

# Viscoelasticity of Zein-Starch Doughs

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## ABSTRACT

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Corn flour, when hydrated, does not form a viscoelastic dough as does wheat flour. Yet when mixtures of zein and corn starch were blended into a composite flour and mixed in a farinograph at 25, 30, and 35°C, viscoelastic doughs resembling those of wheat flour were produced. The properties of such doughs appear to result from zein fibers, produced during mixing, that are similar in appearance to wheat glutenin fibers.

Unlike wheat flour, corn flour, when hydrated, does not form a viscoelastic dough. This difference may result in part from the marked hydrophobicity of corn proteins. Corn flour does not take up water or swell to the same extent as does wheat flour (Hoseney and Rogers 1990). Also, chemical reactivities of corn proteins must differ from wheat proteins because of their different structures. However, polymer chemistry theory suggests that all amorphous macromolecules are, above their glass transition temperature ( $T_g$ ), viscoelastic or rubbery-elastic, depending on their structure (Vollmert 1973, Ferry 1980). The  $T_g$  of a macromolecule can be lowered by adding a plasticizer (Ferry 1980).

Hoseney et al (1986) demonstrated the amorphous polymeric behavior of wheat gluten by showing that it had a glass transition and that its  $T_g$  varied with water (plasticizer) content. These investigators also showed that gluten containing 16% or more water is rubbery at room temperature. Hoseney and Rogers (1990) explained the ability of wheat flour to form a viscoelastic dough in terms of the polymeric behavior of gluten. Gluten proteins are glassy when dry and at room temperature. As water is taken up during mixing, gluten goes through a glass transition that renders it mobile and able to interact with other gluten polymers to form a dough (Faubion and Hoseney 1989).

Hoseney and coworkers suggest that gluten's polymeric nature explains its viscoelasticity upon hydration. If true, other cereal proteins also may be viscoelastic if heated above their  $T_g$ . Some aspects of zein's polymeric behavior, such as its ability to form plastics, have been known for more than 80 years (Desvaux and Alleire 1909, Goldsmith 1909). Zein has been made into fibers, films, and plastics (Croston 1950, Croston and Evans 1950, Reiners et al 1973). MacRitchie (1980) and Bushuk and MacRitchie (1989) state that zein and starch can, at 60°C, be mixed into a dough with properties closely approaching those of a wheat flour dough. They state that under these conditions, zein can be drawn into long fibers and sheets.

In this study, the relationship of dough properties with protein glass transition has been applied to the zeinstarch dough system. In addition, a second plasticizer has been used with water to allow creation of viscoelastic zein-starch doughs at temperatures lower than 60°C. Dibutyl tartrate was chosen as the second plasticizer because it has been used as an industrial plasticizer for zein in the manufacture of films (Reiners et al 1973).

## MATERIALS AND METHODS

### Materials

Commercial zein was from Freeman Industries (Tuckahoe, NY). Reagent-grade L-tartaric acid dibutyl ester was from Sigma (St.

Louis, MO). Corn starch was donated by A. E. Staley Manufacturing Co. (Decatur, IL).

### Flour and Dough Preparation

Dibutyl tartrate was added to zein as a second plasticizer and mixed with a spatula. Composite flours containing starch, zein, and dibutyl tartrate then were prepared by hand-mixing starch and zein in a glass jar with a spatula. All composite flours contained 90% starch and 10% zein, and the zein contained 10% (v/w) dibutyl tartrate. The zein-starch flour (300 g) was mixed with 225 ml of water in a Brabender Farinograph (C. W. Brabender Co., Hackensack, NJ) at four bowl temperatures (21, 25, 30, and 35°C). Formaldehyde-treated dough was mixed at 35°C as described above, except 10 ml of water was replaced with 10 ml of 37% aqueous formaldehyde. The formaldehyde-treated dough was mixed for 30 min. Composite zein-starch flours con-

