

# Effect of Moisture Content on Viscoelastic Properties of Hydrated Gliadin

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## ABSTRACT

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The effect of moisture content on the linear viscoelastic properties of gliadin hydrated to 30 and 40% moisture content [gliadin(30%) and gliadin(40%), respectively] was determined. These two moisture contents bracketed the equilibrium moisture content of gliadin, which was 37.6%. Time-temperature-superposition was used to develop master curves of the elastic modulus ( $G'$ ), viscous modulus ( $G''$ ), dynamic viscosity ( $\eta'$ ), and  $\tan \delta$  ( $G''/G'$ ) from isothermal frequency sweep data obtained at 25–80°C. Smooth master curves were obtained for all of the viscoelastic functions for both gliadins.  $G'$  and  $G''$  showed a power law dependency on frequency (with  $G'' > G'$ ) for frequencies  $<0.1$  rad/sec for gliadin(30%) and  $<1$  rad/sec for gliadin(40%). The low-frequency-limiting slopes on log-log coordinates for  $G'$  and  $G''$  were 0.700 and 0.646 for gliadin(30%), respectively. Corresponding values were 0.658 and 0.614 for gliadin(40%).  $G'$  crossed over  $G''$  at a frequency of  $\approx 0.3$  rad/sec for gliadin(30%), while  $G'$  and  $G''$  for gliadin(40%) only became congruent at higher frequencies. Both gliadin samples showed appreciable frequency dependence of  $\eta'$  over the entire frequency range, while  $\eta'$  was greater for gliadin(30%) than for gliadin(40%) at all frequencies, but especially at the lowest frequencies.  $\tan \delta$  increased gradually from a value of  $\approx 1$  at 0.1 rad/sec to

$\approx 2$  at the lowest frequency of 0.0002 rad/sec for both gliadins, but  $\tan \delta$  decreased rapidly for gliadin(30%) for frequencies  $>0.1$  rad/sec. Thus, the main difference between gliadin(30%) and gliadin(40%) was that elastic effects ( $G' > G''$  and decreased  $\tan \delta$ ) were more prominent for gliadin(30%) at the higher frequencies. In addition, the frequency dependence of  $G'$ ,  $G''$ ,  $\eta'$ , and  $\tan \delta$  for the two gliadin samples was compared directly with two samples of poly(dimethylsiloxane) (PDMS) a linear silicone-based entangled polymer with molecular weights (MW) of 140,000 and 385,000. The substantial differences in the magnitude and overall patterns of the frequency dependence of the viscoelastic functions between the gliadin and PDMS samples was attributed to the dominant effect that noncovalent secondary associations apparently have on the linear viscoelasticity of the gliadins. The energy of activation for flow (determined from the temperature dependence of the shift factors) for the gliadin samples for the range 25–45°C was higher than is typical for entangled linear polymer melts. The activation energy decreased for temperatures greater than  $\approx 60^\circ\text{C}$  for gliadin(30%) and  $\approx 50^\circ\text{C}$  for gliadin(40%). Thus, hydrated gliadin cannot be considered to be a simple viscoelastic liquid.

The gliadin and glutenin proteins are the two primary classes of storage proteins in wheat. Shewry et al (1986), although questioning the fundamental validity of the classification of wheat proteins based on solubility in a series of solvents, do acknowledge an important technological distinction between the two major cereal protein classes. They note that gliadins are considered to contribute to the viscosity and extensibility of gluten, while the glutenins appear to contribute more to the elasticity of gluten. Hosney (1986) describes the functionality of the gliadin and glutenin fractions of gluten a little differently, saying that gliadin appears to be responsible for the dough's cohesiveness, while glutenin apparently gives dough its property of resistance to extension. Hosney also observes that hydrated glutenin itself is resilient but not cohesive.

Both hydrated gliadin and glutenin (i.e., gluten) are needed to obtain a high-quality viscoelastic bread dough, and the proportion of gliadin to glutenin is an important factor in determining the mixing and rheological properties of the dough or gluten (Khatkar et al 1995; Janssen et al 1996; Fido et al 1997; Tsiami et al 1997; Uthayakumaran et al 2001; Wieser and Kieffer 2001; Khatkar et al 2002). Khatkar et al (2002) stated that rheological analysis of gluten subfractions (gliadin and glutenin) and how their interactions affect viscoelasticity of gluten are essential to help explain the molecular basis of gluten viscoelasticity. Leonard et al (1999) also noted that the structure of the gluten matrix is dependent on associations between gliadin and glutenin. In particular, the gliadin proteins are presumed to interact with the glutenin polymers by noncovalent interactions (hydrogen bonds) and the gliadins are traditionally considered to contribute to gluten viscosity rather than strength and elasticity (Khatkar et al 1995; Shewry et al 2001).

However, Belton (1999) has recently discussed how the effect of hydration level on the extent of intermolecular hydrogen bonding between HMW glutenin subunits could play an important

role in the elasticity of these subunits. Belton also points out that, unlike entangled synthetic linear polymers or rubber elastomers above their respective glass transition temperatures ( $T_g$ ), cereal proteins can interact with each other chemically and with the solvent (water) (Belton 1999). But the gliadin proteins also have a high amide content, in the form of glutamine amino acids, and low charge, suggesting substantial hydrogen bonding (Hosney 1986), which may be an important factor in determining the viscoelastic properties of gliadin as well as glutenin. The commonality of amino acid sequences containing glutamine and proline in gliadin and glutenin polypeptides alike (Belton et al 1998) may help to explain the compatibilizing, or plasticizing, effect (Frazier 1993) of gliadin on glutenin.

Despite the fact that gliadin accounts for  $\approx 50\%$  of the gluten proteins, it is apparent that much more emphasis has been placed on the role of the glutenin proteins and their subfractions and the ratio of gliadin to glutenin in gluten than the gliadin proteins per se as the basis for explaining the unique viscoelastic properties of gluten (e.g., Weegels et al 1996; Shewry et al 2001). This may be due in part to the fact that the extracted gliadin fractions of wheat cultivars of different breadmaking quality show quite similar rheological properties, while the glutenin fractions show more differences in their rheological properties as illustrated by Khatkar et al (1995). Tatham and Shewry (1985) characterized the gliadin proteins as associated by hydrogen bonds and hydrophobic interactions, although the use of the term associated by those authors and Leonard et al (1999) was not used in the more general context of synthetic associating polymers, as will be discussed later. The above discussion highlights the important role that noncovalent hydrogen bonds and hydrophobic interactions are thought to play in modulating the viscoelasticity of gluten and in determining the rheological and functional properties of the gluten subfractions including gliadin. However, the effect that noncovalent functional groups can have on the frequency dependence of the linear viscoelastic functions of polymers in general has not been considered in the interpretation of rheological results for cereal systems. More often than not, small and large deformation rheological results for cereal systems have been interpreted in the context of entangled linear polymers, including previous work from one of our labora-

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tories. Singh and MacRitchie (2001) have provided a good review of how the concepts of entanglement couplings have been applied to help explain the rheological properties of gluten and doughs, in particular, the effect of the rate of deformation on the large deformation extensibility. In our view, the concepts related to hydrogen bonding associative synthetic polymers provide a better physical model for interpretation of linear viscoelasticity for hydrated cereal systems. This idea will be explored further here using gliadin as an example.

### Associating Polymers

In a recent publication, Lee and Mulvaney (2003) indirectly quantified the effect of the gliadin fraction on the viscoelastic properties of glutenin gels by comparing results for glutenin and gluten gels at the same moisture content. They also noted that the role of noncovalent intermolecular associations in determining the rheological and functional properties of hydrated cereal systems was more analogous to so-called associating synthetic linear polymers than entangled linear flexible polymers. Associative synthetic polymer refers to a linear synthetic polymer that has been chemically modified to contain noncovalent functional groups spaced evenly along the polymer chain or placed at either end only. Because synthetic polymers have nonpolar backbones, the associating groups are polar, often including hydrogen bonding chemical groups. As discussed in more detail in Lee and Mulvaney (2003) in the context of gluten and glutenin gels and Rao et al (2001) and Edwards et al (2001) for wheat flour doughs, the introduction of just a few mol% of associating groups along the synthetic polymer backbone leads to very high melt viscosities and enhanced viscoelastic properties at low concentration and low molecular weight, relative to the unmodified linear polymer of the same molecular weight. Also, secondary interactions incorporated into synthetic associating polymers can be exploited to enhance the compatibility of polymers or components that are incompatible in the absence of these secondary associations (Klok et al 1999). This sounds qualitatively similar to the plasticizing or compatibilizing effect that gliadin has been shown to exert on glutenin.

The effects of chemical structure and concentration of noncovalent associative groups on the linear viscoelastic properties for synthetic polymers is determined directly by comparison of experimental results with those obtained from the unmodified linear polymer control of the same molecular weight. This direct approach is not feasible for cereal systems. Cereal proteins are a complex mixture of proteins of different molecular weight and chemistry, including a variety of amino acid side chain associating groups, and are always hydrated in any technical use. Thus, the idea of a control without hydrogen bonding for example (that is without water) is impractical. The approach used here will be to compare the patterns of the frequency dependence of the viscoelastic functions for hydrated gliadin with poly(dimethylsiloxane) (PDMS) silicone-based linear polymers directly, and to other linear and synthetic associating polymers by comparisons with results available in the published literature for the latter. Despite obvious differences in chemical structure, certain PDMS associating polymers are qualitatively similar to the gliadin proteins.

### PDMS Polymers

The effect of degree of physical cross-linking on the linear viscoelasticity of physical networks based on PDMS modified to contain hydrogen bonding carboxyl functional groups along the backbone has been determined Klok et al (1999) and Vasil'ev et al (1995). The PDMS associating polymer used by Klok et al (1999) had a molecular weight (MW) of 71,320 and included a linear unmodified PDMS sample for comparison of MW 69,800. The hydrogen bonding associating PDMS polymers used by Vasil'ev et al (1995) ranged from 41,100 to 65,000. The gliadin proteins have reported MW ranges of 30,000–60,000 (Arêas and Cassiano 2001), 11,000–80,000 (Mimouni et al 1998), 25,000–50,000 (Drees

et al 1988), and 30,000–100,000 (Bloksma 1990), which is similar to MW of many published studies involving associating polymers. The associating PDMS polymers described above and their unmodified linear counterparts are qualitatively similar to gliadin molecules in MW and the presence of hydrogen bonding associating groups spaced along the backbone.

