

Starch Participation in Durum Dough Linear Viscoelastic Properties

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ABSTRACT

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The contribution of starch to dough rheological properties has been largely overshadowed by the role of gluten, receiving much less attention in comparison. The influence of starch granule surface properties on durum wheat dough linear viscoelasticity was investigated, and surface interactions between starch granules and gluten were assessed using a model system. Proportions of starch were substituted in dough on a volume basis with an inert filler (glass powder) with a similar particle size range. The doughs were subjected to dynamic and creep

measurements. Dough linear viscoelastic properties were weakened on substitution of starch with glass powder at $\leq 50\%$ substitution, inferring a reduction in adhesion at the matrix-filler (starch and glass powder) interface with declining proportions of starch granules. Surface modification of starch granules or glass powder altered dough rheological properties, confirming the importance of starch granule surface characteristics and the nature of protein-starch bonding on durum dough linear viscoelastic behavior.

Wheat flour dough can be considered a composite material in which gluten forms the continuous matrix and starch granules act as filler particles within that matrix. Assuming insignificant contribution by minor components, the rheological properties of the composite will depend on the material properties of the protein matrix and starch filler, and degree of adhesion and interaction between the starch granules and protein matrix. Material properties that would contribute to rheological properties include the total volume occupied by starch granules, their size distribution, and any interaction between them.

Although starch constitutes the largest volume fraction of solids in dough, comprising $\approx 75\%$ (Colonna et al 1990), limited work has been published describing the contribution of starch to dough rheological properties. In particular, there is little information on starch-protein surface interactions, although the importance of starch granule surface properties to wheat flour dough rheological properties has been established (Larsson and Eliasson 1997).

Starch-protein surface interactions have been discussed in relation to wheat hardness and their effect on milling quality (Greenwell and Schofield 1986; Greenblatt et al 1995). The presence of the protein friabilin on the starch granule surface has been associated with softer endosperm texture (Darlington et al 2000). Hard wheats tend to break around endosperm cell walls and through starch granules during milling or grinding, whereas breakage occurs through cell contents and around starch granules in wheats with soft endosperm texture (Simmonds 1974). Barlow et al (1973) hypothesized that the strength of adhesion between starch granules and protein was responsible for differences in endosperm hardness after finding little difference in indentation hardness between starch and protein components of hard and soft wheats.

Rasper and deMan (1980) studied the effect of starch granule size on dough tensile properties using starch from different botanical sources and glass powder. They concluded that granule particle size did have an effect, but that water-binding capacity of different starches may exert a greater effect. Larsson and Eliasson (1997) studied the influence of starch granule surface properties on rheological behavior of wheat flour doughs by diluting a flour with treated and untreated starch to a fixed protein content. They found that heat-treatment and surface modification of the starch by protein or lecithin adsorption altered dough rheological properties, and concluded that starch granule surface properties are important for dough rheological behavior.

Our objective was to investigate the contribution of starch granule surface interactions with gluten protein on the linear viscoelastic properties of durum wheat dough. The role of starch in durum wheat dough linear viscoelastic properties was investigated by incrementally substituting starch with an inert filler (glass powder) with a particle size range similar to that of starch, and subjecting the dough samples to dynamic and creep measurements. In addition, to investigate the role of starch in gluten-starch interactions, the surfaces of the glass beads and starch granules were modified by adsorption of a protein solution and by heat treatment.

MATERIALS AND METHODS

Wheat

Three cultivars of durum wheat grown at Agriculture and Agri-Food Canada, Semiarid Prairie Agricultural Research Centre, Swift Current, Canada, were supplied by J. M. Clarke and were used as the source of starch throughout this study. The three included Durex, an American desert durum, AC Morse, a registered Canadian cultivar, and Stewart 63, an old Canadian cultivar that is no longer commercially produced. A sample of commercially grown Canadian durum wheat was used as the gluten source.

Milling

All wheats were cleaned and tempered overnight to 16.5% moisture content. Wheats were milled following the procedure of Dexter et al (1990) using a four-stand laboratory mill (Allis-Chalmers, Milwaukee, WI) in conjunction with a laboratory purifier (Black 1966) to produce semolina of $\approx 66\%$ extraction on a clean wheat basis. The milling area was controlled for temperature (21°C) and relative humidity (60%).

Glass Powder

Speriglass A3000 was provided by Potters Industries (Valley Forge, Pa). The powder is made up of solid glass spheres with a particle size range similar to that of purified starch. This was confirmed by comparison of scanning electron micrographs of glass beads and starch (Fig. 1).

Starch Preparation

The starch isolation procedure was based on the method of Morrison et al (1984) with some modifications. Purification of the starch using a cesium chloride gradient was based on the work of South and Morrison (1990) and Sulaiman and Morrison (1990). Semolina (10 g) was used in place of cracked kernels, eliminating the need for an acid presoak. A presoak in 0.5% sodium metabisulfite (Sigma Chemical, St. Louis, MO) for ≈ 4 hr at 4°C was included to soften the protein matrix before enzymatic digestion. The solution was centrifuged at $4,000 \times g$ for 15 min and the supernatant discarded. The pellet was resuspended in a solution contain-

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ing 5 mg of proteinase K (Roche Diagnostics, Mannheim, Germany) and was left to digest overnight in a 25°C shaking water bath. The solution was again centrifuged at 4,000 × g for 15 min, and the supernatant discarded. The pellet material was resuspended in a small amount of water and gently mashed through a 75-μm aperture sieve, washing with distilled water until the water ran clear.