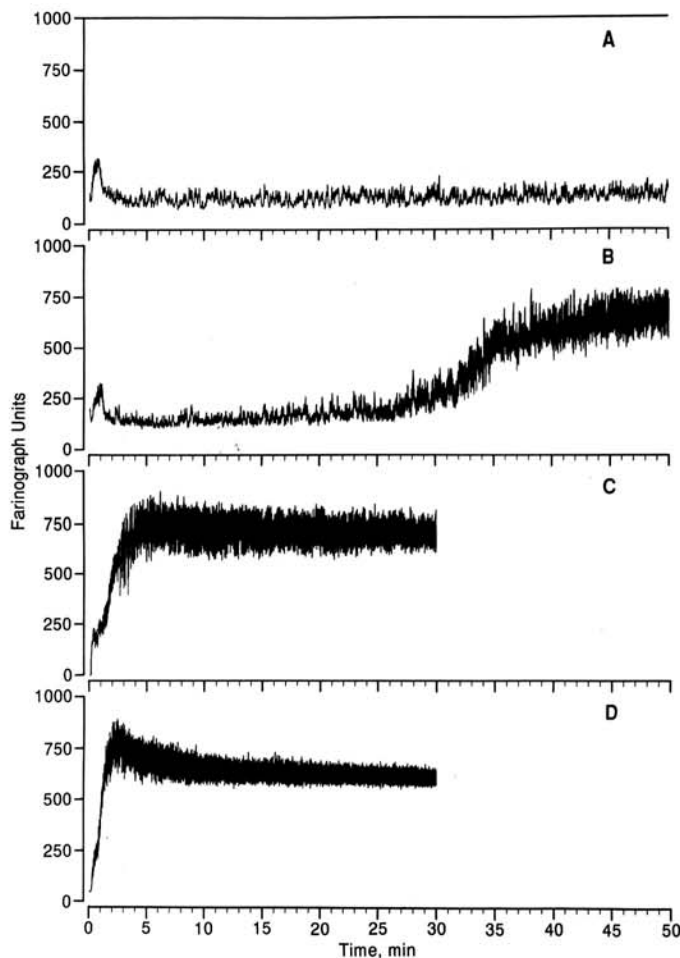


Fig. 1. Farinograms of zein-starch doughs with dibutyl tartrate obtained at bowl temperatures of 21, 25, 30, and 35°C (A-D, respectively).

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taining no dibutyl tartrate were mixed with 225 ml of water in a farinograph at a bowl temperature of 35°C.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on commercial zein samples of various moisture contents to determine their  $T_g$  using a Perkin-Elmer (Norwalk, CT) DSC-7 instrument. The moisture content of the samples was adjusted in aluminum DSC pans by drying or tempering in a desiccator over  $P_2O_5$  or water, respectively. Samples were periodically removed from the desiccator, sealed, and weighed, and moisture contents were determined from changes in weight.

Zein-dibutyl tartrate mixtures were prepared by adding the desired amount of dibutyl tartrate to zein and mixing with a spatula. The mixture was placed in a sealed container for 48 hr to equilibrate and then weighed into aluminum DSC pans and sealed.

All samples were scanned from a minimum of 0°C to a maximum of 160°C. Because  $T_g$  can be affected by the thermal history of the polymer (Richardson 1978), two scans were performed on each sample. In the first scan, zein samples were heated and cooled at 20°C/min to establish their thermal history. Samples then were rescanned at 20°C/min (for samples with a high [above 40°C]  $T_g$ ) or at 10°C/min (for samples with a low  $T_g$ ). The  $T_g$  was then determined by analysis of the second scan using Perkin-Elmer TAS-7 thermal analysis software.

A different heating rate was used for the higher moisture samples (lower  $T_g$ ), because it took about a minute for the differential scanning calorimeter to establish a baseline after the heating started. When heating at 20°C/min, this put the temperature of the DSC instrument at 20°C. This meant that between the establishment of the baseline and the  $T_g$  of the high-moisture samples, the baseline was too short to show a shift. A heating rate of 10°C/min was used for the high-moisture samples to give a good baseline before the  $T_g$  occurred. Because of the kinetics

of heating in the differential scanning calorimeter, lower heating rates will give lower  $T_g$  values. The  $T_g$  values obtained in using the lower heating rate shift about 1–2°C.