In addition, PDMS is a well characterized linear polymer that can be purchased commercially in a wide range of molecular weights and corresponding viscosities. PDMS is a polymer melt or gel-like material at 25°C depending on MW (viscosity) and is more convenient to handle than a plastic polymer melt that would show similar physical properties only at temperatures well above 100°C. Also, because PDMS polymers are commercially available in a wide range of molecular weights with narrow molecular weight distributions, and with or without reactive groups, they make excellent model systems for separating out the effects of incorporation of noncovalent associative groups of different complexity and chemistry on the linear viscoelasticity of linear polymers (de Lucca Freitas et al 1987). Of course, to compare experimental rheological data for these gliadins with synthetic linear and associating polymers, the data must be reported in the same format. This required the use of time-temperature superposition.

### Time-Temperature Superposition

Linear viscoelasticity of entangled synthetic polymers is most often presented as so-called master curves obtained by time-temperature superposition. Time-temperature superposition is used to expand the experimentally available frequency scale so that the viscoelastic functions in the plateau and terminal zones of viscoelasticity for uncross-linked linear polymers can be observed at a single reference temperature ( $T_0$ ). In the terminal or polymer melt flow zone of linear viscoelasticity for uncross-linked linear polymers, the frequency dependence of the dynamic loss modulus ( $G''$ ) and elastic modulus ( $G'$ ) reach their limiting values of 1 and 2, respectively, on logarithmic coordinates and  $G'' > G'$  (Ferry 1980a). As the frequency is increased  $G'$  will crossover  $G''$  for entangled linear polymers, marking the beginning of the plateau region of viscoelasticity for entangled linear polymers, where  $G' > G''$ . Depending on the molecular weight of the linear polymer and the temperature difference ( $T_0 - T_g$ ), the experimentally available frequency range of oscillatory rheometers may not extend to frequencies low enough to observe terminal zone behavior; one may find that for all experimental frequencies at the desired temperature that  $G' > G''$ .

In practice, time-temperature superposition involves first obtaining isothermal frequency sweep data at different temperatures (multifrequency temperature sweeps) and then shifting the data horizontally to obtain a composite master curve at the desired reference temperature (see Marin et al [1982] and Raju et al [1981] for examples for synthetic polymers in the plateau and terminal zones). The temperature shift factors ( $a_T$ ) are usually obtained empirically by determining the horizontal shift required along the logarithmic frequency scale needed to superpose data at a given temperature onto that of the reference temperature. The shift factors themselves, which are a function of temperature, can be analyzed using either the Williams-Landel-Ferry (WLF) or Arrhenius equation to determine the activation energy for the viscous flow process in the terminal zone (Ferry 1980b). The presence of noncovalent associative groups dramatically affects the plateau and terminal zone linear viscoelastic properties of synthetic polymers in increased viscosity, increased relaxation times, and increased activation energy for flow relative to the unmodified polymer (deLucca Freitas and Stadler 1988; Vasil'ev et al 1995). We found that it was necessary to apply the principle of time-temperature superposition to obtain the terminal zone viscoelastic behavior for hydrated gliadin at 25°C.

Published results for the frequency dependence of the dynamic moduli for hydrated gliadin are very limited. Madeka and Kokini

(1995) determined the effect of temperature and moisture content on the dynamic moduli of gliadin for frequencies of 0.1–100 rad/sec but they focused on the physical cross-linking process that occurred at temperatures  $>70^{\circ}\text{C}$ . Khatkar et al (1995) reported some limited data for  $G'$  for gliadins extracted from good and poor breadmaking wheat cultivars but only for frequencies  $>0.628$  rad/sec. Cornec et al (1994) reported results for the dynamic moduli of several subfractions of gluten with increasing proportion of HMW glutenin subunits in the frequency range 0.00628–226 rad/sec but noted that the viscoelasticities of the gliadin fractions themselves were too low to be measured on the rheometer used.

### Objectives

The main objective of this work was to compare the frequency dependence of the dynamic viscoelastic functions in the plateau and terminal zones for hydrated gliadin with those of linear synthetic polymers. If hydrated gliadin is a simple viscoelastic liquid, then the master curves for  $G'$  and  $G''$  should show the limiting slopes of 2 and 1 versus frequency on logarithmic scales, respectively. Failure of the gliadins to show this pattern would indicate that uncross-linked linear synthetic polymers (entangled or not) do not make a good physical model for explaining the linear viscoelasticity of hydrated gliadin.

## MATERIALS AND METHODS

### Gliadin

Crude gliadin from wheat gluten (EEC #232-707, Lot #56H7105) was obtained from Sigma Chemical Co. (St. Louis, MO). According to Sigma, their gliadin is obtained using the method of Blish and Sandstedt (1926). In this method, dried crude gluten is dispersed in dilute acetic acid and, because of the drying step, the glutenin proteins precipitate out of the solution, leaving the gliadin proteins to be easily recovered from the supernatant liquid. Blish and Sandstedt (1926) reported that their gliadin fraction was soluble in 70% ethanol but was purer than gliadin fractions extracted directly with alcohol.

The gliadin was ground in a grinding mill (Arthur C. Thomas Co., Philadelphia, PA) and then passed through a 60-mesh screen (particle size  $< 250\ \mu\text{m}$ ). This process provided a more uniform particle size distribution and helped break up clumps that may have formed during processing and packaging. This ground gliadin will simply be referred to as gliadin. The moisture content of the ground gliadin was determined to be 6.0% using a moisture balance (Cenco Scientific Co., Fairfax, VA) according to Approved Method 44-40 (AACC 2000).

### PDMS Polymers

Viscoelastic properties were obtained for a sample of PDMS (catalog # PS448) from Petrarch Systems (Bristol, PA). According to the manufacturer, this silicone polymer is terminated at each end with a vinyl group and has a MW of 140,000 and a kinematic viscosity of 100,000 cSt ( $\approx 98\ \text{Pa}\cdot\text{sec}$  using the manufacturer's value of 1.02 for the specific gravity of this sample). This sample was tested at  $4^{\circ}\text{C}$  to eliminate flow from between the parallel plates during testing and showed fully developed terminal zone behavior in the experimental frequency range of the rheometer. LMW PDMS samples were essentially silicone oils at  $25^{\circ}\text{C}$ . A second HMW PDMS sample SE30 (General Electric silicones, www.gesilicones.com) was used as an example of an entangled polymer that showed a transition from the terminal zone to the plateau zone of viscoelasticity at  $25^{\circ}\text{C}$  in the experimental frequency range of the rheometer. According to a representative of GE, the approximate number average molecular weight of this PDMS sample was 385,000.

The MW of these PDMS samples are larger than those reported for the gliadins. However, because the plateau and terminal zone

viscoelastic properties of linear synthetic polymers show a universal similarity (Raju et al 1981; Marin et al 1982), the choice of polymer to demonstrate the universal patterns of the viscoelastic functions for uncross-linked linear polymers is arbitrary. These two PDMS samples were chosen because the combination of their molecular weight and the temperature of testing resulted in the shifting of the desired frequency dependence of the viscoelastic functions into the experimental frequency window of the rheometer without application of time-temperature superposition.

### Equilibrium Moisture Content of Gliadin

The gliadin was mixed with distilled water ( $52^{\circ}\text{C}$ ) to 30% MC in a small plastic cup (Solo Cup Co., Highland Park, IL). Samples were mixed using a metal laboratory spatula until no light or dark spots were visible and the sample had a homogeneous surface appearance. Once mixed, the sample was transferred to a small screen basket that was suspended inside an enclosed chamber above a bath of distilled water. The chamber was sealed and the sample was allowed to rest for several days at  $25^{\circ}\text{C}$  and 94% rh. The gain in sample weight was noted for several days and the equilibrium MC was 37.6%, which was achieved after  $\approx 48$  hr.

### Gliadin Sample Preparation for Rheometry

Gliadin was reconstituted to 30 or 40% MC with measured amounts of distilled water ( $52^{\circ}\text{C}$ ) in a plastic cup as described above to obtain one sample with MC  $< 37.6\%$  and one somewhat  $> 37.6\%$  to ensure full hydration. The hydrated gliadin was allowed to further hydrate for 30 min at room temperature ( $25^{\circ}\text{C}$ ). After this rest period, the gliadin sample was removed from the cup and divided in half. One half was hand-shaped into a disk  $\approx 25$  mm in diameter. The other half was placed back into the container and sealed for use in replicate measurements. This additional rest time did not affect the rheological results for the second sample. Data are reported as the average of rheological measurements for the two samples obtained from a single batch of hydrated gliadin. The results from the two samples had a range of standard error (SE) of 0.7–57.3% (3.5–21,750 Pa) at 30% MC and 3.6–78% (13–3,700 Pa) at 40% MC. At both MC, the highest error came at the lowest temperature, highest frequency, data point ( $25^{\circ}\text{C}$ , 6.28 rad/sec).

### Viscoelastic Measurements

Viscoelastic measurements were obtained using a rheometer (VOR-M, Bohlin Instruments, Cranbury, NJ) fitted with a 1.445 g-cm torsion bar, utilizing parallel plate geometry (25 mm plate diameter, 2.5 mm gap) as a function of frequency and temperature. Gliadin disks were loaded into the rheometer, and glue (Quick Tite, Loctite North America, Rocky Hill, CT) was used to secure the sample to the smooth bottom plate to eliminate or minimize slippage. The cross-hatched top plate was slowly lowered until a final sample thickness of 2.5 mm was achieved. Excess gliadin was carefully trimmed from around the edge of the plates using a razor blade.