The resulting starch suspension was divided among 50-mL centrifuge tubes and centrifuged for 10 min at 28,000 × g. The supernatant was discarded, and the pellets combined using the

minimal amount of water, followed by centrifugation at 28,000 × g for 10 min, and the supernatant discarded. The pellet was resuspended in ≈3 mL of water, which was carefully layered over 20 mL of 80% (w/v) cesium chloride (BDH, Toronto, ON) in 50-mL centrifuge tubes. Rinse water was added to the starch-water layer. The tubes were centrifuged for 30 min at 28,000 × g and the cesium chloride was carefully removed. The pellets were washed three times with distilled water, centrifuging for 5 min at 28,000 × g after each wash. The purified starch pellets were suspended in distilled water and collected on a 0.45-μm membrane filter (Millipore Corp., Bedford, MA) by suction filtration, rinsed with ethanol, and air-dried. Once dried, the starch was gently ground using a mortar and pestle. Moisture content of the isolated starches was 8.6–9.1%. Starch from each cultivar was a composite of multiple isolation and purification procedures.

Surface Modifications

Heat-treated starch was prepared as described by Seguchi (1984) using purified starch isolated as described above. Before heat treatment, distilled water was added to the starch, which was then equilibrated for one week, bringing the moisture content of the

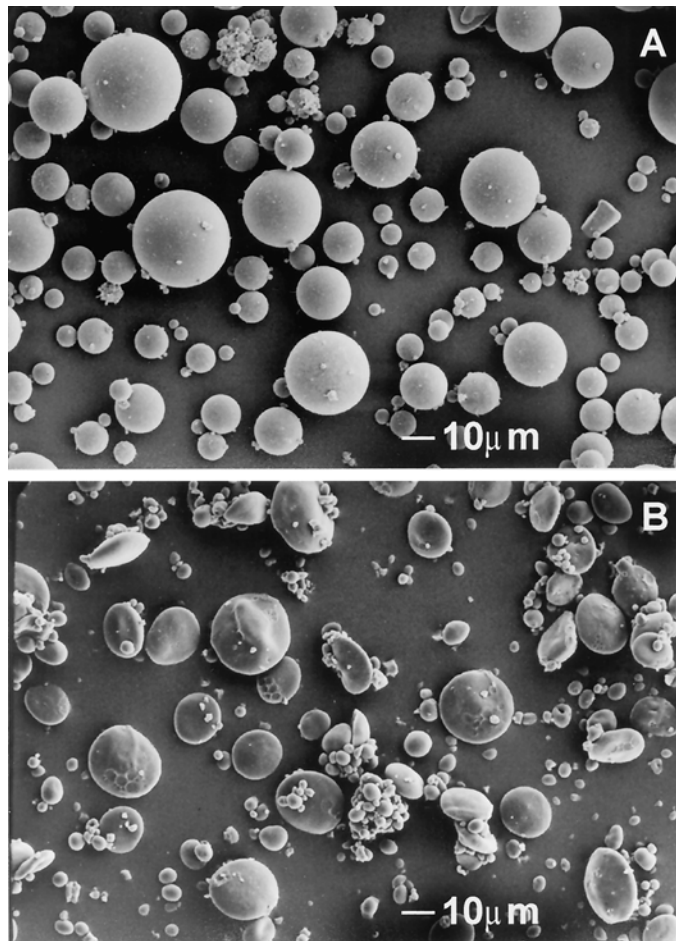


Fig. 1. Scanning electron micrographs of glass powder (A) and starch (B) at 500× magnification.

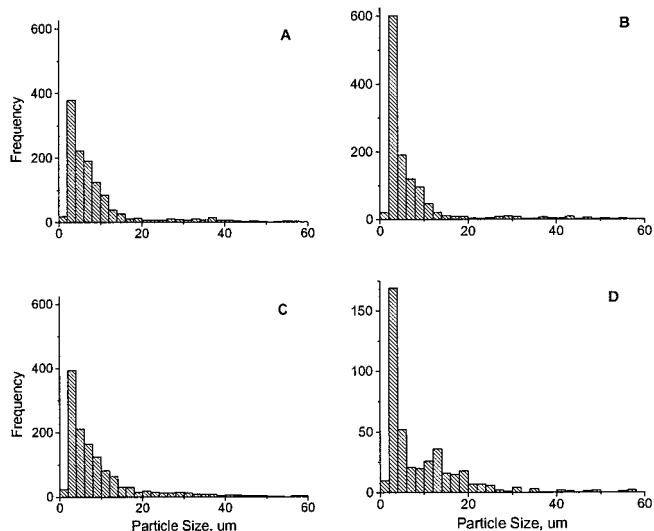


Fig. 2. Frequency distribution of Durex, AC Morse, and Stewart 63 starch granules, and glass beads (A–D, respectively).

