Rheological Properties of Wheat Flour Doughs in Steady and Dynamic Shear: Effect of Water Content and Some Additives

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ABSTRACT

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Dynamic tests and steady flow measurements were made with a controlled stress rheometer to study rheological properties of wheat flour doughs and to examine how rheological properties are related to dough composition (water content, oxidizing and reducing agents, emulsifiers, etc.). Water added to doughs has mainly strong plasticizing effects, but it probably does not change dough structure. The phase angle $tg\delta$, the shift parameter a, related to the extended Cox-Merz rule, and the power law exponent n are practically independent of water content, and these parameters may reflect the structure level of the protein network. Ascorbic acid has strengthening effects, and lecithins have softening effects, but dough structure is little modified by the presence of these components. Beyond 50 ppm, glutathione has strong softening effects, but it simultaneously affects dough structure. In all cases, when dough composition varies, either $tg\delta$, a, or n remain constant, or they vary simultaneously. Results obtained with glutathione lead us to assume that these parameters are closely interrelated.

Methods permitting the rheological characterization of wheat flour doughs have been developed during the last few decades. Most researchers used traditional dough-testing instruments such as the farinograph, the extensigraph, or the alveograph. Those studies have provided much practical information but are limited to empirical correlations. Now the fundamental mechanical properties of wheat flour doughs are most significant to understanding dough handling behavior during processing or to clarify the interactions among dough components. Dynamic testing methods developed for polymer rheology (Ferry 1980) are also most helpful in assessing viscoelastic properties of foods, including doughs. When conducted in the linear range, dynamic tests allow the specific expression of well-defined rheological parameters, such as the storage modulus (G'), the loss modulus (G''), or their viscous counterparts (η'' and η'). In the case of wheat flour dough, the problem of linearity has been discussed by several authors. It is now generally admitted that the behavior is linear or near linear up to strain amplitudes of ~0.2% (Dus and Kokini 1990, Berland and Launay *in press*), 0.25% (Weipert 1990), 0.5% (Amemiya and Menjivar 1992), or 0.8% (Lindhal and Eliasson 1992). When frequency sweep tests are conducted in the linear domain, G', G'', and $|\eta^*| = (\eta'^2 + \eta''^2)^{1/2}$ follow power laws and, in the experimental range, $G' > G''$. A rather low dependence of G' and G'' on frequency has been observed by several authors (Smith et al 1970, Amemiya and Menjivar 1992).

Dough flow properties are also of great relevance for practical applications, and have been studied by several groups. Launay and Buré (1973) used a cone-plate viscosimeter and showed that a power law may express the results. In many instances, flow and viscoelastic properties may be interrelated. The Cox-Merz rule is the simplest relationship between these properties (Cox and Merz 1958) : $\log\eta$ versus $\log\dot{\gamma}$ and $\log |\eta^*|$ versus $\log\omega$ superimpose for $\dot{\gamma} = \omega$. Dus and Kokini (1990) have claimed that wheat flour doughs followed this rule. On the contrary, we demonstrated previously (Berland and Launay, *in press*) that this rule did not apply. However, an extended Cox-Merz rule was applicable by using a frequency shift parameter a, that decreases with shear amplitude beyond the linear range.

The present investigation was undertaken to examine how dough rheological properties in shear, and in particular the shift parameter a, are related to dough composition (water content, oxidizing or reducing agents, and emulsifiers).

