Consequence of Starch Damage on Rheological Properties of Maize Starch Pastes[1]

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ABSTRACT

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Waxy and normal maize starches were damaged to different extents by ball milling, with waxy starch notably more susceptible to damage. Starch damage caused substantial decreases in shear stress or apparent viscosity in both waxy and normal maize starch pastes at a wide range of shear rates (5.6 to 400 1/sec). Shear stress or apparent viscosity decreases were more evident in waxy than in normal maize starch pastes at the same ball milling times. Values of storage moduli were much higher than values of loss moduli, and storage moduli decreased with increase in starch damage in both waxy and normal maize starches, indicating decrease in elastic property. The study showed that starch damage causes substantial rheological changes in gelatinized pastes and that waxy starch undergoes more pronounced changes than normal starch. These results can be used to understand the general behavior of damaged normal and waxy starches in processed foods.

Starch damage is an inevitable consequence of wheat dry milling (Evers and Stevens 1985) and is also found in commercial maize starches (Glennie et al 1987). In wheat dry milling, starch damage is an important quality index of wheat flour (Faridi 1990). Damaged starch swells in cold water, and increases the water absorption of flour (Sandstedt 1961, Tara et al 1972). Damaged starch is also more susceptible to enzymic hydrolysis during dough fermentation, which provides carbohydrate for yeast in the later stages of dough processing (Evers and Stevens 1985).

When starches were mechanically damaged using ball milling, some amylopectin was found broken down into low molecular weight fragments using size-exclusion chromatography (Yin and Stark 1988; Morrison and Tester 1994). The molecular size of fragments tended to decrease with increasing milling time (Morrison and Tester 1994). It was suggested that the low molecular weight fragments of amylopectin were formed by cleavage of glycosidic bonds of intermediate and long chains of amylopectin linking two (B_2 chain), three (B_3 chain), and four (B_4 chain) clusters (Morrison and Tester 1994). Amylose is much less affected by physical impact compared with amylopectin; even severe damage only caused slight amylose depolymerization (Meuser et al 1978; Morrison and Tester 1994). In damaged dry wheat and maize starches, shorter-range crystalline order measured by wide-angle X-ray diffraction and double helix content in amylopectin measured by ^{13}C cross-polarization/magic-angle spinning solid state nuclear magnetic resonance were lost (Morrison et al 1994).

Characteristics of damaged starch in starch-water suspensions have also been studied. When starch is hydrated in cold water, damaged starch granules swell spontaneously, lose birefringence, and give a translucent gel, while few changes can be observed in intact starch granules (Jones 1940; Sandstedt and Schroeder 1960). When a starch and water suspension is heated to different temperatures, damaged starch granules swell more than intact starch granules at low temperature (<60°C), and intact starch granules tend to have a high swelling factor (volume expansion in unlimited water) at higher temperature (60 and 80°C) (Tester and Morrison 1994; Tester 1997). Lipid-complexed amylose strongly inhibits the swelling of intact starch granules during heating in water (Tester and Morrison 1990; Morrison et al 1993), but it has little or no inhibitory effect on damaged starch (Tester and Morrison 1994).

Starch damage causes profound changes in starch granular structure and in amylopectin molecules. Such changes greatly influence the rheological and functional properties of starch. When wheat flour starch was damaged, water absorption and rheological properties of the dough changed, which significantly changed the end product properties (Evers and Stevens 1985; Bloksma and Bushuk 1988; Hoseney et al 1988; Faridi 1990). Extensive starch damage also decreased the viscosity of pastes (Meuser et al 1978). In food processing industries, starch is commonly gelatinized. In-depth characterization of the effect of starch damage on rheological properties of gelatinized starch pastes will aid in understanding changes caused by starch damage and will permit better prediction of final product quality.