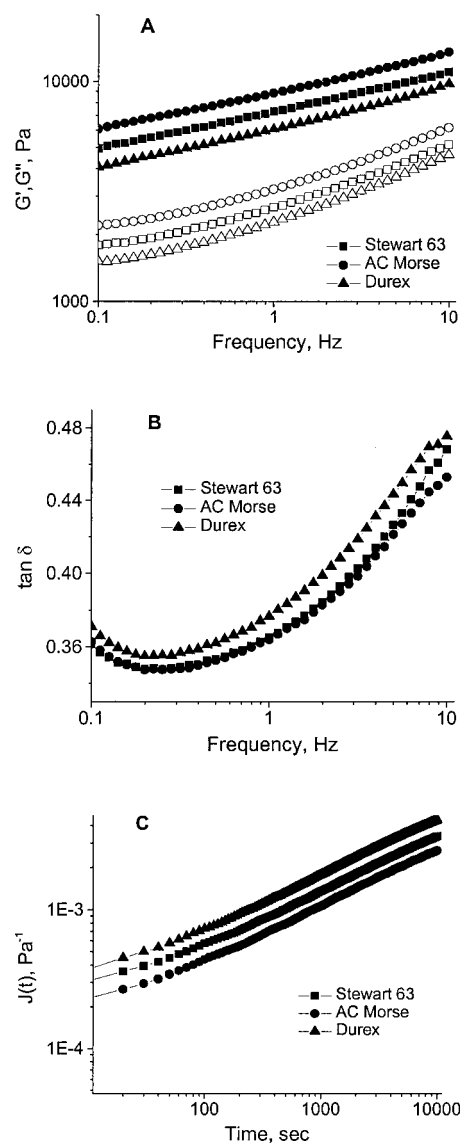


Fig. 3. Effect of starch granule size distribution on dynamic moduli, (A closed symbols = G' , open symbols = G''); $\tan \delta$ (B); and creep compliance (C) of gluten-starch dough.

starch to 24.9%. The equilibrated starch was then heated for 60 min at 120°C in an open container. Final moisture content of the heat-treated starch after equilibrating in an open container at room temperature was 7.5%.

Glass powder and heat-treated starch were coated with bovine serum albumin (BSA) (BDH, Toronto, ON) by mixing the granules in a saturated solution of BSA for ≈ 15 min. Excess liquid was removed by suction filtration using a Millipore apparatus (Millipore Corp., Bedford, MA) with a 0.45- μm membrane filter. The coated glass powder or starch granules were then air-dried, followed by gently grinding with a mortar and pestle to break apart aggregated material. The protein contents (%N $\times 5.7$) of the coated glass powder and starch granules were measured by combustion nitrogen analysis (LECO model FP-428 Dumas CAN Analyzer, St. Joseph, MD) and found to be 1.2 and 1.9%, respectively.

Particle Size Distribution

Starch or glass powder was suspended in a solution of 70% glycerol containing 0.1% KI/I₂. The suspension was placed on a microscope slide using a dropper and a cover glass fixed in place. A minimum of 20 fields of view were captured using a light microscope in tandem with a video camera connected to a computer. Maximum and minimum particle diameter measurements were captured, and the ratio of the two parameters used to identify and eliminate any particles that were not approximately circular, such as broken fragments. Maximum particle diameter was used to generate particle size frequency distribution curves (Fig. 2).

Gluten Isolation

Semolina was defatted with chloroform and air-dried at room temperature. Gluten was extracted by initially mixing the defatted semolina with 0.001M NaCl to form a gluten ball, then washing under a stream of distilled water to remove starch. The gluten ball was freeze-dried, then ground into a fine powder.

Analytical Tests

Moisture content was measured by single-stage air oven using Approved Method 44-15a (AACC 2000). Protein content was determined by combustion nitrogen analysis (model FP-428, LECO Corp., St. Joseph, MI) calibrated against ethylenediaminetetraacetic acid (EDTA). Starch damage was assessed using the Megazyme total starch assay procedure, Approved Method 76-13 (AACC 2000). A 2-g direct drive mixograph (National Mfg. Division, TMCO, Lincoln, NE) was used to obtain mixing data with Mixsmart software supplied with the instrument.

Freezable Water Determination

The amount of free or freezable water was determined using differential scanning calorimetry (DSC model 2920, TA Instruments, New Castle, DE) calibrated against an indium standard. Samples of dough prepared at a range of moisture levels (50–65% absorption) were transferred to sealed containers immediately after mixing. Subsamples (≈ 10 –15 mg) were removed and placed in hermetically sealed aluminum pans for analysis, and the weights recorded. Tap water was tested as a reference. The initial temperature of the DSC chamber was 20°C. The chamber was cooled at 10°C/min to a low of -60°C and held for 5 min so that the sample was fully frozen. The temperature was then ramped at 10°C/min to 50°C and the enthalpy (ΔH) of the endothermic transition recorded. Enthalpy was calculated as J/g based on total sample weight. All tests were done in triplicate and average values are reported. The amount of free or freezable water was determined by extrapolation of the curve generated from measurement of samples with a range of moisture contents to zero ΔH , where there is no freezable water.