MATERIALS AND METHODS

Materials and Dough Preparation

Wheat flour (Table I) was kindly supplied by Grands Moulins de Paris (France). With all relative matter contents expressed on moist flour or on total dough weight basis, except as otherwise stated, doughs were composed of flour, water (43.8–49.4% total water, dwb) and salt (2.2%, fwb). They were mixed at 25°C and 60 rpm for 6 min in the small bowl (50 g) of the Brabender farinograph. Glutathione (GSH) was added as a reducing agent (15–150 ppm, fwb). Ascorbic acid was added (40–300 ppm, fwb), alone or in combination with glutathione. In wheat flour dough, ascorbic acid is enzymatically converted to dehydroascorbic acid by ascorbic acid oxidase (Elkassabany et al 1980, Cherdkiagumchai and Grant 1986) and behaves as an oxidant. The effects of two types of emulsifiers, lecithins and diacetyl-tartaric esters of monoglycerides (DATEM), were also investigated. Lecithins are complex lipid mixtures containing phospholipids. We used three commercial samples of lecithins (Nathin 140, Nathin 3F, and Nathin 5F, Nattermann Co., Rhône-Poulenc) at 0.3% concentration (fwb). Their phospholipid composition differs in that Nathin 140 contains mainly phosphatidyl-choline, while Nathin 3F and Nathin 5F contain specifically phosphatidyl-ethanolamine, phosphatidic acid, and phosphatidyl-inositol. DATEM (Panodan 90, Grinsted) was used at 0.28% (fwb). In all experiments, emulsifiers were combined with ascorbic acid (160 ppm, fwb). Before

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TABLE I
Main Characteristics of the Flour

Composition	Brabender Farinograph[a] (ISO 5530-1)	Chopin Alveograph[b] (NF V03-710)
Water (15.2% moist weight basis) (ISO 712)	Hydration (46.2%)	P (mm) 97
Ash (0.6% dry matter basis) (NF V03-720)		P/L 1.5
Titratable acidity (0.04% dry matter basis) (ISO 7305)		G (cm$^{3/2}$) 18.1
		W (10^{-4} J/g) 223

[a]Hydration: % total water (total weight basis) corresponding to 500 BU maximum consistency.
[b]Dough water content 43.2% (total weight basis).

testing, doughs were stored 1 hr in a small tight box at room temperature, to allow stresses developed during mixing to relax.

Equipment for Rheological Measurements

A controlled stress rheometer (Carrimed CSL 100) with a cone-plate geometry (4°, 40-mm diameter) was used for flow and dynamic tests. Using a truncated cone eliminated unwanted phenomena that may occur near the tip of the cone and facilitated its setting. The temperature was 25°C for all measurements. A dough sample (1.5 g) was deposited on the plate and left 5 min before measurement to allow induced stress to relax. The dough was prevented from drying during the test by use of a solvent trap filled with water and a lid over the cone to create a chamber saturated by water vapor.

In practice, during dynamic tests, the maximum stress applied ($\sigma 0$) was fixed by the computer to maintain the strain amplitude ($\gamma 0$) close to a target value ($\pm 3\%$). G', G'', and $|\eta^*|$ were measured from 0.2 to 20π rad·sec^{-1}, at a strain amplitude of 0.2% (Fig. 1). G', G'', $|\eta^*|$, and $tg\delta$ at 2π rad·sec^{-1} were the parameters chosen to examine the effect of dough composition on viscoelastic properties. Standard deviation was <8% for G', G'', and $|\eta^*|$; <2% for $tg\delta$ (three replicates).

For high consistency materials, the flow properties at low shear rates can be measured by conducting creep tests at several stress levels (40–190 Pa) during 4 min, a duration sufficient to attain a permanent flow regime and to calculate the corresponding shear rates and viscosities. The results in Figure 2 show that the flow properties of wheat flour doughs obey a power law, at least for

shear rates varying between 10^{-4} and 6.10^{-2} sec^{-1}:

$$\eta = K\dot{\gamma}^{1-n} \tag{1}$$

where K is the apparent viscosity for $\dot{\gamma} = 1$ sec^{-1}, and n is the power law exponent (dimensionless). The value of n (~0.2) indicates that wheat flour doughs are highly shear-thinning, which is in agreement with many published results (see Launay and Buré 1973). In our conditions, shear rates of 1 sec^{-1} are not experimentally obtained: we consider K' (apparent viscosity for $\dot{\gamma} = 10^{-3}$ sec^{-1}, a mid-scale shear rate value) instead of K, and the power law relationship is expressed as:

$$\eta = K'[\dot{\gamma}/10^{-3}]^{1-n} \tag{2}$$

where K' and n (standard deviation 5–6%) are the parameters used to study the effect of dough composition on flow properties.

