mixing time and sample differences, even though some data showed less significant changes.

$G'$ decreased and the phase angle increased gradually after 30 to 45 min of resting. In order to ensure the trends after 30 to 45 min of resting, linear regression was performed for the $G'$ and phase angle data measured after 45 min of resting. This confirmed the decrease in $G'$ (negative slope) and the increase in the phase angle (positive slope) with increasing resting time at the 0.05 significance level (data not shown). Among samples of different mixing times, overmixed dough samples showed the least significant change. The decreasing $G'$ and increasing phase angle after 30 to 45 min of resting are probably due to the stress relaxation occurring in the gluten structure. Evart (1977) proposed that, during resting, the extended and unfolded protein molecules revert to the compact state of lower free energy with the help of disulfide bond interchange. Protein concatenation becomes more random, and the stress is relaxed. It could also be explained by the “loops and trains” model proposed by Belton and others (Belton and others 1994, 1995; Belton 1999). During mixing, the number of loops (protein–water hydrogen bonds) decreases and that of trains (protein–protein hydrogen bonds) increases due to the stretching of the protein network. During resting, the structure relaxes to drive the system to more favored conformational equilibrium of those loops and trains.

The observed trends on the rheological properties during the initial 30 to 45 min of resting were more complicated. Consistently, undermixed dough showed a rapid decrease of $G'$ and a rapid increase of the phase angle, whereas overmixed dough showed totally opposite trends. These trends were more obvious for samples made of the strong flour (sample 402). The optimally mixed dough appeared to be more stable to changes during the resting of the 1st 30 to 45 min, showing less changes in $G'$ and phase angle as compared to those for under or overmixed dough. Abdelrahman and Spies (1986) found similar trends. Using reconstructed flour with water absorption of 54%, they found that the storage and loss modulus of the undermixed dough decreased during 30 min of resting, whereas the behavior of overmixed dough was opposite. Strain of 10%, which is probably higher than that corresponding to the linear viscoelastic range for dough (generally less than 1%), was used. Because of the potential nonlinear effects, the absolute values of
Dough influenced by mixing and resting...

storage and loss moduli reported by these authors could deviate from true values, but a relative comparison including increasing or decreasing trends should be meaningful. The same research also found that the closer the dough to its optimum water absorption and optimum mixing time, the fewer changes in the measured viscoelastic parameters during 30 min of resting. G* values illustrated in Figure 2 were redrawn to better visualize the effect of resting time (Figure 3). For the weak flour sample (sample 401), Figure 3A shows that optimally mixed dough (mixing time of 2.89 min) exhibited smaller variation in G* than undermixed dough (mixing time of 1 min). However, G* of overmixed dough (mixing time of 5 min) showed a similar amount of variation to that of optimally mixed dough.

For the strong flour sample 402 (Figure 3B), the optimally mixed dough (mixing time of 5.75 min) showed much less variation in G*, compared to both under-(mixing time of 2 min) and overmixed (mixing time of 10 min) dough during the initial period of resting, but similar small variations for longer resting periods.

Large deformation test

As described previously, 2 parameters from the stress growth curve, the peak stress and the strain at the peak, were measured (Figure 1). These parameters were plotted as a function of resting time and are presented in Figure 4. Stress growth curves for undermixed dough samples did not show any noticeable peak. For this reason, strain at peak data for undermixed dough is omitted in Figure 4. In this case, the maximum attainable stress in the experiment was recorded instead of the peak stress.

Dough prepared with the strong flour (sample 402) consistently showed a higher peak stress than that observed in doughs prepared with the weak flour (sample 401), except when the dough was undermixed. Optimally mixed dough showed the highest peak stress followed by over- and undermixed doughs for both samples. Differences observed in the measured rheological parameters of undermixed dough from the other two were greater in the strong flour compared to the weak flour. Only after 3 h of resting, optimally and overmixed dough showed similar peak stress values. Conversely, during the whole resting period, the strain at the peak of optimally mixed dough was consistently higher than that of overmixed dough for both samples. It appears that the 2 parameters measured in these tests could be used to evaluate conditions of optimum mixing.

The general trend in the change of the peak stress during resting is similar to that observed in G* (Figure 2). After the initial 30 to 45 min of resting period, the peak stress of optimally and overmixed dough gradually decreased during the remaining resting period. Overmixed dough prepared with sample 402 showed a less significant change of peak stress after the initial 30 to 45 min
of resting period, which agreed well with the result for \( G' \). The decreasing peak stress also could be related to the relaxation phenomenon of dough as discussed previously. A fast increase in the peak stress during the initial 30 to 45 min of resting was also observed for optimally and overmixed dough, similarly as observed from dynamic rheological properties obtained at a low strain (Figure 2). The undermixed dough samples did not exhibit any distinct change in the peak stress during the whole resting period. This is possibly due to the low degree of dough development.