Dough Preparation

Gluten-starch doughs (15:85, gluten to starch) were prepared at 60% absorption (46.3% moisture content) using a 2-g mixograph

and mixed to 1 min past peak. Glass powder was substituted for starch on a volume basis to account for considerable differences in density, replacing 0–100% of the starch in the blend. Density of starch was taken to be 1.536 g/cm³ (Rasper and deMan 1980). Density of glass powder was 2.5 g/cm³ according to the supplier specifications. Substitution of starch with glass powder necessitated adjustment of the amount of water added to the mixture. Glass powder does not absorb water per se, but does hold it in interstitial spaces, and complete elimination of water proportional to the amount of glass powder resulted in very dry dough and very erratic mixograph curves (data not shown). Absorption was therefore adjusted to 30% for the portion of the blend made up by glass powder to provide mixograph curves similar to those without any glass powder.

Rheology

Dynamic and creep measurements were made using a Rheometrics SR-500 (Rheometric Scientific, Piscataway, NJ) fitted with serrated 25-mm parallel plates. A preset gap of 2.75 mm was used for all samples. Temperature was maintained at 25°C. Dynamic measurements were conducted at 0.35% strain, over a frequency range of 0.1–10 Hz. Creep compliance measurements were conducted within the linear regime at 20 Pa over 10,000 sec. The creep linear regime was determined as described by Edwards et al (2001) by running a series of tests at different levels of applied stress and identifying the linear region based on agreement of compliance curves. Once loaded in the rheometer, each sample was carefully trimmed and the exposed edges coated with silicon grease. In addition, the rheometer was fitted with a humidity chamber to further prevent moisture loss during testing. All tests were conducted in duplicate and the average result reported. The overall coefficient of variation for dynamic testing was 4.0% and for creep compliance was 9.1%.

RESULTS AND DISCUSSION

Starch Granule Particle Size Distribution

The isolation procedure resulted in average recoveries of 62% starch from semolina, with a starch protein content of 0.28% \pm 0.05. There was good representation of both large and small starch granules as can be seen in the particle size distribution histograms (Fig. 2). The particle-size distribution of starch granules was in general agreement with the results of other studies. A-type granules (10–35 μm) constituted >70% of the total weight, while B-type granules (≤ 10 μm) accounted for <30% by weight but >90% of the total number of granules (Evers and Lindley 1977; Denegate and Meredith 1984; Morrison and Gadan 1987). It was also evident from the histograms (Fig. 2) and the SEM micrographs (Fig. 1) that the diameter of the glass beads fell within the same range as purified starch, and like starch, the smallest beads represented the largest proportion.

Particle Size Effect

AC Morse starch had a greater proportion of granules in the 0–10 μm range compared with the other two starch sources. It also demonstrated greater elastic character when used in gluten-starch dough, possessing higher G' and lower $\tan \delta$ (Fig. 3) than starch from the other two cultivars. Dough creep compliance also was lowest for the model system prepared from starch with a greater proportion of smaller granules (Fig. 3).

Ahmed and Jones (1990) cited several studies on filled synthetic polymers where an increase in modulus with decreasing particle size was evident, suggesting that increasing surface area provided more efficient interfacial bonding. Increasing the proportion of large starch granules has a sufficiently negative impact on gas cell wall stability of fermented doughs, disrupting the protein matrix, to result in coalescence of gas cells (Hayman et al 1998). Lelievre et al (1987) suggested that granule-specific surface area affected the area over which gluten could spread, thereby affecting crumb properties of bread made from gluten and starch. In other words, a larger proportion of small granules provides greater surface area,

allowing for greater interaction with gluten with less disruption of the matrix. Our data appear to support the positive effect of small starch granules on dough strength, but further studies using starch granules segregated by size would be useful in confirming this observation.

Glass Powder-Starch Interchange Experiments

The glass powder used in these experiments was assumed to be chemically inert and would, therefore, offer no means of surface interaction with protein or starch components of the dough. Starch granules, on the other hand, exhibit hydrophilic surface characteristics (Seguchi 1984). One of the limitations that must be recognized in making comparisons between gluten-starch doughs and gluten-glass powder arises from the difference in shape of the filler particles, glass beads being spherical and starch granules being lenticular. Composite mechanical properties are affected by size, shape, and aspect ratio of the reinforcing particles (Ahmed and Jones 1990).