The results in Figure 2 demonstrate that the Cox-Merz rule did not apply; under our conditions, the slopes of $\eta(\dot{\gamma})$ and of $|\eta^*(\omega)|$ are the same or almost equal. Therefore, it is possible to superimpose these straight lines using a shift factor a on the frequency axis (Berland and Launay, in press). The shift factor is calculated as:

$$a = [(\log K - \log K^*)/1 - N] \tag{3}$$

$$\eta = K\dot{\gamma}^{1-n} \tag{4}$$
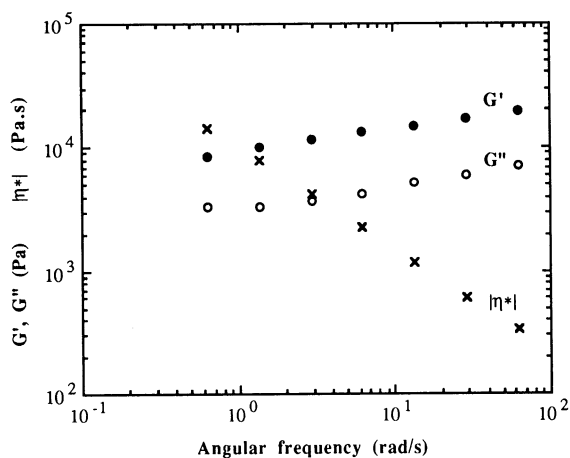
$$|\eta^*| = K^*\omega^{1-n^*} \tag{5}$$

Fig. 1. Dynamic properties versus frequency in the linear domain (strain amplitude 0.2%). Dough water content 46.2%. G' = storage modulus, G'' = loss modulus, $|\eta^*|$ = complex viscosity.
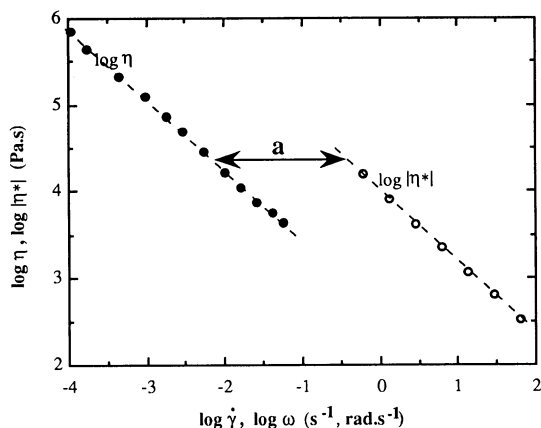

Fig. 2. Test of the Cox-Merz rule. ● = steady state viscosity, ○ = modulus of the complex viscosity (strain amplitude 0.2%), a = frequency shift factor. Dough water content 46.2%.
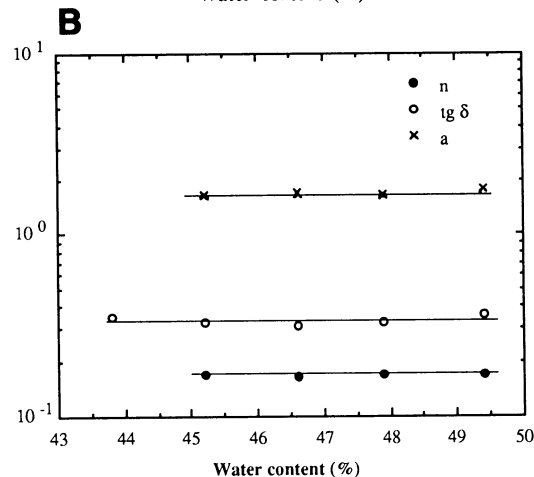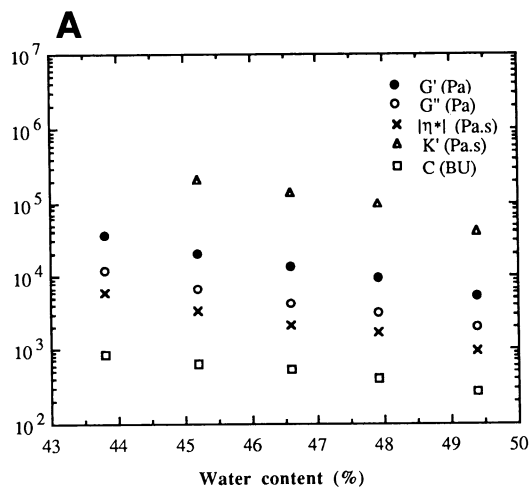

Fig. 3. A, Dependence of storage modulus (G'), loss modulus (G''), complex viscosity ($|\eta^*|$), viscosity at 10^{-3} sec^{-1} (K'), and consistency (C) on dough water content. **B,** Dependence of phase angle ($tg\delta$), power law exponent (n), and shift parameter (a) on dough water content.