The objectives of this study were to 1) investigate the effects of starch damage on the rheological properties of starch pastes during pasting and under different shear rates; 2) determine the viscoelastic properties of starch pastes in relation to starch damage, and 3) compare rheological differences between normal and waxy maize starch pastes after starch damage.

MATERIALS AND METHODS

Normal and waxy maize starches were provided by A. E. Staley Mfg. Co., Decatur, IL. Starches (0.15 g) were damaged using a ball mill (model MM2, Brinkmann, Germany) at 0, 15, 30, 45, and 60 sec at half speed (setting 50) to create different levels of starch damage. Starch damage was determined in triplicate according to Approved Method 76-31 (AACC 2000) using a damaged starch assay kit (Megazyme, Ireland).

Apparent amylose content was determined using a modified method of Juliano (1971). Starch (100 mg) was gelatinized in 2*N* NaOH (5 mL) for 1 hr (60°C) and diluted to 100 mL. Diluted solution (2.5 mL) was transferred to a 100-mL volumetric flask and further diluted with 50 mL of purified water. Phenolphthalein (two drops) was added to the solution, and pH was adjusted by 0.1*N* HCl until the color just disappeared. Iodine solution (2%, 2 mL) was added and the solution was diluted to 100 mL. The solution rested for 30 min and absorbance was measured by spectrophotometer at 600 nm. Amylose content was calculated according to a known standard curve of absorbance and amylose concentration.

For chromatographic analysis of normal maize starch (0.5 g) at different levels of starch damage, samples were extracted with 5 mL of water at room temperature for 30 min, centrifuged at 3,000 × *g* for 10 min, filtered through a 0.45-µm polypropylene filter (Life Science Products, Denver, CO), and separated by size-exclusion chromatography. An HR 16/50 Pharmacia column containing Sephacryl S 500HR gel (exclusion range M_r $4 \times 10^5 - 2 \times 10^7$) was used in combination with an HPLC system (Varian, Inc., Walnut Creek, CA). The other parameters were reported earlier (Han and Hamaker 2001).

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For pasting and flow tests, starch suspensions (7%, w/v, based on 10% moisture content) were prepared using purified water. Suspensions (1.2 mL) were transferred onto the center of the plate of a controlled stress/strain rheometer (ReoLogica Instruments AB, Sweden). Measurements were conducted using a cone and plate system with a cone of 4 cm diameter and 4° angle. Water evaporation was prevented using a sealed cell. Starch suspensions were heated at a rate of 5°C/min from 25 to 95°C under a shear rate of 5.6 1/sec. The pasting curves were recorded. Pastes were then cooled to 80°C. Steady shear measurements were conducted at 80°C using a range of shear rates of 5.6–542 1/sec, and the resulting flow curves were analyzed. Measurements were conducted in triplicate.

For dynamic measurements, starch suspensions (7%, w/v, based on 10% moisture content) prepared using 1.2 mL of purified water were transferred onto the center of the plate of a controlled stress/strain rheometer. A cone and plate system with a cone of 4 cm diameter and 4° angle was used. Starch suspensions were heated at a rate of 5°C/min under a shear rate of 5.6 1/sec from 25 to 95°C, and then cooled to 80°C. Dynamic measurements were performed over a frequency sweep of 0.08–1.5 Hz in the linear viscoelastic range. Measurements were conducted in triplicate.

RESULTS AND DISCUSSION

Starch Damage by Ball Milling

Ball milling of starch for increasing time periods caused a linear increase in starch damage in both normal and waxy maize starches (Table I). Waxy starch was far more susceptible to ball milling damage than normal maize starch, which is in agreement with the work of Tester (1997) and Bettge et al (2000). After ball milling, percent starch damage in waxy maize starch is about double that of normal maize starch (Table I). The different extent of damage between normal and waxy maize starches caused by the same impact logically originates from compositional or structural differences between these two starches. In studies by others (Meuser et al 1978; Morrison and Tester 1994), amylose in normal starch was much less affected by physical damage compared with amylopectin. The apparent amylose content of normal starch in this study was almost unchanged with increasing ball milling time (Table II), which confirms that amylose is not significantly affected by ball milling. Because amylose is much less susceptible to damage, existence of amylose reduces the proportion of starch molecules that could be damaged by ball milling of normal starch. Also, the presence of amylose in normal starch may strengthen the starch granule structure, resulting in less damage.