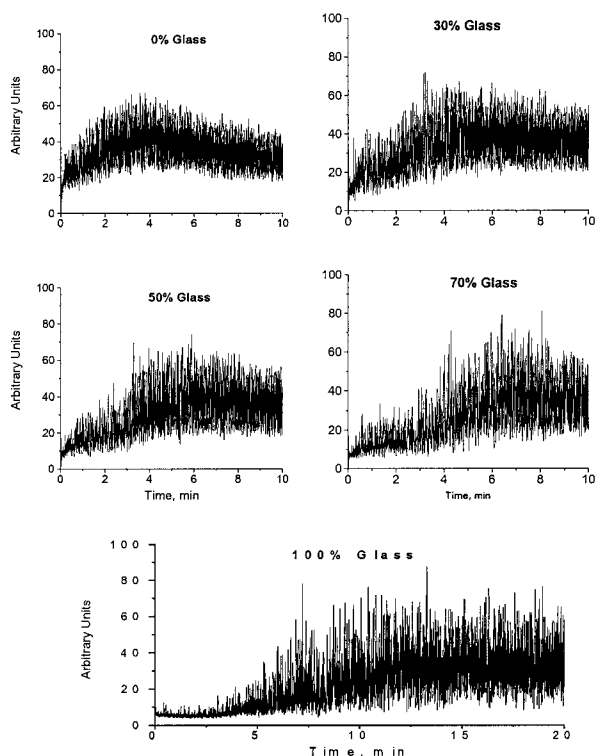


Fig. 4. Mixograph curves of gluten-starch dough; gluten-starch-glass powder dough, and gluten-glass powder dough. Percentage of glass powder substituted for starch: 0, 30, 50, 70, and 100% glass.

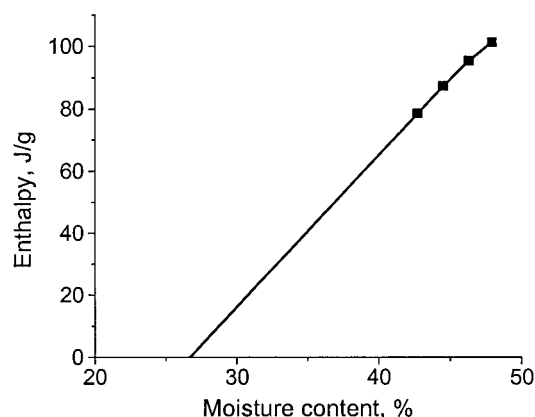


Fig. 5. Dough freezable water content determined by extrapolation of ΔH for a series of gluten-starch dough samples of known moisture content.

To confirm that cohesive dough could be produced when substituting starch with glass powder, a series of blends were prepared ranging from gluten and 100% starch to gluten and 100% glass powder in a 2-g mixograph; water absorption was adjusted to produce a 'reasonable' mixing curve. Eliminating water proportional to the amount of glass powder resulted in very dry dough with erratic mixing curves, while maintaining 60% absorption for the entire sample weight of glass powder blends, resulted in dough that was far too wet with very poor mixing quality (data not shown). Adjusting the water absorption to 30% for the glass powder proportion, while maintaining the gluten and starch proportion at 60% absorption, produced acceptable mixing curves. Rasper and deMan (1980) found similar water retention levels ($\approx 30\%$) for glass powder of similar particle-size range. Mixing time to peak increased with increasing proportions of glass, but in all cases, a cohesive dough sample was produced (Fig. 4).

In addition to assessing the mixing characteristics of the blends, freezable water was determined to establish that sufficient water was available to fully hydrate the gluten, particularly after substitution of starch with glass powder and adjustment of water absorption levels. The range of absorption levels used (50–65%) was somewhat limited because the mixograph was unable to mix very dry stiff dough at very low moisture content, and very high moisture content doughs were too sticky to handle and transfer to the DSC sample pans. The absorption levels used corresponded to 42.7–47.9% dough moisture content. By extrapolating the curve to a ΔH of 0 J/g, freezable water in gluten-starch dough was observed to be

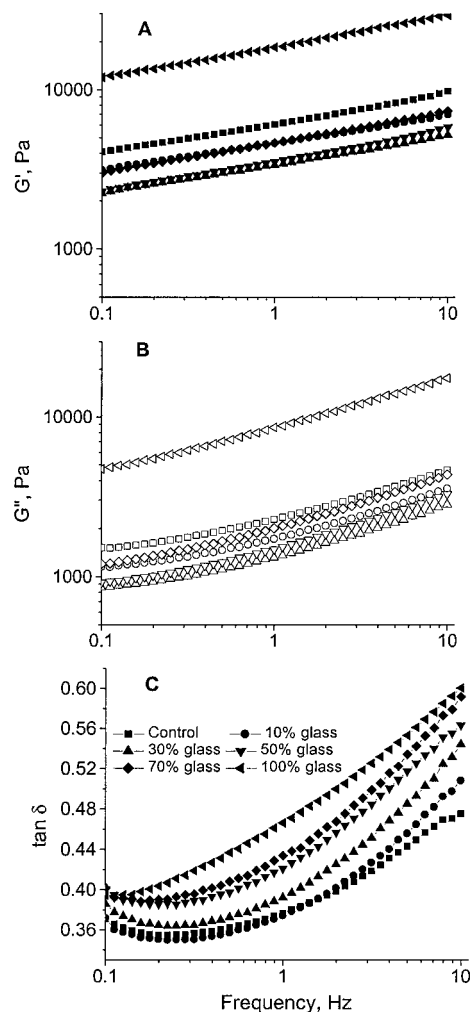


Fig. 6. A and B, Dynamic moduli (closed symbols = G' , open symbols = G''); and C, $\tan \delta$, measurements made on gluten-starch doughs where glass powder replaced 0–100% of Durex starch.