$n \sim n^*$, but we have used the mean value $N = (n + n^*)/2$ to take into account any small difference (5% at most) between the slopes of the regression lines. The extended Cox-Merz rule (Berland and Launay, *in press*) is:

$$|\eta^*|(\omega) = \eta(\dot{\gamma}), \text{ with } \omega = 10^a \cdot \dot{\gamma} \qquad (6)$$

RESULTS AND DISCUSSION

Dependence on Water Content

When dough water content is increased from 43.8 to 49.4%, G', G'', and $|\eta^*|$ decrease exponentially (Fig. 3a). Several groups have published similar results (Hibberd 1970, Hibberd and Parker 1975, Navickis et al 1982, Dreese et al 1988, Cavella et al 1990). Flow properties have also been determined from 45.2 to 49.4%, and we observed that K' also decreases exponentially, while, at least in this range of water content, $n \sim n^* \sim$ constant. It is important to note that G', G, $|\eta^*|$, and K' are more sensitive to water content than is dough consistency. In semi-log scales, G', G'', $|\eta^*|$, and K' vary with water content according to a slope of ~ -0.14, compared to -0.09 for consistency. $Tg\delta$ is independent of water content (Fig. 3b) because G' and G'' vary similarly. In the same way, n and the shift factor a do not vary with water content. This lead us to conclude that in normal doughs, water has mainly strong plasticizing effects, changing the values of the rheological parameters but without modifying the structure. In this connection, we propose that the shift factor a might reflect the level of dough structure.
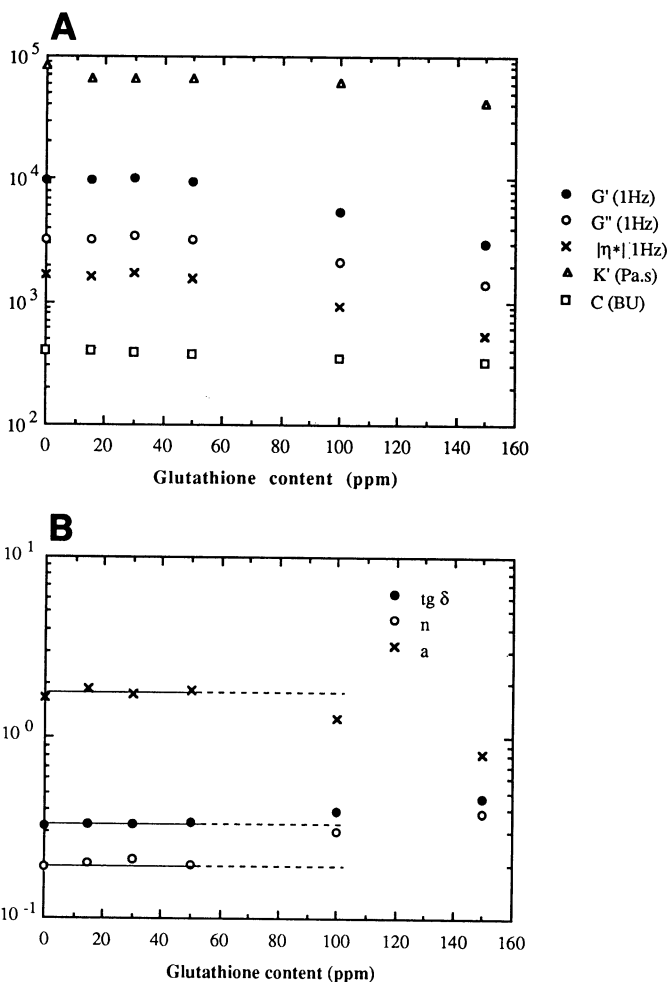

Fig. 4. A, Dependence of storage modulus (G'), loss modulus (G''), complex viscosity ($|\eta^*|$), viscosity at 10^{-3} sec^{-1} (K'), and consistency (C) on glutathione content. Dough water content 47.9%. **B,** Dependence of phase angle ($tg\delta$), power law exponent (n), and shift parameter (a) on glutathione content. Dough water content 47.9%.