To minimize moisture loss during measurements, a thin layer of mineral oil (Rite Aid Corp., Harrisburg, PA) was applied to the exposed sample edges. Additionally, humidified air was circulated around the parallel plates to further reduce possible sample moisture loss. The gliadin samples were allowed to rest in the rheometer for 1 hr before measurements were started. This allowed the stresses induced by loading the sample into the rheometer to relax completely, as indicated by the percent torque reading on the rheometer falling to 0.0%. All measurements were made at a strain of 0.00985, which will be referred to as 1% in this work. Previous work in our laboratory has shown that the linear viscoelastic limit of hydrated gliadin extended to at least 10% for the geometry used here at 38% moisture content. The multifrequency temperature sweep feature of the rheometer was used to obtain  $G'$ ,  $G''$ , and  $\eta'$  at three frequencies ( $\omega = 0.0628, 0.628, \text{ and } 6.28$  rad/sec)

to 25–80°C at 5°C intervals for the gliadin samples. A soak time of 300 sec was used at each temperature interval to allow for thermal equilibrium in the sample.  $G'$  and  $G''$  were measured at each frequency-temperature combination. The tangent of the phase angle between the storage and loss modulus was determined as  $\tan \delta = G''/G'$ . Basic viscoelastic results are reported as master curves referred to 25°C for  $G'$ ,  $G''$ ,  $\eta'$ , and  $\tan \delta$  obtained by time-temperature superposition. Horizontal shift factors were determined by superposing frequency sweep data obtained at each temperature >25°C onto the data obtained at 25°C at frequencies where overlap occurred (Ferry 1980b). Vertical shift factors were not used here because adequate superposition was achieved with horizontal shift factors only. Frequency sweeps from 0.6.28e<sup>-3</sup> to 12.5 rad/sec were used to obtain  $G'$ ,  $G''$ , and  $\eta'$  for PDMS385 at 25°C and for PDMS140 at 4°C.

The master curves obtained here for  $G'$ ,  $G''$ ,  $\eta'$ , and  $\tan \delta$  for the gliadin samples were plotted together with similar data obtained for the two PDMS samples (Figs. 1–3).  $G'$  and  $\tan \delta$  for these gliadins were also compared with results published for a series of linear polystyrene melts (160°C) MW 8,900, 58,700, and 275,000 (Onogi et al 1970) (Fig. 4). The polystyrene sample of MW 8,900 was unentangled. Thus, these comparisons will allow determination

of whether the viscoelasticity of gliadin is qualitatively similar to that of linear polymers, either with or without entanglements, but without the complicating factor of secondary associations.

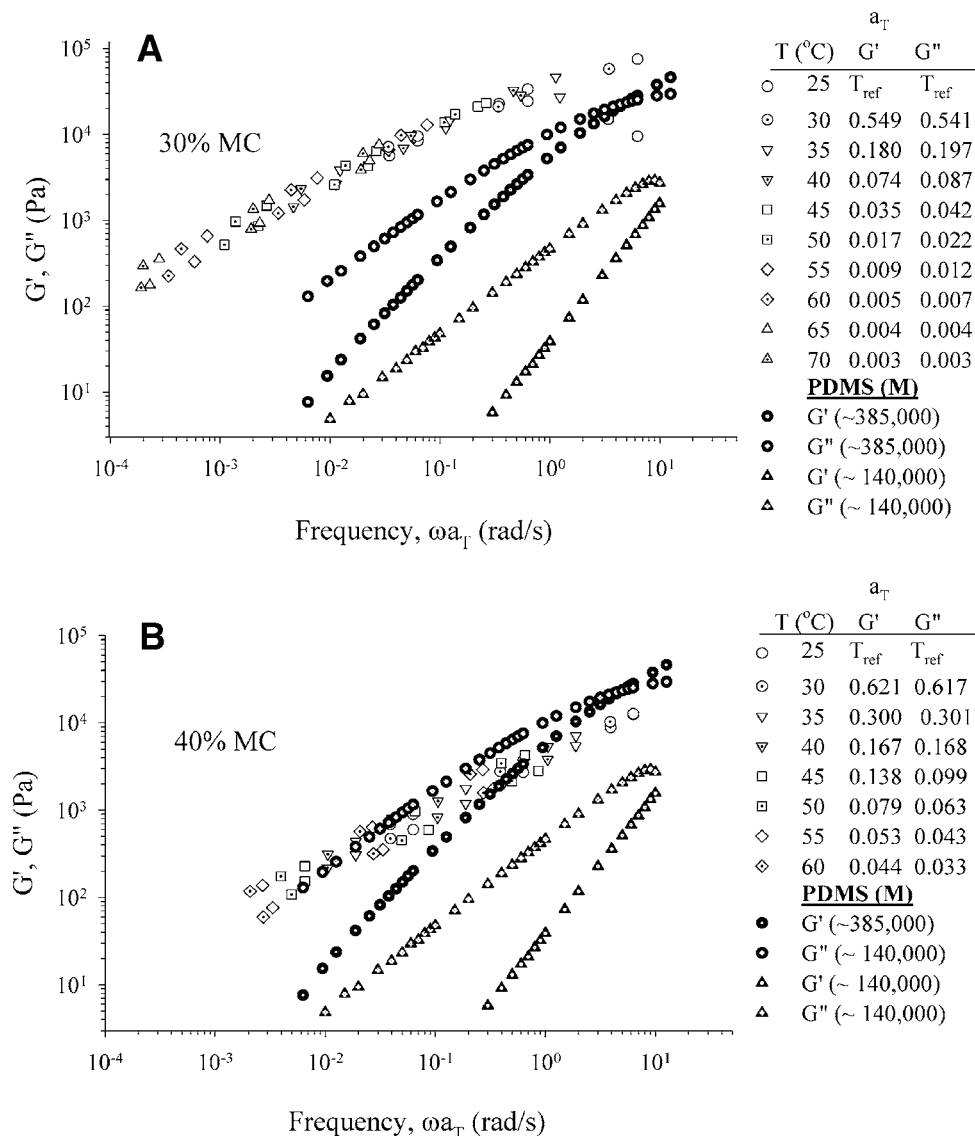
## RESULTS AND DISCUSSION

### Physical Appearance of Gliadins

Gliadin samples at both moisture contents were easily hand-shaped into disks that held their shape while loading onto the rheometer fixture, as were the PDMS samples. However, while resting between rheological measurements ( $\approx 4$  hr), the gliadin(40%) resting in the plastic cup flowed under gravitational stress while the gliadin(30%) held its shape and did not show any visible indications of flow. The PDMS samples also flowed readily at 25°C under gravitational stress. These observations suggest that a network structure (or at least a very high viscosity) was present initially in gliadin(30%) at 25°C, but not in gliadin(40%) or PDMS at 25°C.

### Dynamic Moduli

Master curves obtained by time-temperature-superposition for  $G'$  and  $G''$  (referred to as  $G'_R$  and  $G''_R$ ) for gliadin(30%) and



**Fig. 1.** Master curves for reduced dynamic moduli ( $G'_R$ ,  $G''_R$ ) obtained by time-temperature superposition of hydrated gliadin at moisture content (MC) of 30% (A) and 40% (B). Reference temperature 25°C.  $G'$  and  $G''$  data obtained at 4 and 25°C for poly(dimethylsiloxane) (PDMS) MW 140,000 and 340,000, respectively, shown for comparison.

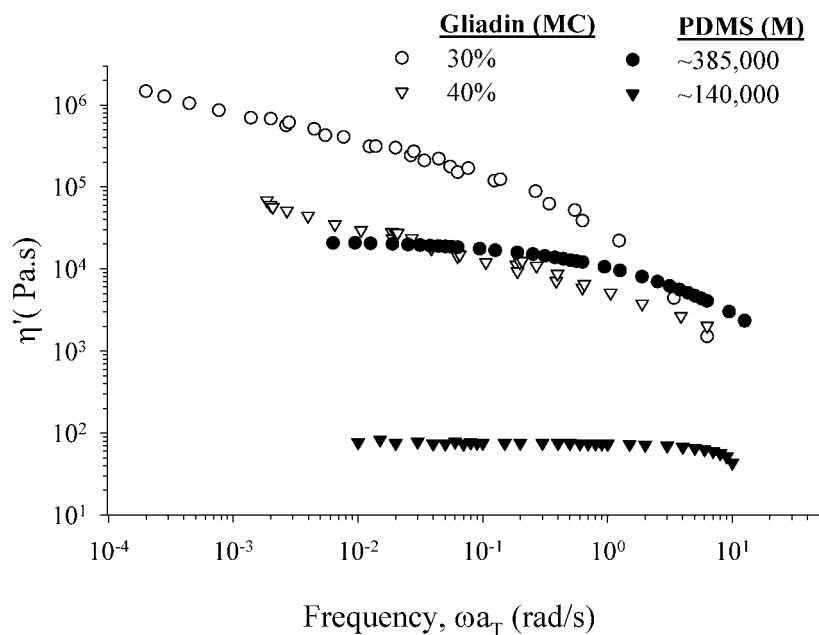
gliadin(40%) at 25°C are shown in Fig. 1A and B, respectively. Frequency sweep results for PDMS385 at 25°C and PDMS140 at 4°C are also shown in Fig. 1A and B for comparison of the gliadin results to linear polymers without any associative groups. Results will be discussed first for the gliadin samples themselves and then versus the PDMS samples. The frequency dependence of  $\eta'$  and  $\tan \delta$  will be discussed separately, as will the temperature dependence of the shift factors obtained by time-temperature superposition.