available at >27% moisture content (Fig. 5). This value was intermediate to the 18% moisture content observed for hydrated gluten (Cherian and Chinachoti 1996) and 33% moisture content for white bread crumb (Vodovotz et al 1996). Dough moisture content was lowest when starch had been completely replaced by glass powder. Even in that dough, ΔH was 54 J/g, well above 0 J/g, indicating that there was excess water in the system, so that more than

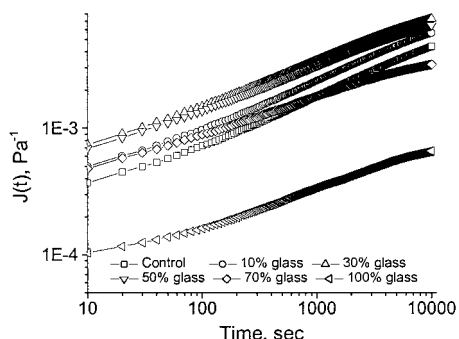


Fig. 7. Creep compliance measurements made on gluten-starch doughs where glass powder replaced 0–100% of Durex starch.

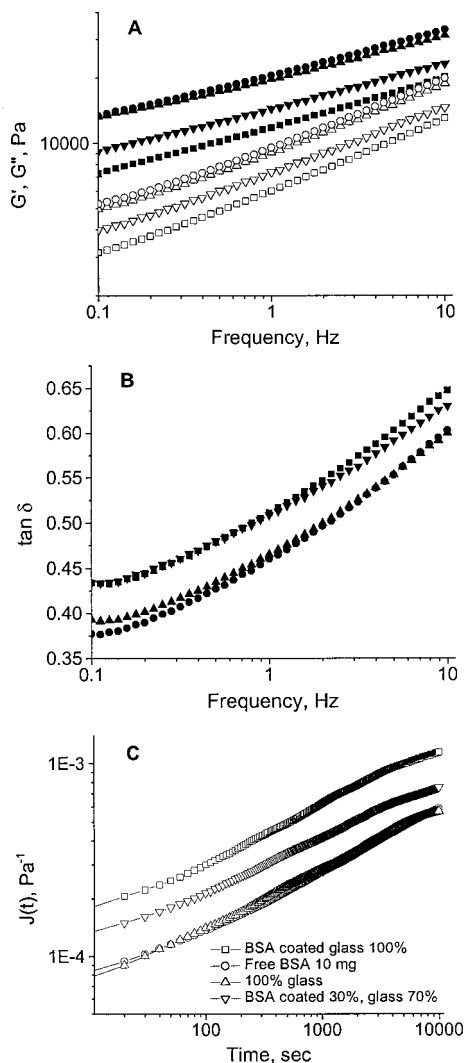


Fig. 8. Effect of bovine serum albumin (BSA) coating of glass powder compared with noncoated glass powder used in gluten-glass powder doughs and a 30:70% BSA coated-noncoated glass powder-gluten blend dough. **A**, dynamic moduli, (closed symbols = G' , open symbols = G''); **B**, $\tan \delta$; and **C**, creep compliance.

sufficient water was available to fully hydrate the gluten. Therefore, any differences observed in mechanical measurements of glass powder gluten blends (with corresponding reductions in water absorption levels) were not attributable to insufficient gluten hydration and resultant dough stiffness.

Both G' and G'' declined as starch was replaced up to 30% with glass powder, then remained essentially unchanged to 50% substitution (Fig. 6). Except at low frequencies, $\tan \delta$ increased with increasing proportion of glass powder. As starch was replaced with glass powder from 0% up to $\approx 50\%$, the dynamic moduli decreased, inferring a reduction in degree of adhesion between the filler (starch/glass powder) and the gluten matrix (Kubat et al 1990). Edie et al (1991) stated that in composite materials consisting of elastic fillers embedded in a viscoelastic matrix, deformation energy is mainly dissipated in the matrix and at the matrix-filler interface. They demonstrated that increasing the volume fraction of filler that adhered poorly to the matrix resulted in substantial increases in energy dissipation attributable to filler-matrix interface. In the current study, the incremental effect of bulk rheological properties of the filler became greater than the filler-matrix interface effects at 30 and 50% substitution with glass powder. At substitution levels in >50% glass powder, the bulk rheological properties of the filler became dominant. The moduli increased and increasing $\tan \delta$ resulted from increasing friction between the rigid glass beads, leading to dissipation of energy as heat. Moduli exceeded those of the gluten-starch control sample once all of the starch had been substituted with glass powder.

Creep compliance exhibited behavior similar to the dynamic measurements (Fig. 7). Compliance, $J(t)$, increased to a maximum at 30% substitution with glass powder. Increasing compliance of durum semolina dough has been related to decreasing overall dough strength (Edwards et al 2001). At 50% substitution, $J(t)$ was slightly lower than at 30%, but the trajectory of the curve at longer times began to flatten off (Fig. 7). By 70% substitution, $J(t)$ trajectory was much flatter and dropped below the gluten-starch control dough after $\approx 1,000$ sec. Once all the starch had been replaced with glass powder, $J(t)$ was much lower than the gluten-starch control dough, and exhibited the flatter trajectory seen at 70% substitution. Flattening off of the compliance curve at 50% substitution and higher indicated a transition to a more solid-like system. A similar phenomenon was also observed by Rayment et al (1998) with increasing volume fraction of rice starch filler in a guar galactomannan entanglement solution.