### Extension

After doughs were mixed in the farinograph, they were scaled into three 150-g pieces. Each piece was rolled into balls by hand and then rolled into 3-cm-diameter cylinders using a three-roll wooden molder (National Manufacturing, Lincoln, NE). Dough pieces were not rounded and molded using the extensigraph molder because zein-starch doughs stuck to the molder. Molded pieces were clamped into the extensigraph dough holders and tested on a Brabender Extensigraph. Samples were analyzed 1) immediately after mixing, 2) after resting 15 min at mixing temperature, and 3) after resting 15 min at ambient temperature.

### Scanning Electron Microscopy

Scanning electron microscopy was performed on zein-starch doughs to examine their microstructure. Dough was frozen in liquid nitrogen immediately after mixing and lyophilized. Dry samples then were mounted on aluminum studs and vacuum-coated with gold-palladium. Samples were examined with an International Scientific Instruments (model ISI-SS130, Milpitas, CA) scanning electron microscope.

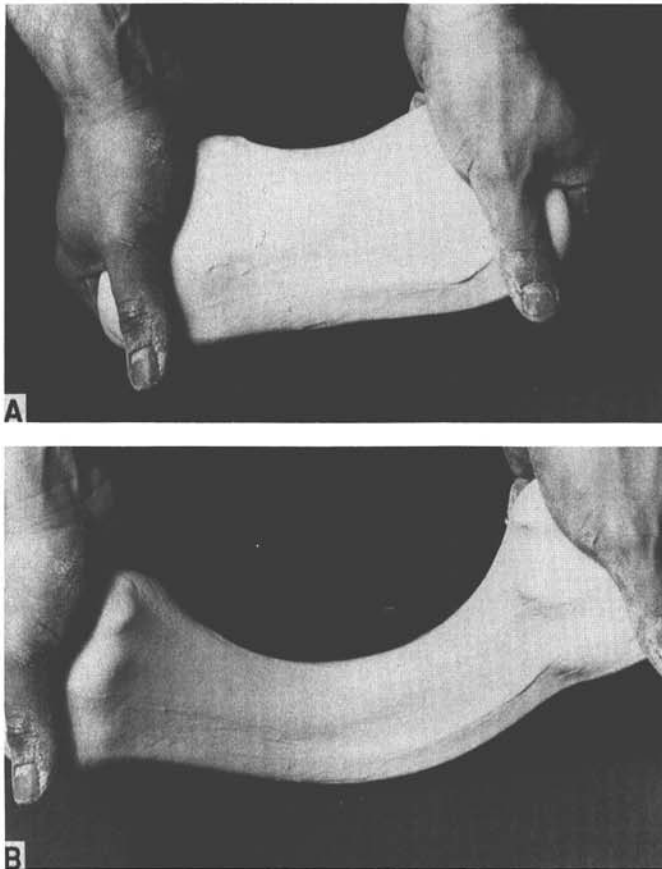


Fig. 2. Photographs of zein-starch dough containing dibutyl tartrate. A, Relaxed; B, extended.

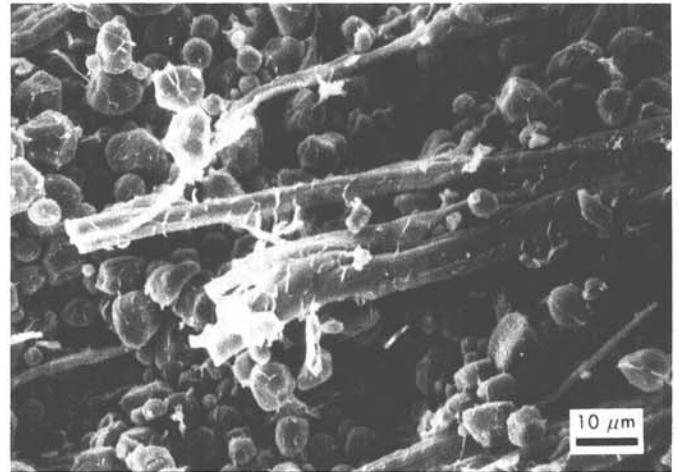


Fig. 3. Scanning electron micrograph of zein-starch dough containing dibutyl tartrate.

