RHEOLOGY

Rheological Properties of Dough Made with Starch and Gluten from Several Cereal Sources

K. E. PETROFSKY and R. C. HOSENEY

The range in moduli for isolated starch and vital gluten doughs showed the existence of starch-gluten or starch-gluten-water interactions in dough. Starches isolated from different wheat cultivars and mixed into dough with a constant gluten, both amount and source, gave large rheological differences. This shows that starch had an active role in determining dough rheological characteristics. Soft wheat and nonwheat starch doughs had higher moduli compared to the hard wheat starch and the control (commercial gluten and starch) doughs, possibly because of greater inter-

action of the starch with the gluten. The source of gluten also had a significant effect on dough rheology, as indicated by the range of elastic (\(G'\)) and loss (\(G''\)) moduli for isolated wheat gluten and commercial starch doughs. Hard wheat gluten doughs had low \(G'\) and \(G''\) values, indicating a greater extensibility and possibly less starch-gluten interaction. Soft wheat gluten doughs had higher \(G'\) and \(G''\) values, possibly because of increased starch-gluten interaction.

Bread dough exhibits the viscoelastic behavior combining the properties of both purely viscous fluids and purely elastic solids (Hibberd and Parker 1975, Billington and Tate 1981). For example, because of its viscous component, a freshly mixed dough will flow under the force of gravity. The same dough when rapidly stretched and then released will spring back (elastically recover). That elastic component helps to determine the dough’s resistance to deformation.

On a moisture-free basis, wheat flour contains ~80% starch, 14% proteins, 4-5% lipids, and 2% pentosans (Chung 1986). The gluten proteins constitute the predominant fraction controlling the viscoelastic properties of wheat flour doughs (Faubion and Hoseney 1990).

The most critical component in bread dough, the flour, is responsible for much of the viscoelastic character and is also the focus of much dynamic rheological research. A dough formula simplified to flour and water still encompasses a complex series of flour component interactions. Gluten and prime starch mixtures often are used in rheological testing, not only to control the protein content in the dough, but also to avoid complex interactions of other flour constituents. These include damaged starch, water-soluble and insoluble pentosans, cellulose, lipids, and insoluble proteins including enzymes.


The rheological response of any material is expressed physically by stresses, which, in turn, are mathematically expressed as functions of either strain and strain rate, or strain and time (Menjivar 1990). Dynamic oscillatory rheometers simultaneously measure the elastic as well as the viscous components of a material’s complex viscosity and can assess the frequency-dependent properties of materials being tested (Weipert 1990). Dynamic deformation patterns commonly utilize parallel-plate sample geometry and sinusoidal oscillation for measurement of simple shear stress (Faubion and Hoseney 1990). Dynamic measurements are particularly useful in measuring short-time or high-rate rheological behavior, as well as behavior at very low deformations and strains (Faubion et al 1985). The absolute validity of the calculated fundamental rheological parameters (\(G'\), \(G''\), \(G^*\), and \(\tan \delta\)) requires that the samples be linearly viscoelastic (Faubion and Hoseney 1990). Wheat flour dough appears to behave linearly at low strain levels (Faubion et al 1985). Nonlinearity may occur over the whole range of deformations even at the smallest strains, but an initial essentially linear portion is chosen to evaluate the apparent \(G'\) and \(G''\) values (Matsumoto 1979). Linear behavior under low strains implies that the small deformation is not injurious to the dough’s structure (Weipert 1990).

A number of factors affect dough rheology during the time after mixing. These include relaxation of the stresses induced during mixing, continuing hydration of flour components, and redistribution of water (Hibberd 1970a). Another possibility is that thiol-disulfide interchange occurs continuously during dough resting, and, as a result, the average molecular weight of the protein decreases and produces a lower \(G'\) (Dong 1992). That author showed that dough tested immediately after mixing had a higher \(G'\) and a smaller loss tangent than the same dough that was allowed to rest in a bowl for 15 min before testing. Dough does not relax appreciably after being placed between the parallel plates of the rheometer (Dreese 1987).

While most of the differences in doughs are usually attributed to the gluten proteins, the starch can cause differences (Medcalf 1968). Those differences are readily apparent in breadmaking (Hoseney et al 1971). The effect of gelatinized starches from different species on doughs rheological properties has also been shown (Lindahl and Eliasson 1986).