The strain at the peak for both overmixed dough samples 401 and 402 showed a similar extent of initial decrease for the first 30 to 45 min of resting, and then did not show any noticeable change during the remaining resting period. However, during the first 30 to 45 min of resting, the strain at the peak for the optimally mixed dough showed an apparent difference between samples. While the weak flour 401 showed a large decrease of strain at the peak during the first 30 to 45 min of resting, it was less evident for the strong flour sample 402. None of the samples exhibited noticeable changes in strain after 45 min of resting. Lindborg and others (1997) performed large deformation tests to study flour samples of different strength during 30 min of resting. As they used mixing times similar or longer than the farinograph optimum mixing time, all of their samples were either optimally mixed or overmixed. They found the greater increase of the peak viscosity for longer mixed dough during 30 min of resting. For the strong flour dough, the strain at the peak viscosity decreased upon 30 min of resting in the overmixed dough, but did not change for optimally mixed dough. Comparing their finding with the above results for the optimally and overmixed dough, both results agreed well. The above results would imply that not only the absolute value of the peak stress and the strain at the peak but also the trend of the strain at the peak during resting might be related to the flour strength and mixing degree.

**Discussion on the rheological behaviors of dough during resting**

No clear explanation of the phenomena occurring during the initial 30 to 45 min of resting was found in the literature. However, the results presented in this study provide evidence, which might bring clues to explain these phenomena. As a possible explanation for the rheological property changes of optimally and overmixed dough during the initial 30 to 45 min of resting, several researchers (Wang and others 1992; Weegels and others 1995, 1997a, 1997b; Don and others 2005) reported the possibility of repolymerization, of gluten proteins and glutenin during resting, which is consistent with the trend observed during small deformation tests. However, as the polymer orientation becomes more and more random during longer resting periods, the secondary forces become less and less effective to make cooperative interactions. From this point the shear stress stays constant or even decreases during the remaining resting period.

As previously discussed, the rheological behavior of undermixed dough during the initial 30 to 45 min of resting was opposite to that of optimally and overmixed dough in small deformation tests. Also, the trend of the measured \( G' \) in small deformation tests for undermixed dough did not agree with that of maximum stress obtained from large deformation tests. The maximum stress for undermixed dough was lower than that of optimally and overmixed dough during the whole resting period. However, \( G' \) of undermixed dough was much larger than that of optimally and overmixed dough immediately after mixing. Higher \( G' \) and lower phase angle of undermixed dough immediately after mixing could be explained by a lack of dough hydration. It is believed that well-developed gluten structure increases resistance to deformation. However, another rheologically active substance in wheat flour dough is starch, whose content is 6 times higher than that of protein. In flour particles, starch granules and proteins are tightly packed. During hydration and mechanical abrasion, proteins are separated from flour particles and form a continuous matrix with starch granules embedded in it. If mixing and hydration time is not sufficient, the resulting dough would resemble the structure of a discontinuous protein network containing a number of unhydrated flour particles composed of starch granules and unseparated proteins (Figure 5B). The presence of rigid flour particles in undermixed dough could increase solid-like behavior in small deformation tests (higher \( G' \) and lower phase angle). However, during resting, flour particles would become hydrated and their rigid structure would be softened (Figure 5B). Due to the lack of developed protein structure in undermixed dough, the hydration of flour particles during resting would directly lead to a decrease in \( G' \) and an increase in phase angle. On the other hand, the discontinuous protein network containing unhydrated flour particles in undermixed dough would provide a number of “weak points” when the sample is subjected to a large deformation. For this reason, the maximum stress of undermixed dough, which lacked in developed protein network, was smaller than that of longer mixed dough. Also, absence of continuous protein network in undermixed dough resulted in the lack of strain hardening during stress growth, a phenomenon regularly observed in dough systems (Amemiya and Menjivar 1992; VanLiet and others 1992). The discrepancy of small and large deformation tests was also evidenced in Figure 6. It shows that even though the maximum stress of both undermixed dough samples hardly changed, the stress at a lower strain (yield stress values in stress growth curve, inside circles) decreased during the initial 30 min of resting, which is consistent with the trend observed during small deformation tests. The initial stress at a lower strain and \( G' \) values for optimally and overmixed dough also showed good agreement in their trends. It would be difficult to expect a perfect correlation between the initial stress and \( G' \), because the smallest strain recorded for each stress growth curve was around 50% to 60%, which is much greater than 0.5% strain used for small deformation tests. However, the fact that, after 5 min of resting, the initial stress for undermixed dough is higher than or at least similar to that of optimally or
Dough influenced by mixing and resting...