TABLE I
Starch Damage of Waxy and Normal Corn Starches After Ball Milling

	Starch Damage (%)	
Ball Milling Time (sec)	Waxy Corn Starch	Normal Corn Starch
0	2.1 ± 0.1[a]	1.4 ± 0.0
15	12.0 ± 0.1	6.6 ± 0.0
30	20.9 ± 0.1	10.9 ± 0.5
45	28.3 ± 0.3	15.2 ± 0.2
60	34.7 ± 0.3	19.2 ± 0.4

[a] Values are means ± standard errors. Data were significantly different between different ball milling times at α = 0.05.

TABLE II
Apparent Amylose Content of Normal Corn Starch After Ball Milling

Ball Milling Times (sec)	Amylose Content of Normal Starch (%)
0	23.9 ± 0.18[a]
15	24.1 ± 0.25
30	24.0 ± 0.37
45	24.0 ± 0.25
60	23.2 ± 0.13

[a] Values are means ± standard errors. All amylose contents are not significantly different at α = 0.05.

When barley starch was mechanically damaged, fragmented amylopectin molecules were solubilized in water (Yin and Stark 1988). In this study with maize starch, water-soluble extracts of starch with increasing damage showed increasing peak area in the amylose elution range (Fig. 1), which indicates that amylopectin molecules are depolymerized during ball milling.

Pasting Profiles

Increase in starch damage caused by ball milling considerably decreased the pasting apparent viscosity profiles of waxy (Fig. 2) and normal (Fig. 3) maize starches. For waxy maize starch, peak apparent viscosities decreased most dramatically after 15 sec of ball milling time (12% starch damage), with the most notable drop between 15 and 30 sec of ball milling (12 and 20.9% starch damage). It is possible that starch damage at or before 30 sec of ball milling caused significant cleavage of glycosidic bonds of intermediate and long chains of amylopectin linking two, three, and four clusters, which could have caused significant drop in shear stress or apparent viscosity. Such cleavage sites were indicated by Morrison and Tester (1994). It is conceivable that in longer ball milling times, proportionally higher amounts of shorter chains may be cleaved. The cleavage of long chains of amylopectin likely would have more effect on the paste viscosity than cleavage of short chains of amylopectin because the long chains of amylopectin contribute more to the gyration radius of amylopectin molecules in pastes. However, this speculation needs to be experimentally proved.

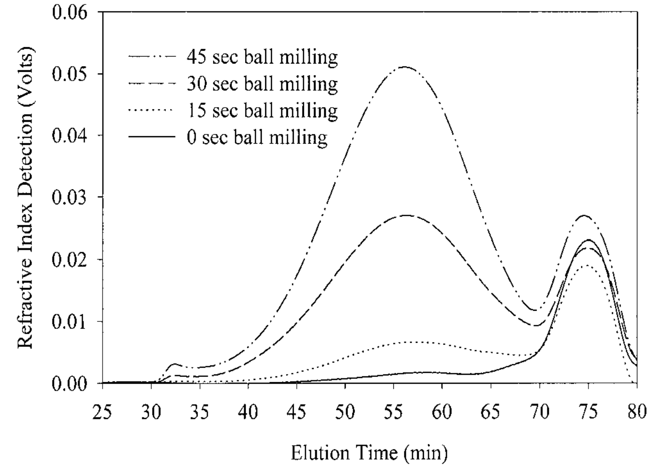

Fig. 1. Chromatographic profiles of water-soluble extracts from normal maize starch with increasing levels of damaged starch.