**Gliadin(30%)**

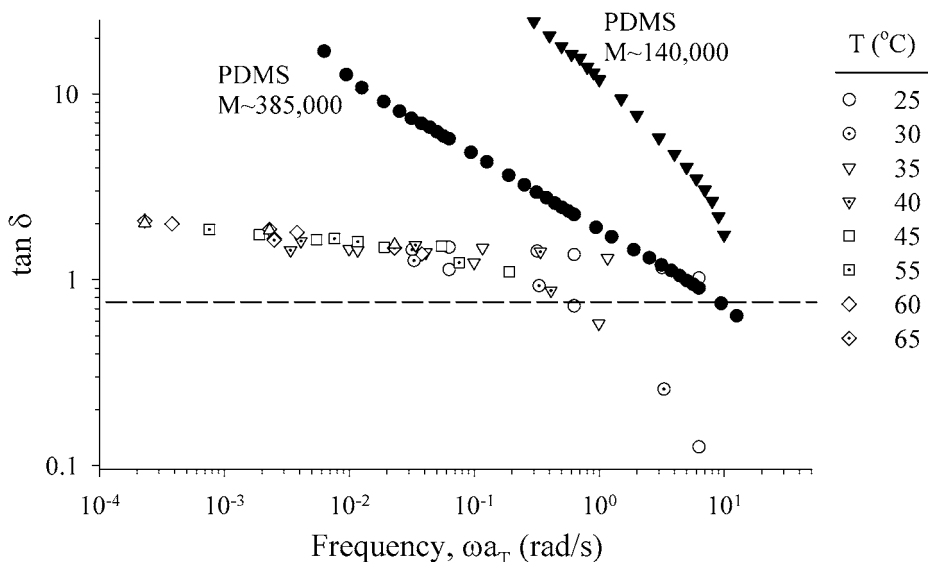
The frequency dependence of  $G'$  and  $G''$  can be expressed as  $G' = G'_0 \omega^{\eta'}$  and  $G'' = G''_0 \omega^{\eta''}$ , where  $\eta'$  and  $\eta''$  represent the slopes on log-log coordinates of  $G'_R$  and  $G''_R$  in the linear region, respectively. These values were determined as  $\eta' = 0.700$  (frequency range  $1.9 \times 10^{-4}$  to  $1.1 \times 10^{-2}$  rad/sec) and  $\eta'' = 0.646$  (frequency range  $2.0 \times 10^{-4}$  to  $1.2 \times 10^{-2}$  rad/sec) for gliadin(30%), where  $G''_R$  was  $> G'_R$ .

$G'_R$  and  $G''_R$  overlaid each other between frequencies of about 0.04 and 0.4 rad/sec, and at higher frequencies  $G'_R$  was  $> G''_R$ . This pattern in the dynamic moduli indicates a transition from a more liquid-like material ( $\tan \delta > 1$ ) to a more elastic material ( $\tan \delta < 1$ ) in this frequency range.

One of the gluten subfractions evaluated by Cornec et al (1994) that contained a high proportion of gliadin, actually showed the same type of interesting frequency dependence observed here for hydrated gliadin, where  $G'$  and  $G''$  essentially overlaid each other and showed power law frequency dependence for several decades of frequency. However, those authors interpreted this power law frequency dependence of the dynamic moduli as transition zone behavior because at one point  $G''$  did cross over  $G'$ . They assumed that the plateau and terminal zones were shifted to even lower frequencies for this fraction. As the proportion of large and medium glutenin polymers increased in the gluten subfractions,  $G'$  became  $> G''$  for the entire frequency range and the frequency



**Fig. 2.** Master curves for reduced dynamic viscosity ( $\eta'$ ) of hydrated gliadin at 30 and 40% moisture content (MC). Reference temperature 25°C. Data for  $\eta'$  obtained at 4 and 25°C for poly(dimethylsiloxane) (PDMS) MW 140,000 and 340,000, respectively, shown for comparison.



**Fig. 3.** Master curves for  $\tan \delta$  ( $G''_R/G'_R$ ) of hydrated gliadin at 30 and 40% moisture content (MC). Reference temperature 25°C.  $\tan \delta$  data obtained at 4 and 25°C for poly(dimethylsiloxane) (PDMS) MW 140,000 and 340,000, respectively, shown for comparison.

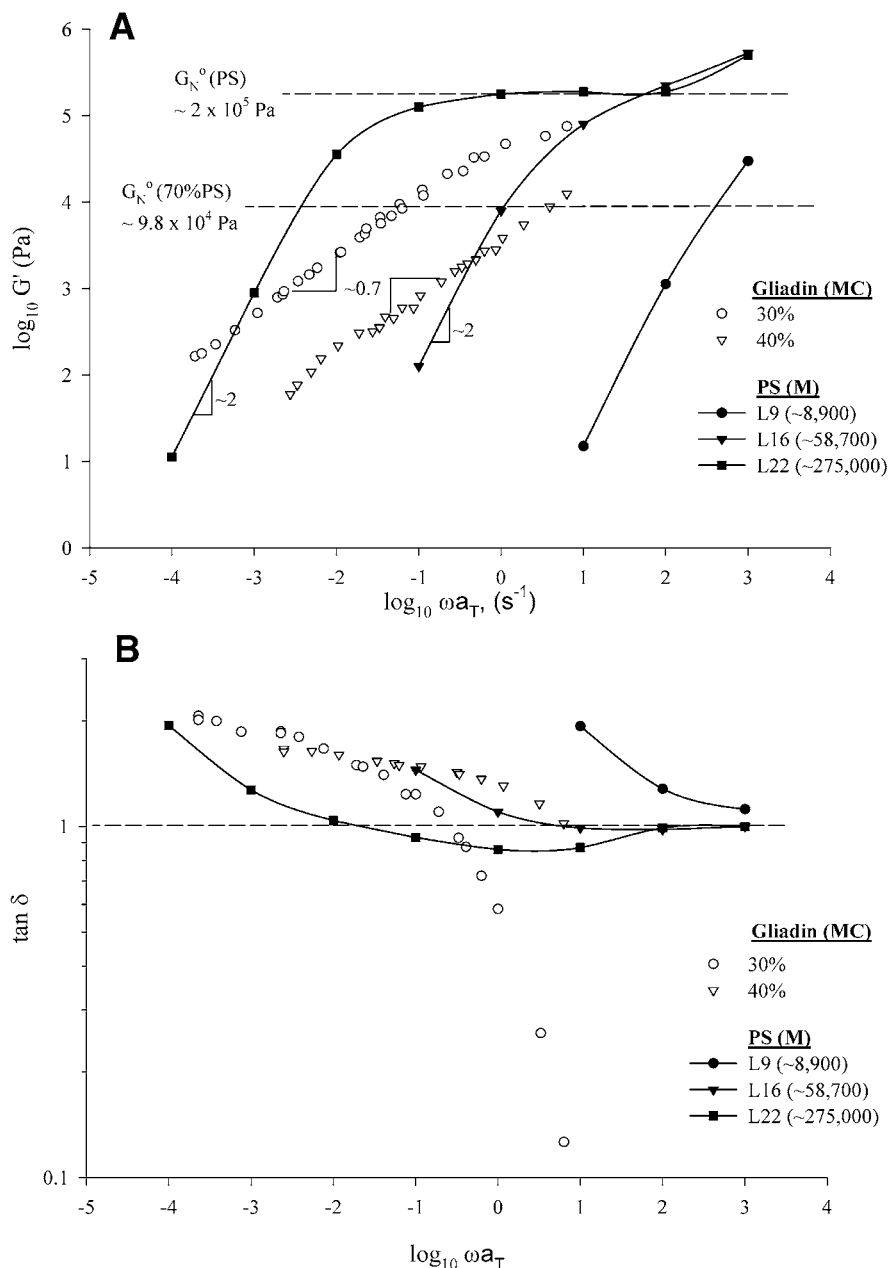
dependence of the moduli themselves decreased, which was indicative of a rubbery plateau due to the presence of some kind of network structure (Cornec et al 1994). But an increase in the proportion of gliadin in a gluten subfraction should enhance its viscous properties, which should result in a shift toward the terminal zone of viscoelasticity. Thus, it must be concluded that the power law behavior observed in the work of Cornec et al (1994) for the gluten subfraction with the highest gliadin content was, in fact, terminal zone behavior.

Madeka and Kokini (1994) also observed a power law spectrum for hydrated gliadin (25% MC) at 50°C. They found that  $G'$  was about equal to  $G''$  at 50°C for frequencies of 0.1–100 rad/sec, and both showed a similar power law slope of 0.45;  $G'$  and  $G''$  were nearly congruent to each other.  $G'$  became  $> G''$  at 70°C over the same frequency range and the power law slope of  $G'$  versus frequency was reduced to 0.26. At 100°C, the dynamic moduli were essentially frequency independent. This indicated the

presence of a well-developed plateau of rubber-like elasticity. Based on those frequency sweeps and additional temperature sweeps at 6.28 rad/sec, Madeka and Kokini (1994) identified three states of gliadin: entangled polymer flow  $\leq 70^\circ\text{C}$ ; a reactive cross-linking state  $\leq 130^\circ\text{C}$  that resulted in a rubbery plateau; and a softer cross-linked rubbery state  $> 135^\circ\text{C}$ . However, these researchers did not obtain data for  $G'$  and  $G''$  for gliadin for frequencies  $< 0.1$  rad/sec, which would have provided additional information on the permanence of the cross-links.

#### Gliadin(40%)

At first glance, the results for gliadin(40%) appear qualitatively similar to those of gliadin(30%), with  $G''_R > G'_R$  for much of the frequency range.  $G'_R$  approached  $G''_R$  for frequencies  $> 1$  rad/sec, but did not cross over  $G''_R$ , although the cross over may exist at higher frequencies. The magnitudes of  $G'_R$  and  $G''_R$  for gliadin(40%) were  $\approx 10\times$  lower than for gliadin(30%) at the same frequency,



**Fig. 4.** Comparison of plateau and terminal zone viscoelastic properties of hydrated gliadins at 30 and 40% moisture content (MC) and narrow-distribution polystyrenes for  $G'$  (A) and  $\tan \delta$  (B). Molecular weights (M) of the polystyrene samples: 8,900 (circle), 58,700 (triangle), 275,000 (square). Polystyrene data estimated from Figs. 2 and 3 of Onogi et al (1970).