The simplest possible case for describing the modulus (E) of a two-phase composite material is given by (Ahmed and Jones 1990):

$$E_c = E_p V_p + E_m V_m \quad (1)$$

Where the subscript c represents the composite, p the particulate filler, and m the matrix. V represents the relative volume fraction. Glass beads are more rigid in comparison with starch granules, and therefore according to Equation 1, if glass beads interact with the gluten matrix in the same manner, the dough should become stiffer as glass powder makes up increasing proportions of the particulate filler. This behavior has been demonstrated in filled polymer systems, using polymers of varying molecular weight with spherical glass beads as the filler (Walberer and McHugh 2001). That, however, was not the case at the lower volume fractions of glass powder in dough blends. Depending on the nature of the matrix and the filler, van Vliet (1988) identified two extremes in composite behavior. In the first case, where there is a strong interaction between the filler and matrix, under conditions of small deformation there would be an increase in modulus of a gel with increasing volume fraction of filler, provided that the filler is stiffer than the gel. At the opposite extreme, where there is no interaction between matrix and filler, there would be a decrease in modulus with increasing volume fraction of filler under small deformation test conditions. These cases hold true only at relatively small volume fractions. In the current study, substitution of starch with glass powder up to $\approx 50\%$ resulted in behavior similar to the second case: a decrease in modulus. G' declined to a greater extent relative to G'' , resulting in increased $\tan \delta$.

Freezable water was measured in both the gluten-starch dough and in the dough where 50% of the starch had been substituted with glass powder to ensure that differences in moduli were not the result of greater free water in the dough containing glass powder. The enthalpy of the starch-gluten dough was 95.4 J/g, whereas the 50:50 glass powder and starch-gluten dough ΔH was 68.4 J/g, indicating that the starch-gluten dough possessed greater “free” water. Therefore, the decline in moduli with increasing proportions of glass powder was not attributable to increased molecular mobility due to the presence of more “free” water in the system. Two conclusions may be drawn from these data: 1) glass powder did not interact with the protein matrix, and 2) starch granules were interacting with the protein matrix, as evident from the continued increase in $\tan \delta$ at all levels of substitution of the glass beads. In excess of 50% substitution of starch by glass powder, the bulk rheological properties of the glass filler exerted greater influence than the filler-matrix interface on the moduli and the dough became stiffer due to the rigidity of the glass beads and the frictional contacts between them.

Filler Surface Modifications

To investigate the effects of surface bonding further, glass powder was coated with BSA to provide H bonding sites in the gluten-glass powder interface and comparison made of its mechanical properties with those of gluten-noncoated glass powder dough. Protein content of the BSA coated glass powder was 1.2%. Completely replacing the glass powder with BSA-coated glass powder reduced dynamic moduli (Fig. 8A), but increased $\tan \delta$ (Fig. 8B), and increased creep compliance (Fig. 8C) in comparison with noncoated glass powder. Tests performed on a gluten-glass powder dough using a 70:30 blend of noncoated glass powder and BSA-coated glass powder, respectively, resulted in dynamic moduli and $J(t)$ that were intermediate to those of noncoated and BSA-coated glass powder. In contrast, $\tan \delta$ of the blend was similar to the dough made with BSA-coated glass powder. BSA (10 mg) simply added to the gluten-glass powder dough had no effect on either dynamic measurements or on $J(t)$. The amount of free BSA added (10 mg) represents approximately the amount of protein that was found in the 70:30 blend of noncoated and coated glass powder. Providing H bonding sites by coating the glass powder with BSA altered the dough rheological properties so as to behave closer to what would be expected for gluten-starch dough. The BSA coating reduced the glass bead-to-glass bead contact, substantially reducing dough stiffness, with an accompanying decline in moduli, particularly G' (Fig. 8A). The greater energy dissipation at the coated interface was evident from the greater decrease of G' relative to G'' resulting in higher $\tan \delta$ than was found for dough comprised of noncoated glass powder (Fig. 8B).

Heat-treatment renders the normally hydrophilic starch granule surface hydrophobic (Seguchi 1984, 2001; Seguchi and Yamada 1988). Hoover and Vasanthan (1994) noted that heat-moisture treatment of wheat starch caused the crystalline arrays to become more closely packed and ordered, resulting in decreased susceptibility to α -amylase and acid hydrolysis, and decreased granule swelling leading to greater amylograph viscosity, overall indicating a reduced ability to absorb water. Others have found that heat-moisture treatments increased water absorbing capacity. In those studies starch with 18–27% moisture content was heated at 100°C for 16 hr or more (Kulp and Lorenz 1981; Donovan et al 1983; Lorenz and Kulp 1983).