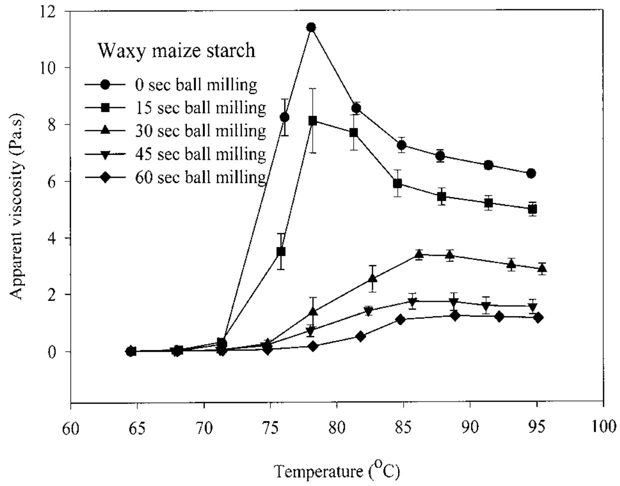

Fig. 2. Influence of ball milling on pasting of suspensions of waxy maize starch and water at shear rate of 5.6 1/sec. Error bars indicate standard errors.

In normal starch, decreases of peak and pasting apparent viscosities also correlated to increases in ball milling time. Furthermore, peak apparent viscosities appeared at lower temperatures with increasing ball milling time (Fig. 3). The gelatinization temperature of normal maize starch decreased after ball milling (Morrison et al 1994), which may be the reason of shift of pasting peaks to lower temperature after ball milling. The influence of ball milling on pasting was more pronounced in waxy maize starch than in normal maize starch as noted by the loss of apparent viscosity peaks in the former with higher ball milling times.

Large Deformation Measurements

The flow curves of gelatinized waxy (Fig. 4A) and normal (Fig. 5A) maize starches show that starch damage caused decreases in shear stress. Accordingly, there were decreases in apparent viscosity (Fig. 4B, 5B) (apparent viscosity equals shear stress divided by shear rate). In the waxy starch, of the 15 sec incremental increases in ball milling times, the 30 sec time (20.9% starch damage) caused the largest drop in shear stress or apparent viscosity, especially at high shear rates. As proposed above, a possible explanation is that significant cleavage of glycosidic bonds of long chains of amylopectin occurred in starches that were ball milled at or before 30 sec. This could lead to the observed significant reduction of paste apparent viscosity at 15 and 30 sec ball milling times (12 and 20.9% starch damage) and less decrease of paste apparent viscosity after 30 sec of ball milling. In waxy maize starch, reduction of shear stress in pastes of damaged starch compared with the control (0 sec) was shear-dependent; greater reductions in shear stress were observed under higher shear rate conditions. This was not seen in normal starch pastes. The cause of this phenomenon is unknown. The susceptibility of gelatinized waxy starch granules to high shear (Han et al 2002a) and the lack of amylose in waxy maize starch might be the causes of the difference.

Overall, shear stresses or apparent viscosities were much lower in normal starches than comparable waxy starches (Figs. 4 and 5). Accordingly, there was a lower apparent viscosity decrease with increasing ball milling time in normal compared with waxy starches. In normal starch, flow curves at different ball milling times showed an incremental decrease in shear stress or apparent viscosity unlike that of corresponding waxy starches (Fig. 5A). When similar starch damage levels are compared (20.9% starch damage in waxy starch after 30 sec of ball milling and 19.2% starch damage in normal starch after 60 sec of ball milling), relative to the control starches (0 sec of ball milling), waxy starch exhibited higher decrease in shear stress or apparent viscosity (≈52% reduction at 200 1/sec shear rate) compared with normal starch (≈29% reduction). For waxy starch, the high initial apparent viscosity, susceptibility of gelatinized starch granules to shear, and lack of amylose may have caused the dramatic drop of shear stress or apparent viscosity.