Recent work by He and Hoseney (1991a, 1992) showed that gluten-water doughs made with glutens isolated from flours of different baking quality had different rheological characteristics. Surprisingly, doughs made from those flours ranked differently than did the gluten doughs. Those authors attributed this difference to starch-gluten interactions. However, they presented no direct evidence that a starch-gluten interaction, and not some other flour constituent, was responsible for the differences. The same authors (He and Hoseney 1991b) suggested that the strength of the gluten-starch interaction may be responsible for differences in baking quality of flours.

The objectives of this study were to determine whether starch-gluten interactions exist in starch-gluten doughs, and, if so, using a constant starch, determine the influence of gluten on the dough rheological properties, and using a constant gluten, determine the influence of starch type on the dough rheological properties.
MATERIALS AND METHODS

Ingredients

MIDSOL vital wheat gluten and MIDSOL 50 wheat starch (Midwest Grain Products Inc., Atchison, KS) were used as commercial controls throughout the study. Flours from three hard red winter (HRW) wheats, Karl, Abiline, and Tam 107, were donated by the Kansas Agricultural Experiment Station, Kansas State University. Hard white (HW) winter wheat flour (KS-SB-369-7), a blend of soft red winter (SRW) wheats, and a blend of durum wheats were obtained from the Department of Grain Science and Industry, Kansas State University. Hard red spring (HRS) (Spillman 902589), club (Hyak 902560), and soft white (SW) (Daws 902551) wheats were obtained from the Western Wheat Quality Lab (Pullman, WA). HRS, club, SW, SRW, and durum wheats were milled on a Buffalo mill to produce flour. Other cereal grains used were white corn, oats, rye, and medium-grain rice. Food-grade potato starch was purchased from AVEBE (Foxhol, The Netherlands).

Fractionation

Wheat flour was fractionated. Flour (500 g) and distilled water (275 ml) were mixed into a dough for 10 min at low speed in a Hobart mixer. Distilled water (500-ml aliquots) was added, and the dough was massaged by hand to wash the starch from the gluten. The rinse water then was sieved through a 10XX cloth. This was repeated six times or until the rinse water was clear. The wet crude gluten was frozen (−18°C) and lyophilized (about 3% moisture). The rinse water was collected and centrifuged at 500 × g for 30 min to separate starch (sediment) and water soluble (supernatant). After centrifugation, the upper layer (starch tailings), which contained insoluble pentosans, bran, damaged starch, and small-granule starch, was separated physically with a spatula from the lower layer of the pellet (prime starch). The starch fractions were frozen and lyophilized.

Starch was isolated from the other cereal grains (corn, oats, rye, and rice). All grains (except corn) were steeped in distilled water for 30 hr at 4°C. Corn was steeped in a 0.1% sulfur dioxide solution to weaken the gluten matrix and aid in starch recovery (Watson 1984). Three parts distilled water and one part steeped grain were ground on low speed in a Waring blender for 10 min to disperse the starch, and the slurry then was sieved with a 180-mesh screen. Overs were suspended in distilled water, reground, and sieved again. This was repeated until no more starch was obtained. The rinse water was collected and centrifuged at 500 × g for 30 min. The prime starch was redispersed in distilled water and centrifuged at 2,800 × g for 30 min for further purification. Prime starch then was frozen and lyophilized.

A small-granule wheat starch was prepared by blending equal amounts of the wheat starch tailing fractions with water in a Waring blender. The starch was purified by repeated resuspensions and centrifugations.

After drying, starch and gluten samples were ground in a Wiley mill to pass through a 0.5-mm screen. Samples then were rehydrated to about 12% moisture by holding at 29°C and 100% rh for 3 hr and storing at 4°C.

Moisture and protein contents of duplicate starch and gluten fractions were measured by AACC methods 44-15A and 46-16, respectively (AACC 1983).

Starch-Gluten Blends

The average protein content of the wheat flours was 11.8% (14% moisture basis). This value was used for the formulation of starch-gluten blends. The wheat gluts from the nine samples were combined with commercial wheat starch to determine the effect of various gluts on dough rheology. Fifteen starches (10 including the small-granule starch, 4 other cereal starches, and potato starch) each were blended with commercial vital wheat gluten to determine the starches' influence on dough rheology. A sample composed of vital wheat gluten plus commercial wheat starch was used as a control (MIDSOL).

Mixograph Testing

Starch and gluten samples were blended thoroughly and given at least 24 hr for moisture equilibration before mixograph testing (AACC method 54-40A). Optimum moisture content and mix time for starch-gluten doughs were determined with the mixograph (National Manufacturing Co, Lincoln, NE) and are given in Table I.