In the current study, dough prepared from gluten and heat-treated starch had considerably greater elastic character than the gluten-starch control dough, with higher dynamic moduli (Fig. 9A), lower $\tan \delta$ (Fig. 9B) and lower $J(t)$ (Fig. 9C). Hydrophobic surface characteristics of the heat-treated starch increased its affinity for hydrophobic areas of the gluten protein. Larsson and Eliasson (1997) also suggested the possibility of hydrophobic interactions when they observed increases in moduli with addition of heat-treated starch to wheat

flour. It could be argued that heat treatment of starch could increase the rigidity of the granules, or alter their shape or size as a result of partial gelatinization if there was sufficient water in localized areas. To alleviate these concerns DSC testing was conducted on the heat-treated starch. No evidence of gelatinization was observed (data not shown), although the possibility of increased granule rigidity could not be ruled out as also contributing to increased stiffness of the dough containing heat-treated starch.

To confirm the importance of surface interactions at the starch granule-protein interface, heat-treated starch was coated with BSA in the same manner as the glass powder. Coating of the starch granules increased the protein content of the starch from 0.25% to 1.9%. Masking of hydrophobic sites by coating with BSA reduced starch granule surface interactions with the gluten protein. Dynamic moduli, $\tan \delta$ and $J(t)$ of the BSA coated, heat-treated starch-gluten dough were in all cases intermediate to gluten-starch control dough and gluten-heat-treated starch dough (Fig. 9). Altering the bonding sites in the interface region dramatically altered the linear viscoelastic properties of the gluten-starch model system, confirming the importance of the starch granule surface characteristics and the nature of protein-starch bonding on durum dough linear viscoelastic behavior.

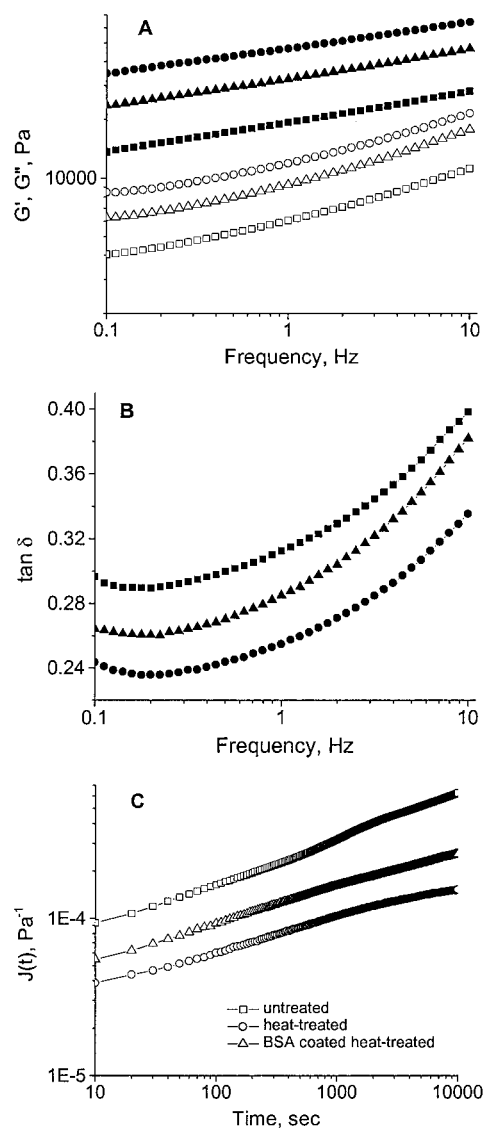


Fig. 9. Comparisons of gluten-starch doughs prepared from untreated (hydrophilic) and heat-treated (hydrophobic) AC Morse starch, and bovine serum albumin (BSA) coating heat-treated starch. **A**, dynamic moduli, (closed symbols = G' , open symbols = G''); **B**, $\tan \delta$; and **C**, creep compliance.

CONCLUSIONS

Starch measurably contributes to durum dough rheological properties. Increased proportions of smaller granules increased dough elastic character, similar to behavior observed in filler polymers (Ahmed and Jones 1990). Substitution of starch with glass powder confirmed the importance of interface interactions between matrix and filler in determining dough linear viscoelastic properties. Increasing substitution of starch with glass powder to $\approx 50\%$ resulted in increasing $J(t)$ and declining dynamic moduli. The reduction in G' was greater than for G'' , resulting in increasing $\tan \delta$, which was attributable to lowering of overall adhesion of the filler particles (starch granules and glass beads) to the gluten matrix. Once the proportion of glass powder exceeded 50%, rigidity of the beads and friction between them exerted a greater influence than the matrix-filler interface in determining the linear viscoelastic properties of the system. At 100% substitution of starch with glass powder, moduli exceeded the gluten-starch control dough. Altering the surface properties of the filler affected the filler-matrix interface, which in turn affected the moduli and compliance functions. Heat treated starch exhibited greater adhesion between filler and matrix with increased moduli and decreased compliance. Coating of the heat-treated starch with BSA reduced the degree of adhesion between the starch granules and gluten protein, while coating of the glass beads reduced frictional contact between beads. In both cases, altering filler surface properties resulted in reduced moduli and increased compliance of the filler-gluten dough in comparison with the noncoated filler particles, confirming the importance of the nature of protein-starch bonding on durum dough linear viscoelastic behavior.

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