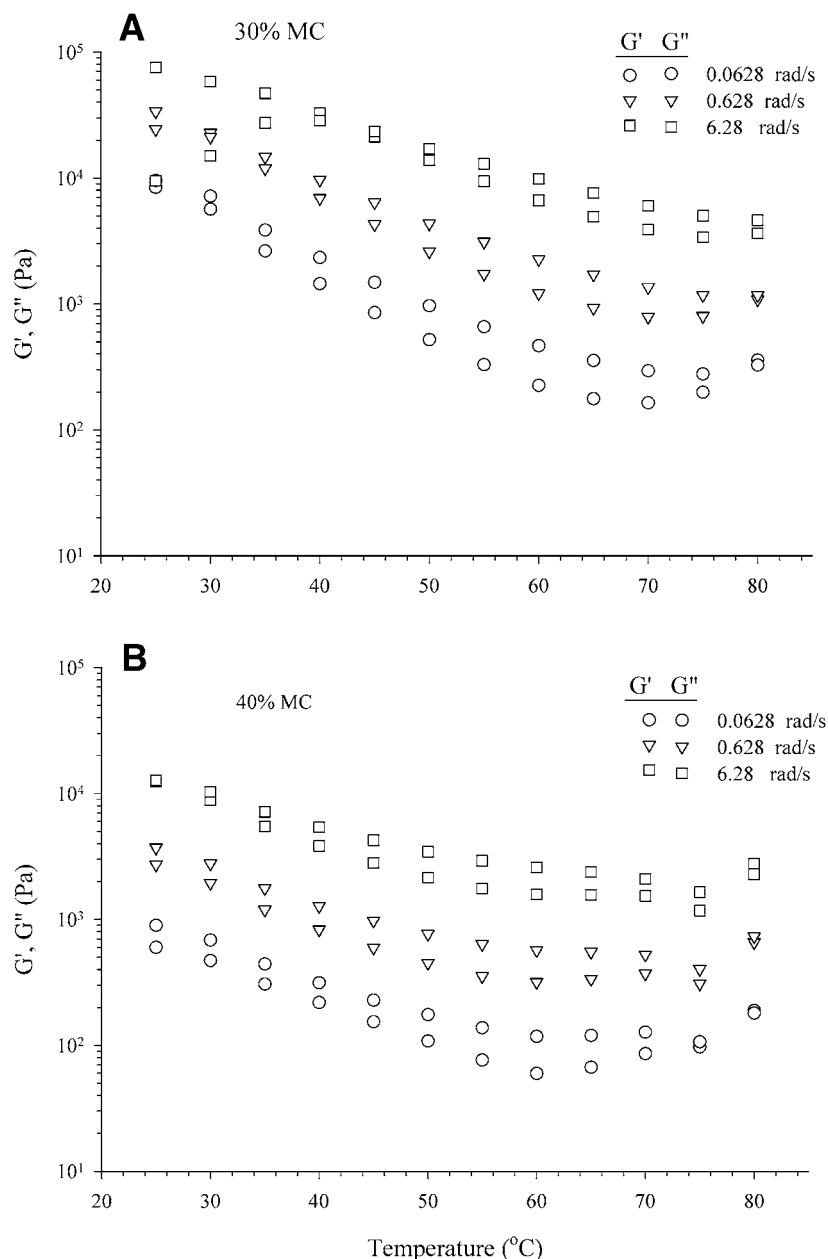
which would be expected due to the higher moisture content. The shifted frequency range for the gliadin(40%) master curves did not extend to as low a frequency as for gliadin(30%). This was due to the absence of experimental data at 65 and 70°C as compared with gliadin(30%). The upper temperature limit for time-temperature superposition was kept lower for gliadin(40%) because physical cross-linking apparently started at a lower temperature than for gliadin(30%), based on the decrease and then increase in  $G'$  with temperature as shown in Fig. 5.

The slopes in the linear range of  $G'_R$  and  $G''_R$  for gliadin(40%) were  $\eta' = 0.658$  (frequency range  $2.7 \times 10^{-3}$  to 0.1 rad/sec) and  $\eta'' = 0.614$  (frequency range  $2.1 \times 10^{-3}$  to 0.1 rad/sec), respectively, compared with the values of  $\eta' = 0.700$  and  $\eta'' = 0.646$  obtained for gliadin(30%). Given the similarity in these limiting slopes for both gliadin samples, it can be concluded that the main effect of higher moisture content was to shift the region of congruency of  $G'_R$  and  $G''_R$  and the crossover to elastic behavior to higher frequencies than observed here. Also, it is apparent that the limiting

slopes for linear uncross-linked polymers in the terminal zone of 2 and 1 for  $G'$  and  $G''$ , respectively, were not achieved at the lowest frequencies attained here.

### Comparison to Linear PDMS Samples

Frequency sweep data is also shown in Fig. 1A and B for the two PDMS samples. It is interesting that the magnitudes of  $G'_R$  and  $G''_R$  for gliadin(30%) were greater than for both PDMS385 and PDMS140.  $G'$  and  $G''$  for the PDMS samples showed the patterns expected for an increase in molecular weight for PDMS (Macosko and Benjamin 1981).  $G'$  and  $G''$  for HMW PDMS385 show more curvature in this frequency range than the LMW PDMS140 sample. The PDMS140 sample shows terminal zone melt flow behavior in this frequency range, where the slopes of  $G'$  and  $G''$  on logarithmic coordinates were essentially 2 and 1, respectively. For the PDMS385, the transition between the plateau and terminal zones occurred at  $\approx 2$  rad/sec, while  $G'$  and  $G''$  did not attain the limiting slope values of 2 and 1 in this frequency



**Fig. 5.** Temperature dependence of the dynamic moduli ( $G'$ ,  $G''$ ) extracted from iso-frequency temperature sweep data of hydrated gliadin at 30 and 40% moisture content (MC).

range. The values of  $\eta'$  and  $\eta''$  for PDMS385 were 1.5 and 0.94, respectively. The plateau value of  $G'$  ( $G_N^0$ ) for PDMS could not be determined from this data because the molecular weight of the PDMS samples was too low.

Macosko and Benjamin (1981) obtained a value of  $G_N^0$  of  $2.4 \times 10^5$  Pa for a PDMS sample with  $MW$   $2.1 \times 10^6$ . Thus, the  $G'_R$  values seen here for gliadin(30%) are actually greater than  $G_N^0$  for PDMS, even though the gliadin sample is diluted relative to the bulk (undiluted) PDMS sample.  $G''_R$  values for gliadin(40%) were similar in magnitude to  $G'$  for PDMS340 for frequencies  $<0.1$  rad/sec, but  $G'_R$  values were  $\approx 10\times$  greater than  $G'$  for PDMS385 at 0.01 rad/sec. This difference decreased at high frequencies and eventually  $G'$  and  $G''$  for PDMS385 exceeded that of the gliadin(40%) sample. Both gliadin(30%) and gliadin(40%) showed  $G'_R$  and  $G''_R$  values well above those of PDMS140 at the same frequency. Said another way, the same value of  $G'$  or  $G''$  for the gliadin samples was shifted to lower frequencies relative to PDMS140, which was unexpected given the lower average molecular weight of the gliadin proteins. The usual effect of an increase in molecular weight for uncross-linked linear polymers is a shift in the terminal zone to lower frequencies, as was seen for the PDMS samples.

It is not just the enhanced magnitudes of the viscoelastic functions of gliadin observed here relative to PDMS that are interesting, but the overall patterns of the viscoelastic functions for the gliadin samples also show clear differences relative to the linear PDMS samples. In particular,  $G'_R$  and  $G''_R$  were essentially parallel to and close to each other for about three decades of frequency, which was not seen for the linear PDMS samples. This pattern was also evident in the gliadin-enriched gluten subfractions of Cornec et al (1994). On the other hand,  $G'$  and  $G''$  diverged rapidly for the linear PDMS samples below the crossover frequency due to the steeper frequency dependence of  $G'$  relative to  $G''$ . These differences in the frequency dependence of  $G'$  and  $G''$  between the gliadin and PDMS samples will also affect the frequency dependence of  $\eta'$  and  $\tan \delta$ .

### Dynamic Viscosity

Differences between the two gliadin samples and the PDMS samples are also evident in the  $\eta'$  master curves as shown in Fig. 2. Both gliadin samples showed appreciable frequency dependence of  $\eta'$  over the entire frequency range, with no indication that a constant value of  $\eta'$  was close to being reached. The lowest frequency value of  $\eta'$  for gliadin(30%), which was  $>10^6$  Pa-sec, was actually much higher than  $\eta_0$  for a PDMS sample of MW 633,000, which was reported to be only 56,234 Pa-sec (Cosgrove et al 2002). The  $\eta'$  for gliadin(40%) was  $\approx 10\times$  less than for gliadin(30%) for frequencies  $<0.1$  rad/sec and was similar in magnitude (but not shape) to that of PDMS385. The  $\eta'$  for both gliadins became similar for frequencies  $>3$  rad/sec and were less than  $\eta'$  for PDMS385, but still significantly greater than  $\eta'$  of the PDMS140 sample. It can not be determined from this data what the high-frequency-limiting behavior of  $\eta'$  for the gliadin samples would be. Extending the high frequency portion of the master curve would involve frequency sweep data at temperatures  $<25^\circ\text{C}$ , which was not done here. This indicates that differences in moisture content had a greater effect on  $\eta'$  at low frequencies.

In contrast to the gliadins, PDMS140 showed a constant value for  $\eta'$  at low frequency, which is a good approximation to the steady shear Newtonian viscosity ( $\eta_0$ ), because the frequency dependence of  $\eta'$  is analogous to the shear rate dependence of the non-Newtonian shear viscosity (Ferry 1980c). The  $\eta'$  showed more curvature for PDMS385 versus frequency than did PDMS140 due to its higher molecular weight, but would be expected to show a frequency independent  $\eta'$  at lower frequencies. The critical molecular weight ( $MW_c$ ) that characterizes the onset of the effect of entanglement couplings on the molecular weight dependence of the Newtonian viscosity ( $\eta_0 \approx M^{3.4}$ ) for PDMS is  $\approx 30,000$

(Cosgrove et al 2002). Because the molecular weight of both of the PDMS samples exceeded  $MW_c$ , the Newtonian viscosity for PDMS385 was significantly greater than for PDMS140. The value of  $MW_c$  is apparently unknown for gliadin, which makes it unclear whether the crossover to the rubberlike plateau observed here for gliadin(30%) was due to entanglements, the presence of noncovalent associative groups, or some combination of the two.