Dynamic Rheological Testing

Doughs were mixed to optimum time and absorption in a 10-g pin mixer (National Manufacturing Co.) and rested in covered bowls for 30 min. Dynamic oscillation was performed on a Bohlin VOR rheometer (Bohlin Reologi, Lund, Sweden) using 30-mm diameter parallel plates. Dough was placed between the plates, and the gap adjusted to 2 mm. The dough's edges were trimmed and immediately coated with automotive lubricating grease to prevent drying (Dreesen 1987). The dough was rested between the plates for 5 min before testing, so that the residual stresses would relax (Faubion et al 1985). A constant gap was used for all doughs, so that sample size would not be critical to reproducibility (Abdelrahman and Spies 1986). Doughs were sheared at 0.2% strain through a frequency sweep from 0.1 to 20 Hz at a constant temperature of 25°C. A 300-g torsion bar was used for measurement of dough.

The software package provided by Bohlin allowed calculation of rheological parameters including shear storage modulus (G'), shear loss modulus (G''), shear complex modulus (G*), tan (δ), and complex viscosity (κ*).

RESULTS AND DISCUSSION

In undertaking a study such as this, certain assumptions must be made. These assumptions are forced by the fact that the dough must be mixed and some amount of water must be used to make the dough. Most cereal chemists are comfortable with the fact that different flours may require different amounts of water and mixing to produce an "optimum" or satisfactory dough. Thus, in this study we used the mixograph to determine the optimum water and mixing time for each sample. As can be seen, both absorption and mixing time varied widely (Table I). Samples prepared under those conditions were then used for the rheological measurements. One problem inherent in such an approach is that the rheological measurements are made at small strain and the mixograph is operating at very large strain. It is also a fact that any change in the dough will result in a change in the optimum water. Thus, an interaction between starch and gluten will affect both optimum water and the rheological properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vital Gluten + Starch</th>
<th>Gluten + Commercial Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimum Mixograph Absorption (%)</td>
<td>Optimum Mix Time (min)</td>
</tr>
<tr>
<td>MIDSOL</td>
<td>60.0 11'10&quot;</td>
<td>60.0 11'10&quot;</td>
</tr>
<tr>
<td>Karl</td>
<td>58.0 9'15&quot;</td>
<td>59.0 9'20&quot;</td>
</tr>
<tr>
<td>Abiline</td>
<td>57.0 9'30&quot;</td>
<td>62.0 13'40&quot;</td>
</tr>
<tr>
<td>Tam 107</td>
<td>59.0 9'00&quot;</td>
<td>59.0 13'00&quot;</td>
</tr>
<tr>
<td>SRW</td>
<td>55.0 10'40&quot;</td>
<td>52.0 4'00&quot;</td>
</tr>
<tr>
<td>HRS</td>
<td>56.5 8'30&quot;</td>
<td>58.0 3'00&quot;</td>
</tr>
<tr>
<td>Club</td>
<td>58.0 8'30&quot;</td>
<td>56.0 4'10&quot;</td>
</tr>
<tr>
<td>HW</td>
<td>58.0 9'50&quot;</td>
<td>64.0 20'30&quot;</td>
</tr>
<tr>
<td>SW</td>
<td>56.0 9'00&quot;</td>
<td>58.5 4'20&quot;</td>
</tr>
<tr>
<td>Durum</td>
<td>58.0 10'00&quot;</td>
<td>44.0 2'00&quot;</td>
</tr>
<tr>
<td>Corn</td>
<td>64.0 15'00&quot;</td>
<td></td>
</tr>
<tr>
<td>Oat</td>
<td>66.0 10'50&quot;</td>
<td></td>
</tr>
<tr>
<td>Rye</td>
<td>52.0 12'50&quot;</td>
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</tr>
<tr>
<td>Rice</td>
<td>70.0 16'00&quot;</td>
<td></td>
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<tr>
<td>Potato</td>
<td>66.0 16'45&quot;</td>
<td></td>
</tr>
<tr>
<td>Small Granule</td>
<td>62.0 7'40&quot;</td>
<td></td>
</tr>
</tbody>
</table>

* MIDSOL = vital gluten and commercial starch; SRW = soft red winter; HRS = hard red spring; HW = hard white; SW = soft white.
Starch plus Vital Gluten Doughs
Doughs made with starches isolated from flours of the HRW wheats (Karl, Abilene, and Tam 107) had lower moduli (both $G'$ and $G''$) than the MIDSOL dough (Fig. 1). The dough made with Karl starch had the lowest values. Although mixed at optimum moisture, the Karl starch dough acted as though it had excess water (slack), causing a decrease in $G'$ (Hibberd 1970a, Dreese et al. 1988). Interestingly, the ranking of the three starches (Karl lowest, Tam 107 highest) was the same for both $G'$ and $G''$.