Effect of Oxidizing and Reducing Agents

Glutathione. At the smallest concentrations (15 or 30 ppm), glutathione has no detectable rheological effects, but when it is increased from 50 to 150 ppm, the G', G'', $|\eta^*|$, and K' decrease (Fig. 4a). High glutathione contents lead to weakening of the dough. As with water content, G', G'', $|\eta^*|$, and K' are more sensitive to glutathione content than is dough consistency. However, in this case, the decrease (in log scale) of G', G'', $|\eta^*|$, and K' is six to eight times higher than the decrease of consistency. The phase angle increases with glutathione content (Fig. 4b). High levels of glutathione modify the balance between viscous and elastic properties: G' decreases more rapidly with glutathione content than does G''. Bloksma (1972, 1975) has published similar results. In creep, both elastic and viscous compliances of dough decreased with glutathione content. In the same way, Dreese et al (1988) observed that G' decreased and $tg\delta$ increased, when another reducing agent, cysteine, was added. A high $tg\delta$ value may be tentatively associated with a sticky behavior. At the smallest concentrations (<50 ppm), the power law exponent n and the shift factor a are not affected by glutathione content. Nevertheless, at higher levels, n increases and a decreases with glutathione content (Fig. 4b). Under these conditions, dough is less shear thinning and deviates less from the Cox-Merz rule.

The sensitivity of rheological properties of dough to oxidation or to reduction suggests that disulfide bonds play a major role in dough rheology. Dough rheology is connected to gluten structure, and several models have been proposed to describe it. According to Miflin et al (1983) among others, gluten properties agree with a model in which viscoelastic behavior is caused by a temporary three-dimensional network, built by entanglement of long linear polymer chains (glutenins). These chains are composed of subunits connected by intermolecular disulfide bonds. In wheat flour dough, glutathione behaves as a reducing agent and is able to cause gluten breakdown, rupturing disulfide cross-links in gluten by SH/SS interchange. At low levels, glutathione has no detectable effect on dough rheological properties. Some authors (Bloksma 1972, Jones et al 1974, Bloksma 1975) proposed that only a fraction of the thiol and disulfide groups are rheologically effective. Recent models proposed for gluten structure suggest an analogy with entangled uncross-linked polymers of high molecular weight, where one can define a critical molecular weight above which the steady-state compliance J becomes independent of molecular weight instead of being inversely proportional to it (Ferry 1980). The incorporation of glutathione at low concentration leads to the reduction of some disulfide bonds, but the mean molecular weight of glutenins would not be sufficiently reduced, and no significant change in dough structure can be observed. On the contrary, when glutathione is incorporated at a higher level, the size reduction of glutenins would affect dough rheological properties by modifying its structure, and this structural alteration might be reflected by a change in the values of a, n, or $tg\delta$.

Ascorbic acid. When ascorbic acid is incorporated at the lowest level (40 ppm), G', G'', $|\eta^*|$, and K' increase slightly, but the effect is barely significant. Beyond this concentration, and up to ~ 160 ppm, G', G'', $|\eta^*|$, and K' increase (Fig. 5a), in agreement with its well-known dough strengthening effects. Indeed, ascorbic acid is converted to dehydroascorbic acid, and it is generally believed that this compound oxidizes thiol groups from low molecular weight peptides (glutathione, for example). These oxidized molecules are no longer rheologically active and will not depolymerize glutenin chains. However, when ascorbic acid is incorporated at a higher level (300 ppm), G', G'', $|\eta^*|$, and K' decrease. We consider that, under our mixing conditions, not all of the ascorbic acid is oxidized, and therefore, it behaves in part as a reducing agent, with almost no effect. $Tg\delta$ is little affected by the presence of ascorbic acid, whatever its level (Fig. 5b). Similarly, Dreese et al (1988) observed that iodate increased G' relative to controls but had little effect on $tg\delta$. Bloksma (1972, 1975) published comparable results; he found that both elastic and viscous compliances increased when iodate level in dough increased. We noted also that n and the shift factor a are not

modified by addition of ascorbic acid, whatever the level (Fig. 5b). However, pooled measurements on a great number of samples (results not shown) allow us to detect a slight but significant decrease of $tg\delta$ with ascorbic acid level. Therefore, ascorbic acid could weakly modify the balance between viscous and elastic properties, G' increasing a little bit more than G''.