Furthermore, the difference in overall shapes of the  $\eta'$  master curves for gliadin(30%) and gliadin(40%) means that the principle of time-concentration superposition does not apply as it does for linear synthetic polymers, even though time-temperature superposition was successful at each individual moisture content. This, in turn, implies that some structural change has occurred in the samples over this moisture content range and that the activation energies for flow were different for the two gliadins, and not just their viscosities. Changes in molecular structure of the cereal proteins have been reported to occur in this moisture range. Gil et al (1997), based on NMR studies, suggested that a  $\beta$ -sheet conformation may predominate in hydrated gliadin for  $MC \leq 35\%$ , whereas a looser  $\beta$ -turn conformation may form at  $MC > 35\%$ . Belton (1999) also noted that, as the degree of hydration of HMW glutenin subunits increases, there should be an increase in the amount of  $\beta$ -turn structures. The results for  $\eta'$  also imply that the degree of hydration of gliadin in gluten may have a dramatic effect on the viscosity of the gliadin component and, in turn, presumably the overall viscoelastic properties of gluten.

### Tan $\delta$

Another way to differentiate the gliadins and the PDMS samples is to compare the master curves for  $\tan \delta$ , which are shown in Fig. 3. Master curves for  $\tan \delta$  give information on the relative balance of viscous and elastic behavior as a function of frequency. Both gliadin samples showed similar values of  $\tan \delta$  for frequencies  $<0.1$  rad/sec. There was a gradual increase in  $\tan \delta$  from a value of  $\approx 1$  at this frequency to  $\approx 2$  at the lowest frequency of 0.0002 rad/sec. This pattern for the frequency dependence of  $\tan \delta$  is indicative of near-critical viscoelastic behavior, as at the gel transition point itself,  $\tan \delta$  is independent of frequency (Winter 1991). For frequencies  $>0.1$  rad/sec,  $\tan \delta$  for gliadin(30%) decreased rapidly with increased frequency to a value of  $\approx 0.1$ , while  $\tan \delta$  for gliadin(40%) remained above or close to 1 over the entire frequency range. Thus, gliadin(30%) showed a dramatic transition to predominately elastic behavior over just two decades of frequency (0.1–10 rad/sec), which was not seen with the gliadin(40%) sample. The combination of such a high value of  $\eta'$  at low frequency and such a drop off in  $\tan \delta$  at high frequency suggests that the secondary associations, which are likely the cause of the high viscosity, become frozen in place at higher frequencies, resulting in a relatively high degree of cross-linking, thus causing a pronounced elastic effect.

The frequency dependence of  $\tan \delta$  for the PDMS samples is strikingly different than that of either gliadin sample. PDMS140 showed a steep increase in  $\tan \delta$  from a value of  $\approx 1$  at 10 rad/sec to a value  $>10$  at  $\approx 0.3$  rad/sec.  $\tan \delta$  crossed through a value of 1 for PDMS385 from below as the frequency decreased, reflecting the crossover of  $G'$  and  $G''$  (Fig. 1A). Relative to the PDMS samples, it is clear that the onset of a predominantly viscous melt flow behavior at low frequency ( $\tan \delta \geq 1$ ) was not attained by either gliadin sample. This is consistent with the observation that the gliadin samples, particularly gliadin(30%), held their shape much longer under gravitational stress than either PDMS sample. The master curves also indicate that the balance of viscoelasticity shifts from more viscous ( $\tan \delta > 1$ ) to more elastic ( $\tan \delta < 1$ ) at a much lower frequency for the gliadin(30%).

### Comparison to Linear Polystyrenes of Different MW

In summary, the above results indicate that both gliadin samples showed enhanced viscoelastic properties relative to PDMS

silicone-based linear polymers of similar or even higher molecular weight. To confirm this observation,  $G'_R$  and  $\tan \delta$  for gliadin(30%) and gliadin(40%) were plotted together with similar master curve data for polystyrenes of different molecular weights ( $T_0 = 160^\circ\text{C}$ ) (Fig. 4). The polystyrene data was extracted from Figs. 2 and 3 of Onogi et al (1970) for narrow molecular weight distribution polystyrenes with MW 8,900, 58,700, and 275,000. The  $T_g$  for polystyrene is  $\approx 100^\circ\text{C}$ , so the polystyrenes master curves at  $160^\circ\text{C}$  reflect the viscoelastic functions for a  $(T_0 - T_g)$  of  $\approx 60^\circ\text{C}$ .

Madeka and Kokini (1994) reported that  $T_g$  reached a constant value of  $-25^\circ\text{C}$  (referred to as  $T_g'$ ) for gliadin with MC  $\geq 25\%$ . This suggests that the difference in the effective degree of physical crosslinking due to dilution was the main effect of differences in moisture content for MC  $\geq 25\%$ . It also means that the effective  $(T_0 - T_g')$  was  $50^\circ\text{C}$  for the master curves for both of the gliadins, which compares well to  $(T_0 - T_g)$  for the polystyrenes of  $60^\circ\text{C}$ . In any case, shifting the polystyrene data to a reference temperature of  $150^\circ\text{C}$  would not change the shapes of the curves at all, only their location along the frequency scale.

$G'$  showed the expected value of 2, indicating terminal zone viscoelastic behavior was achieved for all polystyrene samples. It was clear that the  $G'_R$  curves for gliadin(30%) and gliadin(40%) cut across the terminal  $G'$  curves for polystyrene of increasing molecular weight as the frequency decreased. Thus, at low frequencies, some chemical structure in the gliadins, apparently not present in the linear polystyrenes, impeded the large-scale motions of the gliadin molecules and prevented the characteristic terminal melt flow behavior seen with linear uncross-linked polymers. The effect was more pronounced for gliadin(30%).  $G_N^\circ$  for bulk polystyrene was reported to be  $2 \times 10^5$  Pa (Onogi et al 1970), compared with  $2.4 \times 10^5$  Pa for PDMS. The expected value of  $G_N^\circ$  for a 70% concentrated solution of polystyrene was calculated by us to be  $9.8 \times 10^4$  Pa, assuming the plateau modulus scales with  $c^2$ , where  $c$  is the concentration by weight of polymer (Ferry 1980d). Therefore, the high frequency value of  $G'_R$  for gliadin(30%) exceeded the plateau modulus for both PDMS and a 70% concentration polystyrene.

The shapes of the  $\tan \delta$  master curves for polystyrene and the hydrated gliadins were also quite different (Fig. 4B). The most dramatic difference was in the drop off of  $\tan \delta$  for gliadin(30%) for frequencies  $\approx > 0.1$ , relative to the shallow minimum observed for the entangled polystyrene of MW 275,000. The patterns for gliadin(30%) and gliadin(40%) do not match the frequency dependence of the lowest molecular weight polystyrene either, which was unentangled. The curvature of the gliadin(40%) sample at higher frequencies suggests that it is more likely to follow the pattern of the gliadin(30%) at higher frequencies than the polystyrene.

Based on the distinctly different frequency dependencies of the viscoelastic functions for gliadin relative to PDMS and polystyrene, it can be safely said that linear entangled polymers do not represent a good physical model for explaining the linear viscoelastic properties of gliadin. Better matches were found between the patterns seen here for the viscoelastic properties of hydrated gliadin and synthetic hydrogen bonding associating polymers.

## DISCUSSION

As the concentration of secondary interactions per unit volume increases in a synthetic associating polymer, one will approach the critical concentration required for gelation, that is, the conversion of a viscoelastic liquid to a viscoelastic solid (Rubinstein and Semenov 1998). More extensive substitution along the backbone in bulk associating polymers can actually result in the formation of thermoplastic elastomers that display a well-developed rubbery plateau similar to a covalently cross-linked rubber, except that the material can be melted and recycled, unlike a cross-linked rubber (Hilger et al 1990). Those authors showed that development of such a rubber-like quality in thermoplastic elastomers resulted

from phase-separation of extended hydrogen bonding domains, which were extensive enough to give rise to a differential scanning calorimetry (DSC) melting endotherm. In contrast, weaker thermo-reversible gels are obtained at intermediate degrees of physical cross-linking above the critical gelation point and generally only show a frequency-independent rubbery plateau at moderate to high frequencies ( $\omega > 6.28$  rad/sec) (or short times in creep), but show a frequency-dependent dynamic moduli at lower frequencies. This latter case is similar to the results seen here for gliadin(30%), other reported results described above for gliadin or gliadin-enriched gluten subfractions and for the hydrogen bonding PDMS samples of Klok et al (1999).

## Dynamic Moduli

The limiting slopes of the master curves for  $G'_R$  and  $G''_R$  on logarithmic coordinates in the terminal zone for gliadin(30%) are qualitatively similar to those of physical and chemical gels near the gel point. Congruency of master curves for  $G'$  and  $G''$  (i.e., the power law slopes of  $G'$  and  $G''$ ) were the same and  $G'$  was equal to  $G''$  over several decades of frequency was observed for chemically cross-linked polyurethanes and PDMS for molecular weights far below  $MW_c$  and with balanced stoichiometries (Chambon and Winter 1987). Balanced stoichiometry means that the number of reactive groups on the precursor polymer molecules was the same as for the cross-linking molecules as discussed in Chambon and Winter (1987). In that work, the critical gel point was determined by stopping a curing reaction at different times and conducting frequency sweeps on the stopped samples. Below the critical gel point,  $G'' > G'$  and both dynamic moduli approached zero at low frequency (i.e., showed viscoelastic liquidlike behavior), while beyond the critical gel point,  $G'$  started to show an equilibrium modulus at low frequency (i.e., viscoelastic solidlike behavior). The congruent power law spectrum, with a slope of 0.5, appeared as a transition between those two behaviors, and the time of curing corresponding to this power law spectrum was denoted as the gel time, and the material the critical gel. In all cases, samples near the gel point were only partially cross-linked, but the exact degree of cross-linking was not reported.