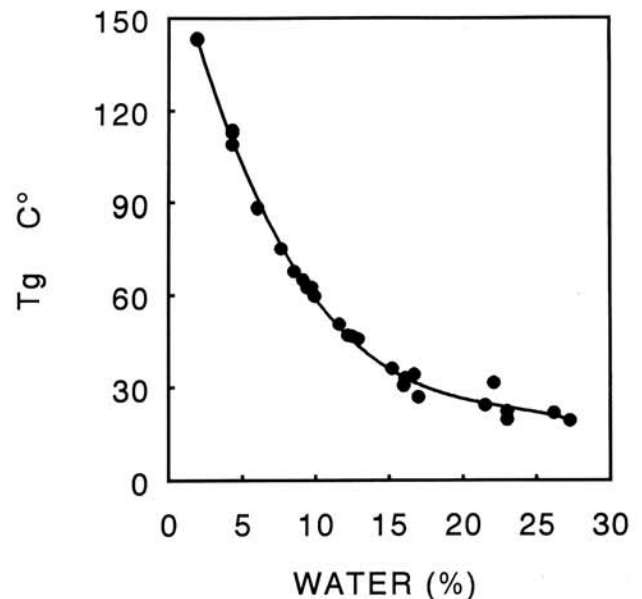


Fig. 4. Glass transition temperature ( $T_g$ ) of zein as a function of moisture.  $R^2 = 0.996$ .

## RESULTS AND DISCUSSION

### Effect of Mixing Temperature on Zein-Starch Doughs

The temperature at which the zein-starch composite flour (with dibutyl tartrate) is mixed influences the dough that is produced and whether a dough is formed. The composite flour with dibutyl tartrate mixed at 21°C did not yield a viscoelastic dough (Fig. 1A). Increasing the mixing temperature to 25°C (Fig. 1B) caused a dough to develop, but only after 35 min. Under these conditions, the final, developed dough temperature increased to 28°C because of friction during mixing. Once above 30°C, the composite flour containing dibutyl tartrate developed a dough in about 6 min (Fig. 1C). The same system mixed at 35°C developed a dough in about 2.5 min (Fig. 1D). Since no dough developed below 25°C, the ability of the composite flour to form a dough is clearly related to the temperature in which the dough was mixed.

Zein-starch dough appeared similar to one made from wheat flour (Fig. 2), but it was not as strong as a wheat dough. As Figure 2 illustrates, zein-starch doughs were, however, very extensible. Scanning electron microscopic analyses of zein-starch doughs prepared above the  $T_g$  of zein (Fig. 3) reveal an extensive protein fiber network. This network is probably responsible for the observed viscoelastic behavior. Fibers of similar appearance have been shown for purified glutenin (Orth et al 1973).

### Determination of $T_g$

The  $T_g$  of macromolecules is very sensitive to plasticizer level (Ferry 1980). Water lowers the  $T_g$  of wheat gluten (Hoseney et al 1986, Doescher et al 1987, Fujio and Lim 1989), glutenin (Cocero and Kokini 1991), gelatin-glycerol systems (Yannas and Tobolsky 1966), and elastin (Kakivaya and Hoeve 1975). The sensitivity of  $T_g$  to water can be seen in commercial zein plasticized by water (Fig. 4). The  $T_g$  of zein decreases rapidly with increasing water content. The rate of change begins to level off at roughly 15% water. As Figure 4 demonstrates, the  $T_g$  of hydrated zein containing plasticizer does not fall much below room temperature at any of the plasticizer (water) contents tested. This means, according to Hoseney's hypothesis, that a dough system involving zein needs to be mixed above room temperature to develop viscoelasticity. In this study, zein-starch composite flours mixed above room temperature developed into dough (Fig. 1), indicating that zein's ability to form dough is dependent on its  $T_g$ .

At a high water content, the  $T_g$  of zein is far below 60°C and close to room temperature (Fig. 4), indicating that zein-starch mixtures should form doughs at temperatures much lower than 60°C. MacRitchie (1980) and Bushuk and MacRitchie (1989)

suggested a temperature of 60°C for formation of zein-starch doughs. This led to the addition of a second plasticizer, dibutyl tartrate, to zein-starch mixtures to attempt to form zein-starch doughs below 60°C. However, the addition of dibutyl tartrate did not lower the  $T_g$  of zein below 50°C for any of the concentrations tested (Fig. 5).

