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Rheological behaviors of doughs reconstituted from wheat gluten and starch

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Abstract Hydrated starch-gluten reconstituted doughs were prepared and dynamic rheological tests of the reconstituted doughs were performed using dynamic strain and dynamic frequency sweep modes. Influence of starch/gluten ratio on rheological behaviors of the reconstituted doughs was investigated. The results showed that the reconstituted doughs exhibited nonlinear rheological behavior with increasing strain. The mechanical spectra revealed predominantly elastic characteristics in frequency range from 10^{-1} rad s⁻¹ to 10^{2} rad s⁻¹. Cole-Cole functions were applied to fit the mechanical spectra to reveal the influence of starch/gluten ratio on Plateau modulus and longest relaxation time of the dough network. The time-temperature superposition principle was applicable to a narrow temperature range of 25°C ~40°C while it failed at 50°C due to swelling and gelatinization of the starch.

Keywords Gluten · Starch · Dough · Rheology · Compliance · Cole-Cole functions

Among the cereal flours, only wheat flour can form three-dimensional viscoelastic dough when mixed with water. Rheological testing in the linear viscoelastic region has been used to follow the structure and properties of doughs and to study the functions of dough ingredients (Miller and Hoseney 1999). Flour doughs can not be viewed simply as a concentrated suspension of starch granules in hydrated gluten matrix. Mixing starches from different wheat cultivars into dough with constant gluten content leads to large rheological differences, indicating an active role of starch (Petrofsky and Hoseney 1995). Starch, making up $\sim 80\%$ of wheat flour on dry basis, is able to form a continuous network of particles together with the macromolecular network of hydrated gluten. The starch fraction is largely responsible for the nonlinear viscoelastic behaviors of flour doughs (Khatkar and Schofield, 2002, Watanabe et al., 2002). The contributions of these two independent networks to the rheological behaviors of doughs are, however, difficult to resolve due to the starch-gluten interaction. Reconstituted doughs made with gluten and starch, on the other hand, behave qualitatively like flour doughs with comparable compositions (Smith et al., 1970) and have been applied as model systems for studying the component interactions (Uthayakumaran et al., 2002; Watanabe et al., 2002). Starches have been added to wheat flour to improve the qualities of noodles and baking performance of wheat flours. The reconstituted flour method is also used to evaluate the role of starch on the food quality (Chen et al., 2003; Huang and Lai 2010). The objective of this study was to investigate the dynamic rheological properties of reconstituted doughs with different starch/gluten ratios.

Materials and methods

Materials

Wheat gluten with protein content \ge 75%, starch content \le 10%, fat content \le 6.5% and ash content \le 0.95% and wheat starch with a particle size of 100 mesh were supplied by Shanghai Wangwei Food Co. Ltd., China.

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Methods

Wheat gluten and starch with three different starch/gluten (7/3, 6/4 and 4/6 in weight) ratios were mixed with deionized water and the doughs were further mixed on a three-rolling mixer (SG-65, Qinhuangdao Funing Chem. Light Machinery Plant, China) for 15 min at room temperature. The formed cohesive doughs were molded at room temperature and 10 MPa for 15 min to form discs of 25 mm in diameter and 2.0 mm in thickness. The discs were immersed in deionized water for 24 h to allow the sample attaining optimized water content. The optimized water content was determined as 45.0 wt.%, 50.7 wt.%, and 51.7 wt.% for the doughs with starch/gluten ratios of 7/3, 6/4 and 4/6, respectively, indicating that gluten absorbed more water than starch. This is consistent with the result of Uthayakumaran et al. (2002) who calculated optimum water by the method of American Association of Cereal Chemists (2000).

Dynamic rheological measurements were performed in duplicate in an advance rheomitric expanded system (ARES, Rheometrics Co., USA) in the modes of strain (γ) and frequency (ω) sweeps. Dynamic strain sweep was conducted with at ω =1 rad s⁻¹ by varying γ amplitude from 0.01% to 100%. Dynamic frequency sweep was performed at γ =0.1% by varying ω from 10⁻¹ rad s⁻¹ to 10² rad s⁻¹. Paraffine oil was coated on the sample surface exposed to air in order to eliminate moisture exchange with the surroundings (Song et al. 2007). With this procedure, the reproducibility error of compliances in the linearity region could be reduced to about 60%. Dynamic frequency sweep was conducted in a limited range from 25°C to 50°C in order to avoid accelerated water volatilization at higher temperatures.