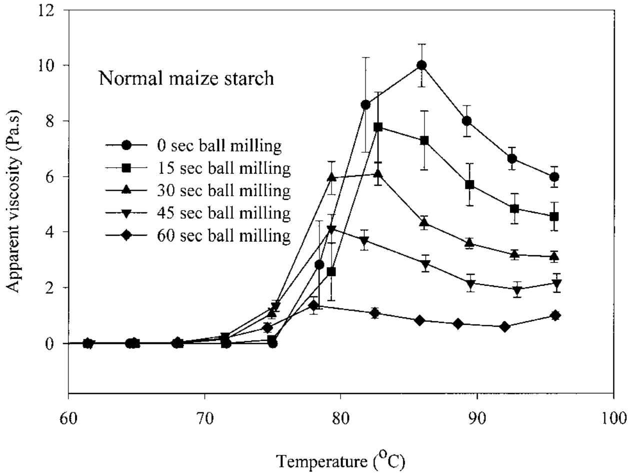

Fig. 3. Influence of ball milling on pasting of suspensions of normal maize starch and water at shear rate of 5.6 1/sec. Error bars indicate standard errors.

Ball milling of normal maize starch at <20% starch damage level has a limited effect on the amylose molecules (Meuser et al 1978; Morrison and Tester 1994), and our data confirm this conclusion (Table II). The contribution of nearly intact amylose to overall shear stress or apparent viscosity of pastes increases with the decreasing role of amylopectin caused by depolymerization. Because amylose is nearly intact after ball milling, it may stabilize the paste shear stress or apparent viscosity after starch damage.

Oscillatory Measurements

In oscillatory measurements, storage moduli were substantially higher for normal than waxy starches, and damage to starch decreased the storage moduli in both starch pastes (Fig. 6A and 7A). It was notable that, again in waxy maize starch, the most significant percentage of decrease in storage moduli was found between 15 and 30 sec ball milling times (12 and 20.9% starch damage). This phenomenon was similar to the profiles found from pasting curves and large deformation measurements (flow curves).

The high storage moduli of gelatinized normal maize starch pastes were likely caused by the presence of amylose and a more rigid gelatinized starch granule structure (Miller et al 1973; Evans and Haisman 1979; Lii et al 1996; Han et al 2002b). The percentage reduction in storage moduli between 15 and 30 sec in normal maize starch (6.6 and 10.9% starch damage) was not as dramatic as in waxy maize starch. In normal starch, amylose is a major contributor to storage modulus (Hsu et al 2000). Waxy starch without amylose cannot form a gel (Whistler and BeMiller 1997). Because amylose is not damaged by ball milling and it is a major contributor to storage modulus, it could have stabilized the elastic property of starch pastes after starch damage.