Figure 4 indicates that the  $T_g$  of hydrated zein is about the same temperature as the minimum mixing temperature needed for dough development. To test whether the second plasticizer is needed for zein-starch dough development, doughs were mixed

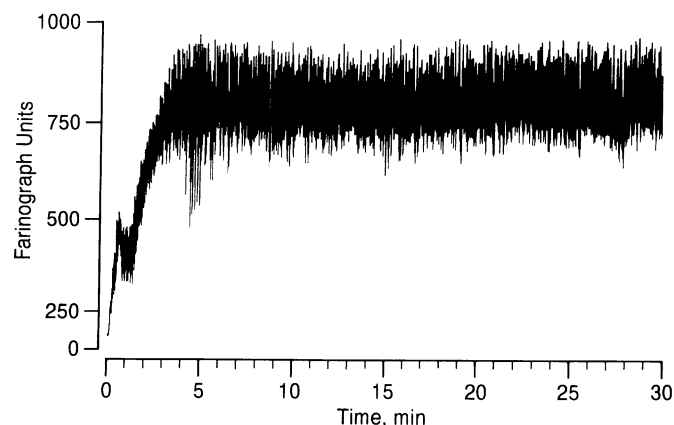


Fig. 6. Farinograms of zein-starch dough without dibutyl tartrate mixed at 35°C.

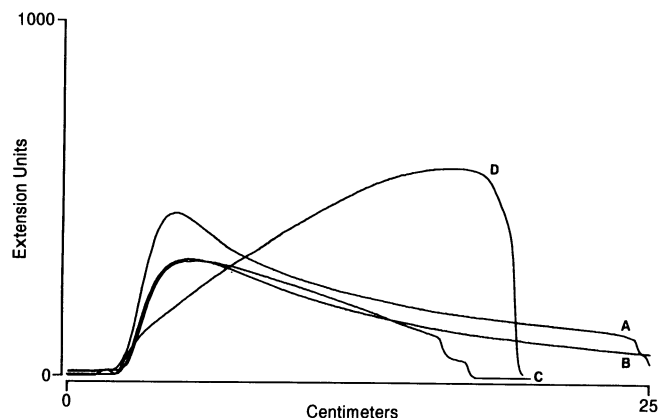


Fig. 7. Extensigrams of zein-starch doughs with dibutyl tartrate tested immediately after mixing. A-C = Doughs mixed at 25, 30, and 35°C, respectively; D = well-developed wheat flour dough after a 90-min rest.

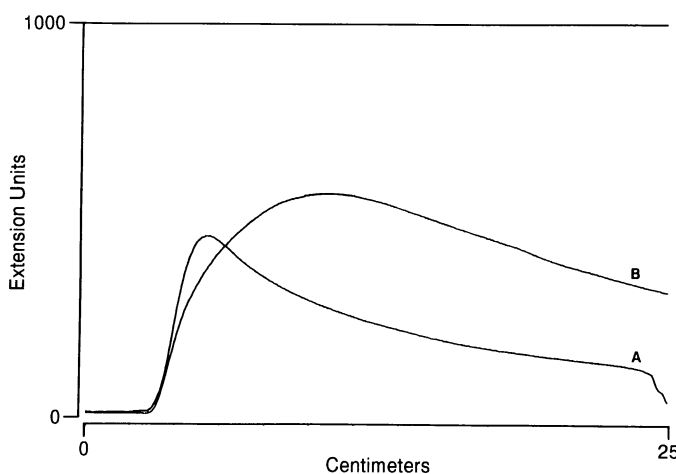


Fig. 8. Extensigrams of zein-starch doughs with dibutyl tartrate mixed at 35°C and tested immediately after mixing. A = Untreated, B = formaldehyde treated.