Fig. 2 Dynamic storage compliance J' (hollow symbols) and loss compliance J'' (solid symbols) as a function of frequency ω at 25°C for the doughs with starch/gluten ratios of 7/3 (\square), 6/4 (\circ •) and 4/6 (Δ \blacktriangle)

Results and discussion

Dough rheology is one of the main factors governing the baking performance of wheat flours. Alternatively, dynamic rheological tests have been used to follow the structure and properties of doughs and to study the functions of dough ingredients for predicting the processibility and quality of food products (Dobraszczyk, 2004; Song and Zheng, 2007). Figure 1 shows storage and loss compliances (J' and J'') as a function of γ for the doughs with different starch/gluten ratios at 25°C. Both J' and J'' exhibit strong γ dependences (Petrofsky and Hoseney 1995). J' and J" remain constants at low strains while they increase rapidly at high γ amplitudes above a characteristic strain amplitude (γ_c). The dough with starch/gluten ratio of 7/3 shows lower compliances and γ_c value than the doughs with starch/gluten ratios of 6/4 and 4/6. The doughs with starch/gluten ratios of 6/4 and 4/6 have optimized water contents close to each other so that they exhibit similar nonlinear rheological behaviors.

The nonlinear viscoelasticity of flour doughs is highly related to the starch fraction (Khatkar and Schofield, 2002,



Fig. 1 Dynamic storage compliance J' (hollow symbols) and loss compliance J'' (solid symbols) as a function of strain γ for the doughs with starch/gluten ratios of 7/3 (\square **n**), 6/4 (\bigcirc **•**) and 4/6 (\triangle **▲**)



Fig. 3 Complex viscosity η^* as a function of frequency ω at 25°C for the doughs with starch/gluten ratios of 7/3 (**u**), 6/4 (**o**) and 4/6 (**A**)

Table 1Influence of starch/gluten ratio on rheologicalparameters of the doughs

Starch/gluten	4/6	6/4	7/3
Plateau compliance $J_{\rm N}^0$, 10^{-3} Pa ⁻¹	3.30	2.00	0.13
Plateau modulus $G_{\rm N}^0$, 10 ³ Pa	0.3	0.5	7.7
Newtonian steady-state viscosity η_0 , 10 ⁵ Pa s	0.25	0.4	3.0
Characteristic frequency ω_0 , rad s ⁻¹	0.18	0.28	0.07
Longest relaxation time τ_0 , s	5.5	3.6	14.3
Exponent <i>n</i>	0.36	0.38	0.32

Watanabe et al., 2002) so that a variation in starch/gluten ratio causes marked changes in the amplitude effect of compliances. It was evident that the dough with a higher starch content behaves more elastically at small strains in the linearity region while the dough structure is more sensitive to shear actions at $\gamma > \gamma_c$, indicating the significant influence of the starch component to the nonlinear viscoelasticity of doughs. On the one hand, starch granules in the dough reinforce the hydrated gluten network (Song and Zheng 2007) due to the active role of starch (Petrofsky and Hoseney 1995). On the other hand, they may also lower the consistency of the gluten network, leading the dough with a higher starch content to be less resistance to strains (Watanabe et al., 2002). The starch fraction shows the propensity to aggregate at high starch contents, which is largely responsible for the nonlinear viscoelasticity of the doughs (Khatkar and Schofield 2002). Starch granules at high contents might form particle network interpenetrating the hydrated gluten network. The starch network develops gradually with increasing starch content, giving rise to enhanced rheological nonlinearity with substantial narrowing of the linear viscoelastic range under shear action, as shown in Fig. 1. The amplitude effect of compliances is the most significant in the dough with starch/gluten ratio of 7/3, suggesting that the strain softening may be related to the breakdown of aggregates of starch granules and also to the local segregation effect caused by differences in viscoelasticity between the gluten network and the starch granules.

Figure 2 shows J' and J'' as a function of ω for the doughs at 25°C at γ =0.1% in the linear viscoelastic region. The mechanical spectra show predominantly elastic characteristics with J''>J' in the whole ω range. Both J'' and J'' decrease nonlinearly with increasing ω and the spectra are rather flat, suggesting that there exists a network structure in the doughs. The network formation might be related to the intermolecular interaction between gluten proteins and also between gluten and starch granules.

Figure 3 shows complex viscosity η^* as a function of ω for the doughs at 25°C. η^* decreases almost linearly with increasing ω . The slopes of η^* against ω are determined as -0.77, -0.74 and -0.73, respectively, for the doughs with starch/gluten ratio of 7/3, 6/4 and 4/6.