On first approximation, one may nevertheless conclude that the use of ascorbic acid in wheat flour dough (80 or 160 ppm) has dough strengthening effects (G', G'', $|\eta^*|$, and K' increase), but the rheological parameters related to dough structure ($tg\delta$, n, and a) do not vary much.

Effect of Emulsifiers

Emulsifiers are well-known for their effect on starch, particularly for their ability to delay starch retrogradation (Stauffer 1990, Kamel and Ponte 1993, Silva 1993). The effect of emulsifiers on dough rheological properties have been studied by several authors. Eliasson and Larsson (1993) noted an increase of the modulus G (stress relaxation measurements) when lecithins were added. Gluten aggregation would increase in presence of DATEM (Stauffer 1990). Polar lipids (phosphatidyl-inositol, for example) would be able to react with gluten proteins and build up a lipoprotein complex (Silva 1993). We noted that, in presence of ascorbic acid, the addition of lecithins has a dough-softening effect; G' (Fig. 6a) and (data not shown) G'', $|\eta^*|$, and K' decrease. This effect is more pronounced for lecithins containing a high level of phosphatidyl-choline (Nathin 140), than for lecithins containing phosphatidyl-ethanolamine (Nathin 3F, Natin 5F). In

contrast, there is no difference in rheological properties (Fig. 6a) between the sample containing diacetyl tartaric esters of monoglycerides (P 90) and the corresponding reference (A 160). In our experimental conditions, the structure parameters $tg\delta$, n, and a are unaffected, whatever the emulsifier used (lecithins, DATEM) (Fig. 6b). In combination with ascorbic acid, they have no additional strengthening effects, and would not cause more gluten aggregation under our experimental conditions.

CONCLUSION

Dynamic tests and steady flow measurements were conducted with wheat flour doughs, and the effects of water content and some additives were studied. Water added to doughs mainly has strong plasticizing effects, but water probably does not modify the supramolecular organization of high molecular weight proteins. Increasing water content leads to softening of the dough (G', G'', $|\eta^*|$, and K' decrease), but does not alter dough structure. The parameters n, $tg\delta$ and a do not vary with water content, and in this connection, they may reflect the structure level of protein network, which also is not modified by addition of emulsifiers in presence of ascorbic acid. However, lecithins have softening effects, while DATEM does not change dough consistency.

It is interesting to compare the oxidizing effects of ascorbic acid and the reducing effects of glutathione, and to examine whether they are symmetrical. In both cases, a similar minimum
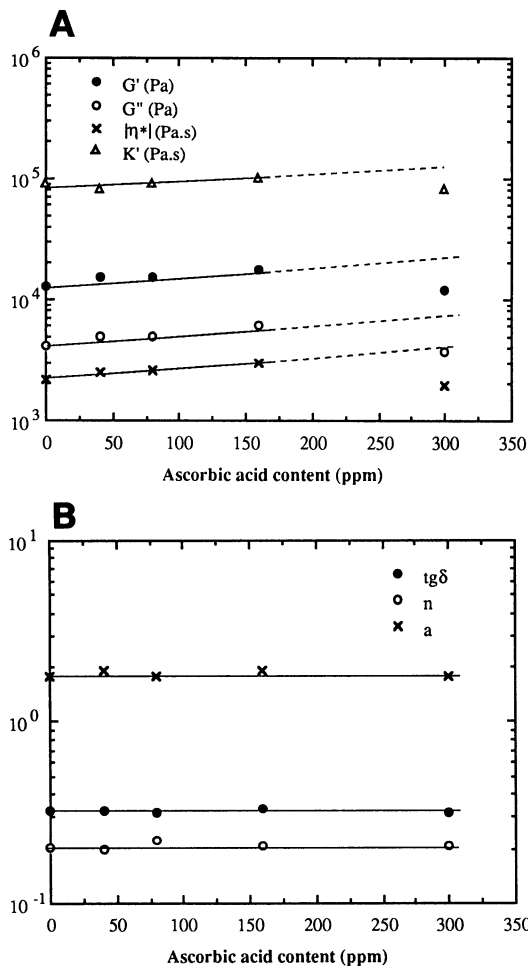