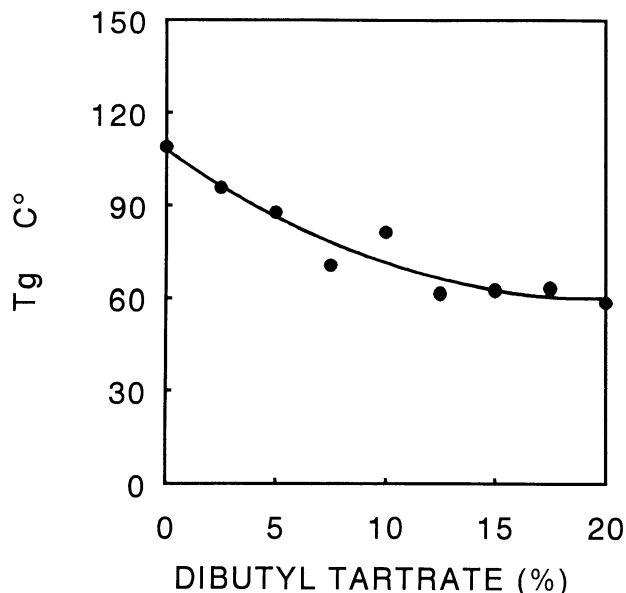


Fig. 5. Glass transition temperature ( $T_g$ ) of zein as a function of dibutyl tartrate. Zein moisture content is 4.3%.  $R^2 = 0.961$ .

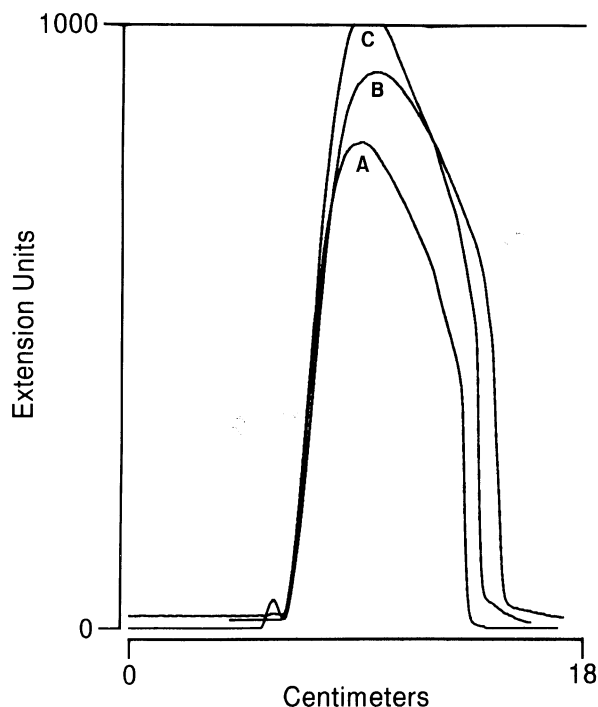


Fig. 9. Extensigrams of zein-starch doughs with dibutyl tartrate rested at room temperature for 15 min before testing. A-C = Doughs mixed at 25, 30, and 35°C, respectively.