Starches isolated from HRS and SRW flours gave doughs that had moduli similar to those of the MIDSOL dough, whereas club starch dough had higher moduli than the MIDSOL dough (Fig. 2). This indicates that starch from club wheat flour caused the dough to act as though it contained less water (stiff). Hibberd (1970a) and Dreese (1987) showed that an increase in $G'$ occurs with a decreasing water content. This also was noticed from the subjective evaluation of dough; it felt drier to the touch. Because the amount and source of wheat gluten remained constant and only the source of the starch was varied, only starch-water, starch-gluten, or a combination of these interactions could cause the changes in dough rheology.

The results for starches isolated from HW, SW, and durum wheats and mixed into doughs with vital wheat gluten are shown in Figure 3. HW starch dough was similar in rheology to doughs made with Karl and Abilene starches. The durum starch dough had the highest moduli of the wheat starches.

The standard deviations for these ten starch and vital wheat gluten doughs were extremely low. Differences between the starch and vital gluten doughs were significant, even within the HRW wheat class.

More dramatic effects were seen when starch-gluten doughs were prepared from small-granule wheat and nonwheat starches. Doughs made from corn, oats, and rye starches and vital wheat gluten all had higher moduli than the MIDSOL dough, except for the $G''$ for corn (Fig. 4). This trend continued with potato, rice, and small-granule wheat starch doughs (Fig. 5). Doughs made with potato starch had significantly higher moduli than the other doughs and also had higher standard deviations. Doughs made with rice starch, on the other hand, had a lower $G'$ than all other starch doughs. These tests have shown that, with a constant gluten, both amount and source, starch-gluten interactions caused large differences in rheology of the starch doughs.

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**Fig. 1.** Storage modulus ($G'$) and loss modulus ($G''$) versus frequency for commercial gluten plus starches isolated from Karl, Abilene, and Tam 107 hard winter wheat flours. The control (MIDSOL) is commercial gluten plus commercial starch.

**Fig. 2.** Storage modulus ($G'$) and loss modulus ($G''$) versus frequency for commercial gluten plus starches isolated from SRW, HRS, and club wheat flours. The control (MIDSOL) is commercial gluten plus commercial starch.

**Fig. 3.** Storage modulus ($G'$) and loss modulus ($G''$) versus frequency for commercial gluten plus starches isolated from SW, HW, and durum wheat flours. The control (MIDSOL) is commercial gluten plus commercial starch.
Commercial Starch plus Gluten Doughs

Rheological measurements of doughs made from glutens isolated from HRW wheat flours and commercial starch show that doughs from Karl and Abilene were similar in rheology to the MIDSOL dough (Fig. 6). Gluten from Tam 107 gave doughs that had higher $G'$ and $G''$. This indicates that Tam 107 gluten caused the dough to act as though it had less water (stiff). This was also apparent subjectively, because the Tam 107 gluten dough felt drier to the touch.

Gluten isolated from HRS flour gave doughs that had moduli...
Gluten isolated from high moisture soft wheat and club flours gave gluten-doughs that were not significantly different from the MIDSOL dough, although the standard deviations for the samples was much higher (Fig. 8). Gluten isolated from durum flour gave a dough with an extremely high modulus compared to the other wheat gluten doughs. The standard deviation for the durum gluten doughs was also high. The dough appeared dry to the touch, had little elasticity, and felt more like clay. It was similar to doughs from many nonwheat starches mixed with vital gluten.

Comparison of Starch-Gluten Doughs

Although many workers have shown changes in dough rheology based on changes in the relative concentrations of starch, gluten, or water (Hibberd 1970b, Smith et al 1970, Faubion et al 1985, Abdelrahman and Spies 1986, Dreese et al 1988, Navickis 1989), relatively little has been reported on changes in dough rheology because of the properties of starch or gluten.

The doughs made with commercial gluten plus starches isolated from flours of bread wheats Karl, Abilene, Tam 107 (Fig. 1), HRS (Fig. 2), and HW (Fig. 3) all had moduli significantly lower than those of the MIDSOL dough. The reverse was true for commercial gluten plus starch isolated from nonbread wheat flours, SRW, and durum (Fig. 3), club, and SW (Fig. 2), which all showed moduli above or equal to those of the MIDSOL dough. This indicates that nonbread wheat starches, as a group, give stronger starch-gluten interactions than the breadmaking wheat starches.