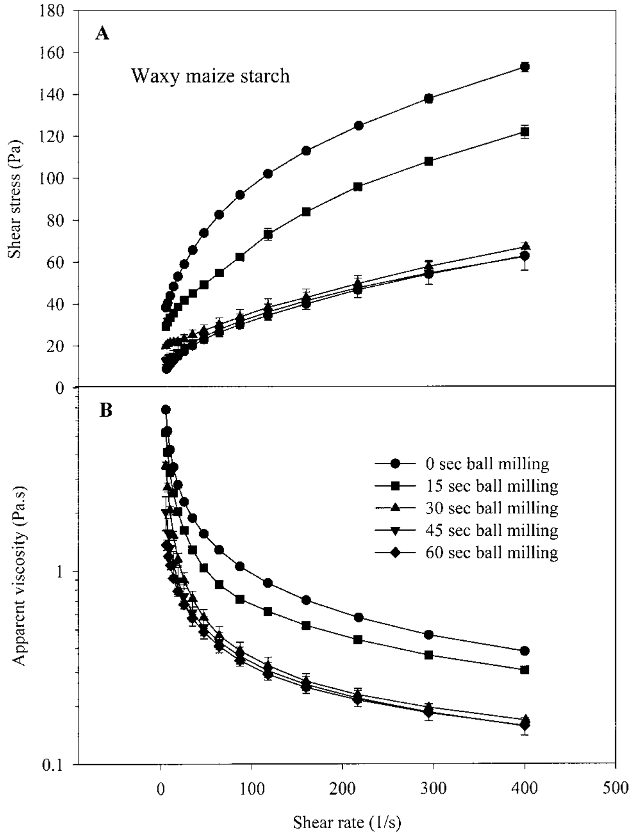

Fig. 4. Influence of ball milling on shear stresses (**A**) and apparent viscosities (**B**) of gelatinized pastes of waxy maize starch over different shear rates. Error bars indicate standard errors.

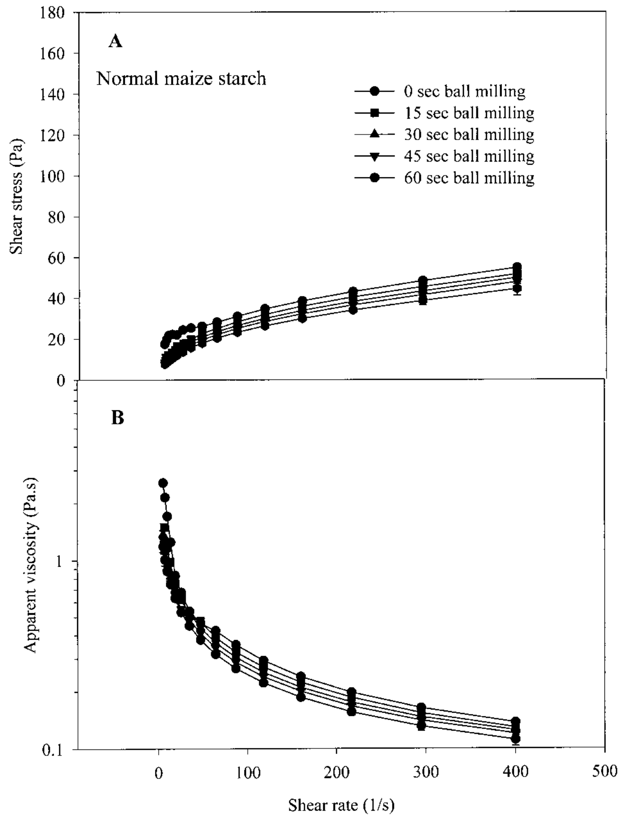

Fig. 5. Influence of ball milling on shear stresses (**A**) and apparent viscosities (**B**) of gelatinized pastes of normal maize starch over different shear rates. Error bars indicate standard errors.