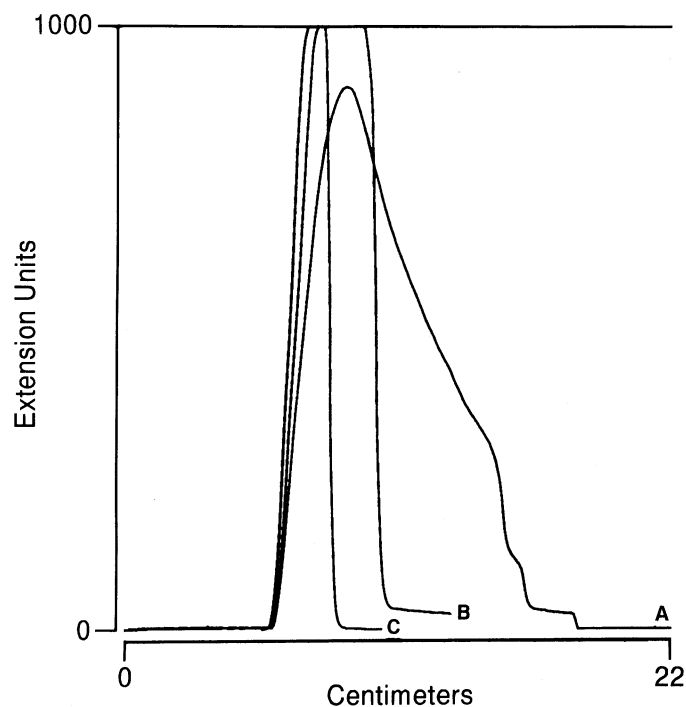


Fig. 10. Extensigrams of zein-starch doughs containing no dibutyl tartrate mixed at 35°C. A = Dough tested immediately after mixing, B = dough tested after resting at 35°C for 15 min, and C = dough tested after resting at room temperature for 15 min.

with no dibutyl tartrate. The zein-starch composite flour prepared without dibutyl tartrate developed into a dough when mixed at 35°C (Fig. 6). Because it appears that dibutyl tartrate is not needed for zein-starch dough development, all composite flours were analyzed on the basis of the  $T_g$  of zein shown in Figure 4.

#### Extensigrams of Zein-Starch Doughs

Extensigrams of zein-starch doughs appear different from those for wheat dough (Fig. 7). The maximum resistance to extension is near the beginning of the curve, and it decreases rapidly as dough is extended. This response is opposite to that of a well-developed wheat flour dough, in which resistance to extension increases as dough is extended (Bloksma and Bushuk 1988). However, zein-starch doughs were very extensible. Doughs mixed at 30 and 35°C stretched the entire length of the extensigraph test without breaking.

Commercial zein contains mostly A and B zeins (Wilson 1988), having only one to two cysteines per subunit, near their amino terminus (Wilson 1987). This suggests that commercial zein could not form the cross-linked matrix or extended polymers of subunits postulated to exist in wheat proteins (Hoseney and Rogers 1990). Consequently, when zein-starch doughs are extended, fewer covalent bonds are available to resist extension than in wheat dough.

To test whether a relative lack of covalent intermolecular cross-links decreases resistance to extension of zein-starch doughs, zein was cross-linked with formaldehyde. Resistance to extension of the resulting dough was greater than that of the untreated dough (Fig. 8). Resistance of the formaldehyde-treated dough also did not decrease as rapidly as dough was extended.

Dough temperature affected extensibility. Zein-starch doughs allowed to rest at room temperature for 15 min lost their extensibility (Fig. 9), possibly because of the  $T_g$  of zein. As dough rests at room temperature, zein cools to below its  $T_g$  and becomes glassy, causing a loss of viscoelasticity. Doughs mixed at 30 and 35°C but rested for 15 min at the temperature at which they were mixed showed no change in extensibility. These doughs did, however, increase in resistance to extension by about 100 extensigraph units. Doughs mixed and rested at 25°C behaved slightly differently. They increased in resistance to extension as did the other two doughs, but they also decreased in extensibility. This

decrease in extensibility may relate to passage back through the  $T_g$  of zein as described above, since 25°C is close to the  $T_g$  of zein measured in the system (Fig. 1).

When extended, the behavior of a zein-starch dough containing no dibutyl tartrate (Fig. 10) differs from that of doughs containing dibutyl tartrate. The former dough has little extensibility immediately after mixing and loses most of its extensibility after resting, whether kept warm or not. Obviously, dibutyl tartrate affects dough extensibility. Whether this is a classical plasticizer effect or some type of lubrication effect will be examined in future studies.

#### CONCLUSIONS

Zein-starch composite flour can be mixed into doughs that are viscoelastic and similar to those prepared from wheat flour. The existence of viscoelasticity seems governed by the  $T_g$  of zein. A composite flour did not develop into a dough if mixed below zein's  $T_g$ . Doughs rested and cooled to below the  $T_g$  of zein lost their viscoelasticity. At temperatures above its  $T_g$ , zein formed fibers during mixing, similar in appearance to those formed from wheat glutenin. These fibers appear responsible for the viscoelasticity of zein-starch doughs. The addition of a second plasticizer, dibutyl tartrate, to the zein starch mixture was not needed to form viscoelastic doughs. Understanding how corn proteins react in dough should make corn more useful in commercial products.

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