However, for cross-linked PDMS with unbalanced stoichiometry (a deficiency in the number of cross-linker molecule functional groups relative to the precursor molecules), master curves for  $G'$  and  $G''$  at the gel point were only parallel to each other but not congruent (Chambon and Winter 1987). Master curves for  $G'$  and  $G''$  were also parallel to each other at the gel point for a physical gelation process, where the transition from viscoelastic liquid to viscoelastic solid was induced by heating (Richtering et al 1992) but congruent for the physical cross-linking of hydrogen-bonding PDMS (Vasil'ev et al 1995). The latter case showed a smooth transition from the viscoelastic liquid state ( $G'' > G'$ ) through the critical gel transition and then to a viscoelastic solid state ( $G' > G''$ ) with increased time of heating as for the chemical cross-linking systems. So, the phenomenon of a power law mechanical spectrum for  $G'$  and  $G''$  over several decades of frequency, at or near the gel point, seems to be common to both chemical and physical gels. It is interesting to note that a similar smooth transition from power law behavior of the dynamic moduli to a rubbery plateau pattern is evident in the gluten subfractions of Cornec et al (1994 [see Fig. 4]), except that the transition was apparently due to an increased concentration of HMW glutenin subunits in the samples rather than due to a physical or chemical cross-linking process, where the relevant parameter controlling the effective degree of cross-linking is time of heating at elevated temperature or time of reaction, respectively. It remains an open question as to why such a change in the frequency dependence of the dynamic moduli occurred as the concentration of HMW subunits increased.

Patterns in the master curves for  $G'$  for gliadin(30%) and gliadin(40%) seen here were qualitatively similar to those reported for the master curves for  $G'$  and  $G''$  in hydrogen bonding polybu-

tadiene samples with increasing mol% of hydrogen bonding functional groups (Stadler and de Lucca Freitas 1986). The molecular weight of the precursor polymer molecules was  $MW \approx 50,000$ , similar to that of the gliadins. The control polybutadiene showed typical terminal zone behavior exhibiting the limiting slopes of 2 and 1, respectively for  $G'$  and  $G''$ . However for the modified samples, the terminal zone was shifted to lower frequencies, and the power law slopes were reduced from 1.2 to 0.66 as the degree of modification was increased from 1 to 2%. In a separate study, de Lucca Freitas and Stadler (1987) showed a similar trend in the slopes of the  $G'$  and  $G''$  master curves in the terminal zone relative to an unmodified control for a polybutadiene sample of  $MW \approx 27,000$ .

In addition, the value of  $G'_R$  for gliadin(30%) for frequencies above the crossover frequency was higher than  $G_N^0$  for PDMS or polystyrene. This could be further evidence of enhanced viscoelastic properties due to associative groups in the gliadin sample. Stadler and de Lucca Freitas (1986) also reported that the value of  $G_N^0$  increased with increased degree of substitution relative to the control for their polybutadiene samples.

The reduced slopes of the  $G'_R$  and  $G''_R$  curves for gliadin(40%) indicate that secondary interactions still apparently exert a dominant influence on the terminal zone viscoelastic properties for gliadin(40%). The tendency to show an increased slope at low frequency for  $G'_R$  may be related to the enhanced fluidity of gliadin(40%) that was observed in the handling of the samples at 25°C. At this temperature, gliadin(30%) did not flow under gravitational stress, but gliadin(40%) did.

Because the backbone chemistry and the effective cross-linking functionality of the gliadin was the same for gliadin(30%) and gliadin(40%), it is logical that differences in the concentration of associative groups per unit volume due to dilution with additional water was the most probable cause of the observed differences seen here in the linear viscoelastic functions between the two gliadins.

### Dynamic Viscosity

Many studies involving associative synthetic polymers include a section on the frequency dependence of  $\eta'$ , because the presence of associative groups has such a dramatic effect on the magnitude of the melt viscosity. Klok et al (1999) showed that the frequency denoting the onset of non-Newtonian behavior of  $\eta'$  for a hydrogen bonding PDMS sample was shifted first to lower frequencies at high temperatures as the rubbery network developed due to physical cross-linking. Eventually,  $\eta'$  became inversely proportional to frequency over the entire accessible frequency window (0.1–100 rad/sec) as  $G''$  became nearly constant with frequency. This final stage of a frequency-independent rubbery network was not seen here for gliadins at 25°C, but the frequency dependence of  $\eta'$  was similar to the PDMS samples of Klok et al (1999) with intermediate degree of cure.

The convergence of  $\eta'$  for both gliadin samples for frequencies  $>4$  rad/sec is qualitatively similar to the high frequency behavior of linear polymers of increasing molecular weight, which often converge to a single curve at the highest frequencies (Ferry 1980c). Also, hydrogen bonding polybutadiene polymers of MW 27,000 and 37,000 with increased mol% substitution resulted in increased values for  $\eta_0$  relative to the unmodified control, but the modified polymers all converged to the  $\eta'$  master curve for the unmodified polybutadiene polymer of the same molecular weight at higher frequency (de Lucca Freitas et al 1987). Thus, as for  $G'_R$  and  $G''_R$ , the gliadin samples showed enhanced  $\eta'$  at low frequency relative to the linear PDMS samples, which is one of the most salient features of associative synthetic polymers in general (Rubinstein and Dobrynin 1999).

Additional comparisons between the patterns of the viscoelastic functions seen here for hydrated gliadin and published results for synthetic associating polymers indicate clearly that hydrated gliadin is not a simple viscous or even a simple viscoelastic liquid

like PDMS. The presence of secondary associations apparently results in a very high viscosity for hydrated gliadin relative to its molecular weight, which in turn decreases the fluidity of hydrated gliadin at 25°C. Also, it is clear that gliadin(30%) can behave elastically at moderate frequencies ( $G' > G''$ ) in the linear viscoelastic regime. Thus, it is possible that hydrated gliadin may also contribute to elastic effects during flow of doughs at higher steady-state shears such as during dough mixing or sheeting. It is also interesting to speculate that the differences in the shapes of the master curves for gliadin(30%) and gliadin(40%) are at least partly due to the conformational change from  $\beta$ -spiral to the looser  $\beta$ -turn in gliadin that occurs at  $\approx 35\%$  MC as discussed above. More work is needed to further explore the relationship between moisture content, temperature, conformational changes, and the viscoelastic properties for a broader range of cereal proteins.

### Iso-Frequency Temperature Sweeps

The presence of associating groups also influences the shape of the iso-frequency temperature dependence of the dynamic moduli and the activation energy for flow. Experimental results obtained here for gliadin(30%) and gliadin(40%) are relative to similar results published for associating synthetic polymers. The experimental multifrequency temperature sweep data was replotted as iso-frequency temperature sweep data after Mours and Winter (1995). For gliadin(30%),  $G'$  decreased strongly for  $T \leq 70^\circ\text{C}$  for all three frequencies (Fig. 5A). At  $T > 70^\circ\text{C}$ ,  $G'$  started to increase with temperature for  $\omega = 0.0628$  rad/sec, while at  $\omega = 0.628$  and 6.28 rad/sec,  $G'$  attained a plateau value at  $>70^\circ\text{C}$ . The effect of temperature was lessened at higher frequencies. The patterns for the temperature and frequency dependence of  $G'$  and  $G''$  for these gliadins are very similar to those seen for the polybutadiene samples of MW 51,000 and with mol% substitution levels of 1 and 2 (Stadler and de Lucca Freitas 1986 [see Fig. 3]).

This was particularly the case for gliadin(30%) at the highest frequency, where  $G''$  was initially less than  $G'$ , but then actually increased initially as the temperature was increased, and became greater than  $G'$  at higher temperatures. Stadler and de Lucca Freitas (1986) reported "The prolonged curvature of the modified samples at low frequency indicates the marked effect of hydrogen bonds on the temperature dependent mechanical properties even at high temperatures". The  $G'$  and  $G''$  curves were approximately one order of magnitude lower for gliadin(40%) for the same frequency but showed curvature at high temperature similar to the gliadin(30%), suggesting that secondary interactions influence the dynamic moduli of gliadin(40%) as well (Fig. 5B). The lower  $G'$  values for the gliadin(40%) indicate a softer material over the temperature range evaluated here.

### Shift Factors ( $a_T$ )

We followed the format and analysis reported by de Lucca Freitas and Stadler (1988) for a series of polybutadiene samples of different molecular weights and degrees of modification with hydrogen bonding groups along the chain. Plots of the log of the shift factors obtained by constructing the  $G'_R$  and  $G''_R$  master curves for gliadin(30%) and gliadin(40%) versus  $1/T$  ( $\text{K}^{-1}$ ) are shown in Fig. 6.

Some associating polymer systems follow the principle of time-temperature superposition, while others do not. de Lucca Freitas et al (1987) showed that smooth master curves for the dynamic moduli could be successfully obtained by time-temperature superposition for a hydrogen-bonding polybutadiene as long as the hydrogen bonds involved only binary contacts between functional groups on different molecules. However, smooth master curves could not be obtained using the same set of temperature shift factors (time-temperature superposition failed) if an additional hydrogen bonding functional group was available (de Lucca Freitas et al 1987). There will be varying degrees of deviation from successful time-temperature superposition of the viscoelastic functions for

associating polymers. Also, it is not clear whether WLF kinetics, based on the increase in free volume due to an increase in temperature only, should be observed for complex biopolymer soft solids in general if  $(T_o - T_g) < 100^\circ\text{C}$  due to the additional plasticizing effects of water. The WLF equation is widely used to describe the temperature dependence of the shift factors for linear polymers and is usually written as

$$\log a_T = -c_1^0(T - T_o)/(c_2^0 + T - T_o) \quad (1)$$

where  $T_o$  is the reference temperature often taken as  $T_g$  of polymers (Ferry 1980b). The WLF equation is generally applicable for linear polymers for  $T_g < T < T_g + 100^\circ\text{C}$  (Ferry 1980b). As mentioned above, the effective  $(T_o - T_g')$  for the master curves for both gliadin(30%) and gliadin(40%) was  $50^\circ\text{C}$  ( $T_o = 25^\circ\text{C}$ ), well within the range of WLF kinetics for linear polymers.