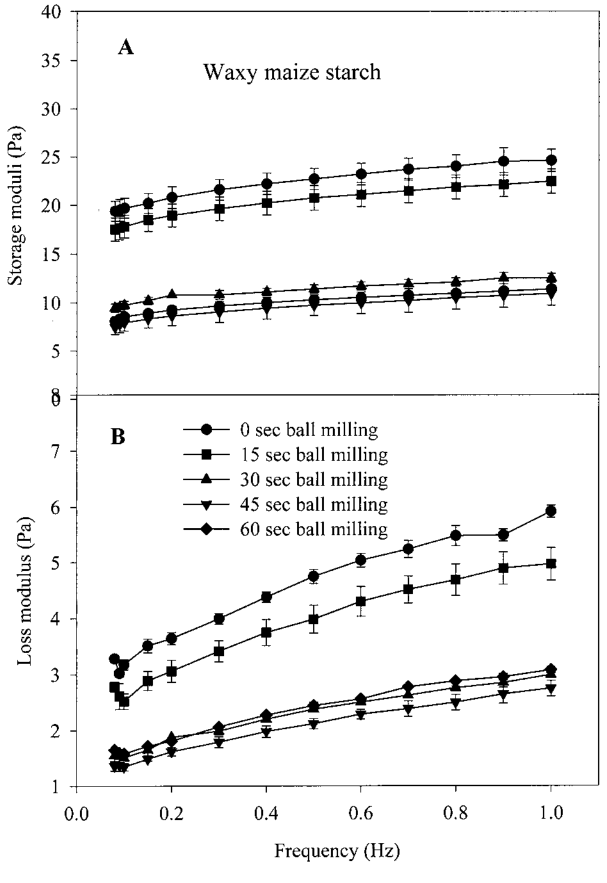

Fig. 6. Influence of ball milling on storage moduli (**A**) and loss moduli (**B**) of gelatinized pastes of waxy maize starch over different frequencies. Error bars indicate standard errors.

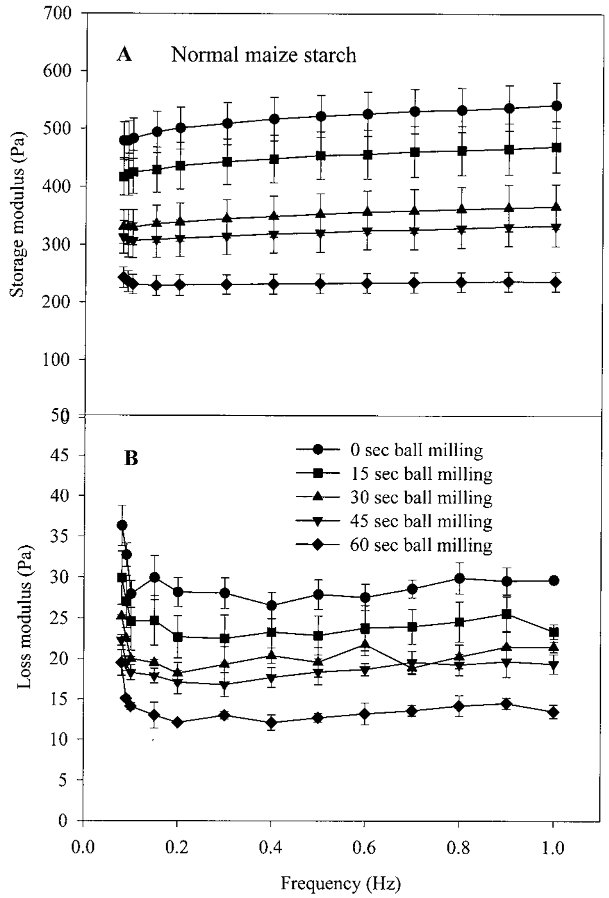

Fig. 7. Influence of ball milling on storage moduli (**A**) and loss moduli (**B**) of gelatinized pastes of normal maize starch over different frequencies. Error bars indicate standard errors.

Increases in starch damage also caused concomitant decreases in loss moduli in both waxy (Fig. 6B) and normal maize (Fig. 7B) starches. Loss modulus is an indication of the viscous nature of the pastes. Values of loss moduli were much less than values of storage moduli.

The properties of the pastes were largely determined by the storage modulus. Starch damage caused dramatic decrease in storage moduli, which indicated that the elastic property of the pastes decreased. Decrease of the elastic property of gelatinized pastes was also shown in tendency of increases in phase angles with increases in starch damage (not shown). Loss of intact gelatinized starch granule structure and fragmentation of starch molecules were likely the primary reasons for decreased elastic behavior of starch pastes by starch damage.

CONCLUSIONS

This study showed that starch damage caused decrease in apparent viscosity and elastic property of starch pastes. Waxy starch was more extensively damaged by ball milling than was normal starch. At same starch damage levels, rheological properties of waxy starch were more affected than in normal starch. The results should aid in understanding and predicting variations in processing starch-containing foods that are caused by starch damage.

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