The mechanical spectra in the linear region shown in Fig. 2 encompass only a part of the viscoelastic plateau (Pruska-Kedzior et al., 2008). Viscoelastic properties in the upper ω region of the plateau can be quantified using Cole-Cole functions (Domenek et al., 2003; Pruska-Kedzior et al., 2008; Redl et al., 2003; Redl et al., 1999) where *J* and *J*" can be expressed as

$$J' = J_{\rm N}^0 \frac{(\omega_0/\omega)^n + \cos(n\pi/2)}{(\omega_0/\omega)^n + 2\cos(n\pi/2) + (\omega/\omega_0)^n}$$
(1)

$$J'' = \frac{1}{\eta_0 \omega} + J_N^0 \frac{\sin(n\pi/2)}{(\omega_0/\omega)^n + 2\cos(n\pi/2) + (\omega/\omega_0)^n}$$
(2)

Here, ω_0 is the loss peak characteristic frequency and *n* is the spread coefficient of the Cole-Cole distribution. ω_0 is located at the boundary between the plateau and transition zones of the mechanical spectrum and its reciprocal τ_0 is the longest relaxation time in the transition zone. The exponent *n* corresponds to the slopes of *J* and *J*" in the plateau to the glassy transition zone. η_0 is Newtonian steady-state viscosity, $J_N^0 = 1/G_N^0$ is plateau compliance and G_N^0 is plateau modulus. Eq. (1) and Eq. (2) were used to fit the data presented in Fig. 2 and the resultant parameters are listed in Table 1. Both G_N^0 and η_0 increase with increasing starch/gluten ratio, revealing the significant



Fig. 4 Master curves at 25°C for storage compliance J' (hollow symbols) and loss compliance J'' (solid symbols) as a function of frequency ω for the dough with starch/gluten ratio of 6/4 at 25°C ($\Box \blacksquare$), 30°C ($\circ \bullet$), 40°C ($\Delta \blacktriangle$) and 50°C ($\nabla \lor$). The inset shows frequency shift factor a_T as a function of reciprocal temperature 1/T

reinforcement effect of starch to the hydrated gluten network. In gluten doughs free of starch, ω_0 is related to the compositions of glutenins and gliadins (Hargreaves et al., 1996; Popineau et al., 1994; Pruska-Kedzior et al., 2008). The characteristic frequency ω_0 is 0.28 rad s⁻¹ and 0.18 rad s^{-1} for the doughs with starch/gluten ratios of 6/4 and 4/6, respectively, while it is reduced markedly in the dough with starch/gluten ratio of 7/3. This means that, in the starch/gluten doughs, ω_0 is affected mainly by the starch/ gluten ratio as well as the dough water content. The longest relaxation time τ_0 of the dough with starch/gluten ratio of 7/3 is 14.3 s and is much longer than those of the doughs with starch/gluten ratios of 6/4 and 4/6. The increase of τ_0 at high starch content reflects contribution of the starch network to the relaxation. The interfacial interaction between the starch granules and the hydrated gluten network might be assigned to the reinforcement effect and retardation of molecular relaxation in the transition zone.

Figure 4 shows master curves of J' and J'' at 25°C for the dough with starch/gluten ratio of 6/4 to check the applicability of the time-temperature superposition principle. The superposition is fairly good at temperature $T \leq 40^{\circ}$ C while it fails at 50°C, suggesting that the dough is not thermorheologically simple (Ferry, 1980). The frequency shift factor $a_{\rm T}$ is shown in the inset as a function of reciprocal temperature 1/T. The temperature dependency of $a_{\rm T}$ at $T \leq 40^{\circ}$ C can be described by the Arrehenius law,

$$a_{\rm T} = A \exp\left\{\frac{E_{\rm a}}{RT}\right\} \tag{3}$$

where E_a is activation energy, R is the universal gas constant, and A is a pre-exponential factor. The E_a value is determined as 36.0 ± 0.8 kJ mol⁻¹ according to least-square fitting to the data at $T \leq 40^{\circ}$ C. The thermorheological complexity of the dough could be ascribed to the swelling and gelatinization of starches at elevated temperatures (Dogan, 2002). The transfer of water from the gluten network to the starch component during heat treatment causes the swelling of starch granules. The starch gelatinization lowers the starch-gluten interactions in the dough, resulting in the failure of the time-temperature superposition principle. On the other hand, heating above 50°C may strengthen the gluten structure due to disulfide/ sulfhydryl exchange reaction that causes gluten in the interspaces between starch granules to coagulate to a continuous network (Hayta and Schofield 2005).

The reconstitution method is effective for investigation the effects of flour constituents and their interaction on rheology of wheat flour doughs. Investigation dynamic rheology of reconstituted flour doughs is of importance for evaluating end-use quality of flours and for establishing relationships between fundamental rheological tests and flour composition.

Conclusions

In conclusion, starch granules are responsible for enhanced rheological nonlinearity of the starch-gluten doughs. $G_{\rm N}^0$, η_0 and τ_0 increase with increasing starch/gluten ratio according to data fitting the Cole-Cole distribution functions to the linear viscoelasticity of the doughs. The starch granules are largely responsible for the reinforcement effect and the retardation of molecular relaxation in the transition zone.

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