A convenient test of the applicability of the WLF equation can be obtained by linearizing the equation used by de Lucca Freitas and Stadler (1988)

$$\frac{T - T_o}{\log a_T} = \frac{-c_2}{c_1} - \frac{(T - T_o)}{c_1} \quad (2)$$

and plotting  $(T - T_o)/\log a_T$  versus  $(T - T_o)$ . The empirical constants  $c_1$  and  $c_2$  can be determined from the slope and intercept of such a plot if the data is linear.

However, such plots of the shift factors obtained here were not linear (data not shown), and it was concluded that the free volume form of the WLF equation failed to describe the temperature dependence of the shift factors. This could be explained by the presence of an Arrhenius-type process related to the secondary associations in hydrated gliadin. This was also the case for the hydrogen bonding polybutadienes studied by de Lucca Freitas and Stadler (1988).

#### Apparent Activation Energies ( $\Delta H_a$ )

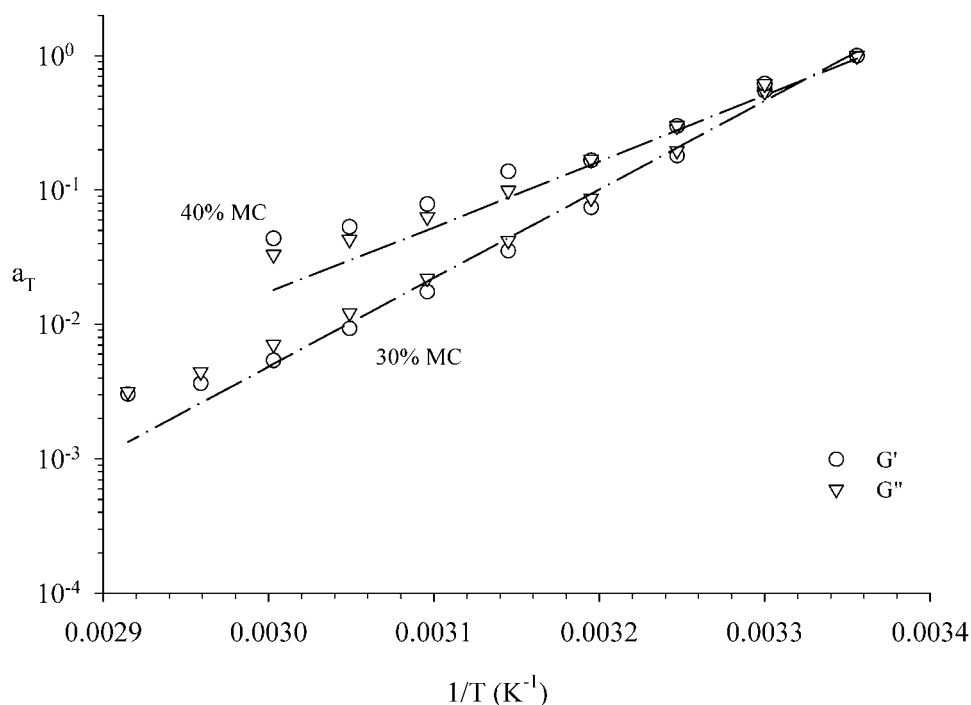
Because the temperature dependence of the shift factors did not follow the WLF equation, it made sense to determine activation energies in the terminal zone. However, as shown in Fig. 6, the

plots of  $\log a_T$  versus  $1/T$  were not linear over the entire temperature range used here. Thus, two values of  $\Delta H_a$  were determined for the gliadins, as suggested by the change in slope of the  $\log a_T$  versus  $1/T$  plots at  $\approx 60^\circ\text{C}$  for gliadin(30%) and  $\approx 50^\circ\text{C}$  for gliadin(40%).

The  $\Delta H_a$  values calculated from the slopes of the regression lines (slope  $\times 2.303 \times 8.314 \text{ J/g - mole K}$ ) were 123 kJ/mol and 93 kJ/mol for the gliadin(30%) and gliadin(40%), respectively for  $25\text{--}50^\circ\text{C}$ . These regression lines are shown in Fig. 6. The  $\Delta H_a$  was reduced to 84 kJ/mol (for  $45\text{--}60^\circ\text{C}$ ) and 65 kJ/mol (for  $55\text{--}70^\circ\text{C}$ ) for gliadin(30%) and gliadin(40%), respectively (regression lines not shown).  $\Delta H_a$  for the higher temperatures corresponds well to a  $\Delta H_a$  value of 49 kJ/mol calculated by us for a bulk, unmodified polyisobutylene (MW 96,600 and  $T_g - 68^\circ\text{C}$ ) using the Newtonian viscosity versus temperature data ( $24.5\text{--}130.2^\circ\text{C}$ ) reported by Agarwal and Lundberg (1984). Vasil'ev et al (1995) reported a  $\Delta H_a$  value for their hydrogen bonding PDMS (MW 37,200) of 22 kJ/mol, which was calculated directly from steady-state viscosity values at  $20\text{--}80^\circ\text{C}$ . This was higher than the  $\Delta H_a$  value for the unmodified PDMS, which was only 15 kJ/mol. It is important to note that over this temperature range, the modified PDMS was still a viscoelastic liquid, that is, below the temperature at which physical cross-linking began (Vasil'ev et al 1995). Those authors attributed the increase in  $\Delta H_a$  for modified PDMS relative to the unmodified PDMS to the presence of some intermolecular hydrogen bonds that were present in the former but not in the latter. However,  $\Delta H_a$  for this same PDMS sample increased to 98 kJ/mol at  $160\text{--}200^\circ\text{C}$ , which the authors attributed to increased intermolecular cross-linking at the higher temperatures.

De Lucca Freitas and Stadler (1988) determined apparent  $\Delta H_a$  values for polybutadiene samples with MW  $\approx 27,000$  and with increasing degree (mol%) of hydrogen bond substitution. They found that  $\Delta H_a$  increased with increased degree of substitution but the increase in  $\Delta H_a$  relative to the unmodified polymer decreased with increased temperature.

The enhancement of  $\Delta H_a$  ranged from 32 kJ/mol at the lowest temperature to 22.5 kJ/mol at the highest temperature, which corresponded to  $(T - T_g)$  values of  $\approx 88\text{--}188^\circ\text{C}$ , respectively. The



**Fig. 6.** Temperature shift factors for reduced dynamic moduli ( $G'_R$  and  $G''_R$ ) plotted as  $\log a_T$  versus  $1/T$  ( $\text{K}^{-1}$ ) for hydrated gliadin at 30 and 40% moisture content (MC). See text for procedure for calculation of activation energies.

highest value of  $\Delta H_a$  reported was 110 kJ/mol for the highest substitution level (7.5 mol%) and lowest temperature. It is expected that all of these  $\Delta H_a$  values would reflect relative differences in the activation energy of melt flow because ( $T - T_g$ ) was generally  $>100^\circ\text{C}$ .

The decrease in  $\Delta H_a$  for both gliadins at the higher temperatures suggests that a relatively small increase in the temperature reduced the effective number of intermolecular associations, which were present initially at  $25^\circ\text{C}$ . It is hard to make direct comparisons of  $\Delta H_a$  values for these gliadins and the synthetic polymers discussed above due to differences in ( $T - T_g$ ), concentration, and chemistry. However, the relatively high  $\Delta H_a$  values for the gliadins at low temperatures could be explained by the very high mol% (40–50) of glutamine residues in gliadin as compared with mol% substitutions of functional groups for associating polymers of  $\leq 7.5\%$  in the literature cited here. On the other hand, the  $\Delta H_a$  values for gliadins at the higher temperatures are in line with those reported for viscous flow of polymer melts but were obtained at a  $\Delta T$  ( $T_0 - T_g'$ ) of only  $50^\circ\text{C}$  as compared with  $\approx 100^\circ\text{C}$  for bulk polymer melts. This could be explained by the additional free volume and dissociation of hydrogen bonds in the gliadins by water as compared with bulk linear polymer melts.

## CONCLUSIONS

Analysis of the linear viscoelastic functions of gliadin hydrated to 30 and 40% MC in the terminal zone suggested that they are dominated by intermolecular, reversible (nonpermanent) secondary interactions similar to that observed for hydrogen-bonding synthetic associating polymers. Master curves for  $G'$  and  $G''$  indicated that if hydrated gliadin does contain entanglements, they only become evident at frequencies  $>1$  rad/sec at 30% MC, and at even higher frequencies for gliadin at 40% MC, so they may not be relevant to the slow flow processes involved in the fermentation and oven rise portions of breadmaking. The temperature shift factors could not be fit by the WLF equation, which is consistent with the idea that secondary associations are the primary factor in affecting the linear viscoelastic properties of gliadin in the terminal zone. The energy of activation decreased for the gliadin(40%) for temperatures of  $45\text{--}55^\circ\text{C}$  relative to the temperature range  $25\text{--}45^\circ\text{C}$  and for temperatures of  $55\text{--}70^\circ\text{C}$  relative to the temperature range  $25\text{--}55^\circ\text{C}$  for gliadin(30%). This suggests some loss of intermolecular associations in the higher temperature range, which apparently precedes physical gelation at even higher temperatures.

In addition, because the linear viscoelastic properties of associating polymers in general do not exhibit the same universal form of linear viscoelasticity in the rubbery plateau and terminal zones as do linear flexible polymers, the linear viscoelastic properties must be determined separately for each associating polymer of interest, at least until some recognizable pattern emerges for that particular class of associating polymer.

The series of articles cited here from the laboratory of Reimund Stadler has demonstrated such patterns for hydrogen-bonding polybutadienes. Further work will be needed to recognize and interpret patterns in the linear viscoelastic properties of hydrated cereal materials representing different classes and strengths of cereal cultivars.

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