Fig. 5. A, Dependence of storage modulus (G'), loss modulus (G''), complex viscosity ($|\eta^*|$), and viscosity at 10^{-3} sec^{-1} (K') on ascorbic acid content. Dough water content 46.2%. **B,** Dependence of phase angle ($tg\delta$), power law exponent (n), and shift parameter (a) on ascorbic acid content. Dough water content 46.2%.
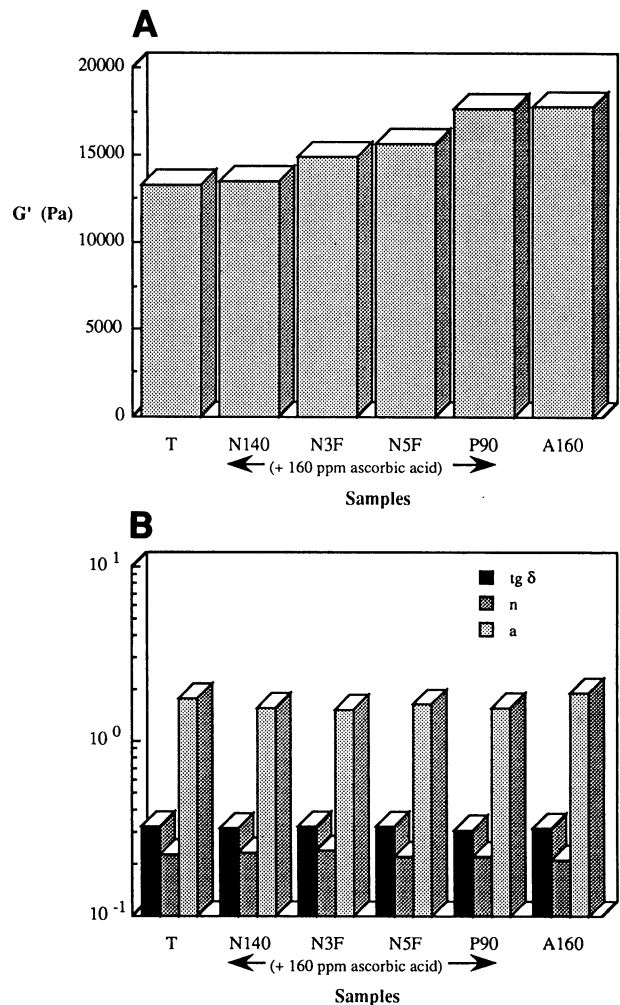

Fig. 6. A, Value of storage modulus (G') for various types of emulsifiers. **B,** Values of phase angle ($tg\delta$), power law exponent (n), and shift parameter (a) for various types of emulsifiers. Ascorbic acid (160 ppm) plus lecithins, 300 ppm (Nathin 140, Nathin 3F, Nathin 5F) or diacetyl-tartaric esters of monoglycerides, 280 ppm (Panodan 90). Ascorbic acid, 160 ppm (A 160). Control doughs (T). Dough water content 46.2%.

level of additives is required, so that strengthening effects can be observed with ascorbic acid ($\approx$40 ppm) and softening effects can be observed with glutathione ($\approx$50 ppm). Yet, only glutathione seems to modify significantly the structure level of gluten proteins, by extended rupture of disulfide cross-links.

In all cases, when dough composition varies, $tg\delta$, n, and a either remain constant together, or they vary simultaneously. Results obtained with glutathione indicate that, when dough is less shear thinning, and when the frequency dependence of G^* increases, the phase angle increases and the shift factor a decreases. Future work is needed to determine whether the existence of such correlated variations may be generalized. In addition, it would be interesting to examine the shear-sensitivity of the shift parameter a beyond the strictly linear viscoelastic domain (Berland and Launay, in press).

ACKNOWLEDGMENTS

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