The rheological properties of doughs made with commercial starch plus gluten isolated from the nine wheat flours showed great variability. The hard wheats, excluding Tam 107 and durum, produced doughs with moduli lower than or equal to those of the control (MIDSOL). The soft wheat glucens, excluding SW, produced greater moduli than the MIDSOL dough. Durum again stood apart from the rest with extremely high moduli. The results with the gluten doughs are difficult to interpret, because they could reflect differences in the gluten itself or in interactions with the starch.

CONCLUSIONS

The range in moduli for the isolated starch and vital gluten doughs shows the existence of starch-gluten interactions in dough. From the data generated in this study, it is not possible to determine the nature of the interaction. It is also not possible to isolate the role of water. Starches isolated from different wheat cultivars and mixed into dough with a constant gluten gave large rheological differences. This indicates that starch had an active role in determining dough rheological characteristics. Soft wheat and nonwheat starch doughs had higher moduli when compared to the hard wheat starch and MIDSOL doughs, possibly because of greater starch-gluten interaction.

Although this initial study into starch-gluten interactions has shown their existence, further investigation into these interactions in dough should include chemical modifications such as removal of surface proteins and lipids from starch granules to determine their importance in dough rheology.

LITERATURE CITED


Sperling (1986) cataloged the causes of stress relaxation into five categories: 1) a decrease in molecular weight caused by chain scission as a result of oxidative degradation or hydrolysis; 2) bond exchanges ongoing constantly in polymers, with or without stress (in the presence of a stress, however, the statistical rearrangements tend to reform the chains, so the stresses are reduced); 3) viscous flow caused by linear chains slipping past one another; 4) thirion relaxation as a reversible relaxation of the physical cross-links or trapped entanglements in elastomeric networks; 5) stress (in the presence of a stress, however, the statistical rearrangements tend to reform the chains, so the stresses are reduced); 6) cross-links or trapped entanglements in elastomeric networks; 7) stress (in the presence of a stress, however, the statistical rearrangements tend to reform the chains, so the stresses are reduced); 8) bond exchanges ongoing constantly in polymers, with or without stress (in the presence of a stress, however, the statistical rearrangements tend to reform the chains, so the stresses are reduced); 9) viscous flow caused by linear chains slipping past one another; 10) thirion relaxation as a reversible relaxation of the physical cross-links or trapped entanglements in elastomeric networks; 11) molecular relaxation, especially near the glass transition temperature (Tg), that tends to relieve any stress of chains during the experiment.

The role of the sulfhydryl groups in dough chemistry has attracted the attention of many cereal chemists. The main premise has been that these sulfhydryl groups are potentially capable of undergoing a disulfide-sulfhydryl interchange that involves the cleavage or reformation of disulfide bonds mediated by sulfhydryl groups in flour or by relatively small amounts of added sulfhydryl compounds.

Reduced glutathione (GSH) and oxidized glutathione (GSSG) are both naturally occurring in wheat flour (Kuninori and Matsumoto 1964, Hird et al 1968, Tkachuk 1969). Graveland et al (1978) reported that flour contained 5–7 mmol of sulfhydryl groups and 11–18 mmol of disulfide per kilogram. Kuninori and Sullivan (1968) studied disulfide-sulfhydryl interchange in wheat flour by adding radioactive glutathione. They reported that significant interchange took place in a flour-water dough, but not in a flour suspension. They postulated that mixing promoted the reaction of disulfide groups and GSH. Another possibility is that a free radical (GS·) is formed during mixing and may be involved in the disulfide-sulfhydryl interchange. Reaction with (GS·) can cause session of protein disulfide forming a protein thiol radical.

When interchain disulfide bonds are cleaved, the resulting

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**Effects of Certain Breadmaking Oxidants and Reducing Agents on Dough Rheological Properties**

**WEI DONG**\(^1\) and R. C. HOSENNEY\(^2\)

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**ABSTRACT**

A dynamic rheometer was used to characterize the effect of glutathione, potassium bromate, and two ascorbic acid isomers on the rheological properties of wheat flour doughs. During resting after mixing (dough relaxation), G' decreased and the loss tangent increased. The major factor causing those changes was suggested to be a sulfhydryl-disulfide interchange. Free radicals appeared to be involved in the sulfhydryl-disulfide interchange. Addition of potassium bromate to dough resulted an increase in G' and a decrease in loss tangent. L-threoascorbic acid was rheologically more effective than D-erythroascorbic acid. This was explained by the presence of an active glutathione dehydrogenase in wheat flour that is specific for both glutathione and L-threoascorbic acid.

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