Overmixed dough regardless of their maximum stress values, supports the above hypothesis that small and large deformation tests could reflect different structural aspects of dough depending on its hydration status.

This study showed that small deformation tests were more advantageous for understanding molecular interactions and microstructure, whereas large deformation tests were useful to evaluate more practical information specifically related to optimum mixing time and flour strength.

Evolution of NMR relaxation time during mixing and resting

Nuclear magnetic resonance (NMR) is one of the most powerful techniques for determining the molecular mobility and dynamic...
molecular interactions. Relaxation of spins occurs because of the interactions between individual spins (the spin–spin relaxation, \(T_2\)) and between a spin and its environment (the spin–lattice relaxation, \(T_1\)). During relaxation, resonant energy is exchanged among spins and environments through the process of molecular motion. In the fast molecular motion environment, such as a dough system, \(T_1\) and \(T_2\) relaxation occurs in a similar way; that is, faster molecular motion (higher molecular mobility) brings about slower relaxation (longer relaxation time). Hence, the analysis of the relaxation time is a very powerful tool for determining changes in molecular mobility (Hore 1995).

A decrease in water mobility during resting was clearly observed by the \(T_1\) relaxation time presented in Figure 7. This phenomenon might be related to a continued hydration of dough after mixing. In a system of restricted diffusion such as dough (Umbach and others 1992; Ohtsuka and others 1994), relatively mobile water molecules would migrate slowly into neighboring compartments, such as starch and proteins, promoting a higher level of molecular interactions between water and the macromolecules. As a result, overall water mobility decreased, as indicated from the gradual decrease of \(T_1\) during resting. Also, as mixing time increased, \(T_1\) decreased for both samples. Each data point was an average value of 3 independent measurements (different sets of resting experiments) and the standard deviation of the triplicates ranged from 0.03 to 0.76 ms for all the data points, showing quite small deviations. Even though \(T_1\) value differences were relatively small (a few ms) among under, optimally, and over mixed dough, those differences should be significant enough when the much smaller standard deviation values were considered. The decrease of \(T_1\) with mixing time was attributed to a decrease in water mobility due to increased molecular interactions during mixing. Interestingly, \(T_1\) difference created by different mixing time remained throughout the resting period. It seemed that mechanical mixing created additional interactions between water and other molecules, probably proteins, which was unachievable from the simple hydration by water migration. Even though mixing times of sample 402 is considerably longer than those of sample 401, sample 402 showed greater \(T_1\) relaxation time at the beginning of the resting period. This implies that there might be inherent compositional or chemical factors of flour, which affect initial molecular interactions with water. Also, the rate of \(T_1\) decrease during resting was quite different between 2 flour samples. \(T_1\) of the strong flour dough (sample 402) (Figure 7B) reached a minimum value within 100 min and then leveled off, whereas that of the weak flour dough (sample 401) (Figure 7A) decreased slowly during the entire resting period of 200 min. At the end of the resting period, 2 flour samples showed similar \(T_1\) values, especially for optimally and overmixed dough.

Conclusions

Fundamental rheological properties of hard wheat flour dough samples of different strength were investigated as functions of mixing and resting time. Both small and large deformation tests consistently showed that stress built up during mixing gradually relaxed during 3 h of resting period. However, during the first 30 to 45 min of resting, structure reformation was evident, probably due to the repolymerization of the gluten polymer. The small deformation test was able to demonstrate a lack of flexibility in undermixed dough, whereas the large deformation test more clearly showed the differences between optimal and under- or overmixing, and between strong and weak flour. From the above studies, it was shown that small deformation tests were advantageous for understanding molecular interactions and microstructure, whereas large deformation tests were useful to evaluate practical information related to the processing of dough, notably optimum mixing time and flour strength. There was no obvious relationship between the evolution of NMR relaxation time \((T_1)\) and the rheological property changes during resting. However, from the NMR relaxation data, molecular interactions between water and other molecules, which depended on mixing, resting, and flour type, could be understood more clearly.

Acknowledgments

Dr. Okkyung Kim Chung and Bradford W. Seabourn of the Hard Winter Wheat Quality Laboratory at Kansas State Univ. are gratefully acknowledged for providing flour samples and flour property data. This work was partly supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-005-J04703), partly by Technology Development Program for Agriculture and Forestry, Ministry of Agriculture and Forestry, Republic of Korea.

References


Dough influenced by mixing and resting...