Eur Food Res Technol (2008) 227:199–207
DOI 10.1007/s00217-007-0710-0

ORIGINAL PAPER

Comparison of viscoelastic properties of gluten from spelt and common wheat

Anna Pruska-Kedzior · Zenon Kedzior · Ewa Klockiewicz-Kaminska

Received: 3 April 2007 / Revised: 7 June 2007 / Accepted: 19 June 2007 / Published online: 27 July 2007

Abstract Rheological properties of gluten from spelt and common wheat were studied. The mechanical spectra of gluten samples were registered over a frequency range of 0.001–200 rad/s. Retardation tests were performed to keep all measurements within a linear regime. The mechanical spectra were fitted with Cole–Cole functions to calculate the viscoelastic plateau modulus G_N^0, the central frequency of the upper dissipative loss peak ω_0, and the spread parameter n. Steady state compliance J_e^0 and Newtonian viscosity η_0 were determined from the retardation tests results. Recovery data were converted from time to frequency domain using the Kaschta method and combined with dynamic data; this enabled the extension of the gluten mechanical spectra down to 10^{-6} rad/s, revealing the lower dissipative peak loss. The width of the viscoelastic plateau τ_m^0/τ_0 was calculated, and substantial qualitative and quantitative differences were found in spelt and common wheat gluten. All differences in gluten rheological properties were related to spelt and common wheat flour baking quality and protein composition.

Keywords Wheat · Spelt · Gluten · Dynamic rheology · Retardation test

Introduction

Spelt wheat, *Triticum aestivum* ssp. *spelta* (L.) Thell. is traditionally used for baking in countries such as Germany, Austria, and Switzerland. Recently emerging in the market as a speciality food, this cereal has received increasing interest from wheat breeders and food technologists due to its genetic potential for improving common wheat cultivars resistance to plant diseases and the potential technological and nutritional value of the species itself [1–8].

Genetic foundations of spelt diversity, especially its prolamins composition, have been extensively examined [9–16]. Many researchers claim that the technological potential of spelt for milling, bread making, and pasta production is very promising [1–3, 5–8, 17]. Spelt is reported to have a higher protein content and a higher participation of the aleurone layer in the kernel than common bread wheat [2]. It is also believed that spelt possesses valuable nutritional potential due to its protein content and composition as well as its lipids and crude fibre [6, 15, 18–22]. Nevertheless, spelt products are not allowed for consumers suffering from celiac disease [20, 21].

Dough made from spelt flours is characterised by lower stability, less elasticity, and higher extensibility than common wheat dough. Spelt dough is very soft and sticky after kneading; thus, handling spelt dough is more difficult, and the loaf volume is generally lower than modern wheat cultivars [1, 5, 8, 9, 17]. Spelt usually observes a higher yield of wet gluten and higher gluten spreadability, i.e. weaker gluten structure [5, 7, 8]. Rheological properties of common and spelt wheat dough depend largely on gluten matrix viscoelastic properties, which are predetermined by the qualitative and quantitative composition of monomeric gliadin(s) and polymeric glutenin(s) fractions.

A. Pruska-Kedzior · Z. Kedzior (✉)
Institute of Food Technology,
The August Cieszkowski Agricultural University,
ul. Wojska Polskiego 31, 60-624 Poznan, Poland
e-mail: kedziorm@au.poznan.pl

E. Klockiewicz-Kaminska
Centre for Cultivar Testing,
63-022 Slupia Wielka, Poland

Schober et al. [12] divided spelt cultivars into three quality groups according to baking quality: similar to modern bread wheat (group 1), typical spelt (group 2), and low quality (group 3). Based on capillary zone electrophoresis (CZE), the authors distinguished pure spelt cultivars and showing traces of crosses with common wheat. Among cultivars without crosses, only cv. "Schwabenkorn" (SKO) was qualified for group 1.

There are some essential differences between spelt and common wheat in the number of fractions and molecular masses of α-, γ-, and ω-gliadins as well as HMW- and LMW-glutenin subunits (GS) [10–12]. RP-HPLC reveals much higher content of total gliadins and lower total glutenins in spelt. The gliadins/glutenins (Gli/Glu) ratio is significantly higher in spelt, and α-gliadins are predominant, followed by γ-gliadins, and LMW-GS; ω-gliadins and HMW-GS are generally minor components [14]. Differences between ω5- and ω1,2-gliadins content and composition have also been observed [1, 13]. Following alleles coding HMW-GS are present in spelt but absent in bread common wheat: *Glu-B1 d** (6.1 + 22.1), *Glu-B1f** (13 + 22*), *Glu-B1g** allele *j** (6.1), and allele *k** (22.1). Alleles coding LMW-GS that are present in spelt but absent or rare in bread common wheat include *Glu-A3h* and *Glu-B3d* [16].

Spelt and common wheat gluten represent convenient natural models of gluten structures differing significantly in their elementary building blocks, i.e. gliadins and glutenin subunits composition and Gli/Glu ratio. The present work compares the fundamental viscoelastic properties of spelt gluten with those of common bread wheat gluten of good and relatively weak baking quality over an extended time scale of observation. Spelt cv. SKO has been chosen as the cultivar for study without any traces of crossing with common wheat but similar in its baking quality to common bread wheat.

Materials and methods

Experimental material

The grain of spelt cv. "Schwabenkorn" (SKO) (HMW-GS composition: 1/6 + 8/2 + 12) [9] and two common wheat cvs, "Begra" (*N*/7 + 9/5 + 10) [23] and "Wilga" (*N*/7 + 9/2 + 12) [23], harvested in 2004 (Plant Breeding Station DANKO, Choryn, Poland) were milled into flours on a Quadrumat Senior laboratory mill. Spelt grain was dehulled before milling. The grain moisture was adjusted to 14% overnight before milling. Gluten samples were washed out manually from the flours, freeze-dried, and stored at 4 °C in an oxygen-reduced atmosphere. Starch removal during gluten washing was controlled using the starch/iodine reaction.

General technological and chemical characteristics of studied samples

The baking quality of common wheat and spelt flours was estimated by a gluten yield and spreadability test [24], a Zeleny test [25], and by farinographic characteristics [26]. Dry matter content and protein content ($N \times 5.7$) were determined for the flours and gluten samples.

Protein fractional composition

The general protein fractional composition of spelt and common wheat flours was determined by the three-step extraction procedure [27, 28]. The flours were defatted with *n*-butanol and air-dried overnight at room temperature. A 10 g defatted flour sample was extracted with 50 ml of a pyrophosphate buffer (0.01 mol L^{-1}, pH 7.0) for 1 h. The mixture was centrifuged for 15 min at 3,000*g*, the supernatant was collected, and the extraction was repeated again three times. The combined pyrophosphate buffer soluble (PBS) protein extracts will be referred to as albumins and globulins. Next, the procedure was repeated using acetic acid (0.05 mol L^{-1}) to isolate the acetic acid soluble (AAS) prolamins. The last step of the procedure consisted of twofold extraction with 50 mL of NaOH (0.1 mol L^{-1}) to extract glutenins. All operations were conducted at 4 °C. Insoluble nitrogen-containing residue would correspond to an insoluble glutenin macropolymer protein (GMP).

Rheological measurements

Samples of freeze-dried gluten were rehydrated using a two-step procedure. First, 500 mg of gluten powder was swelled in 1 mL of distilled water for 30 min to enable the native gluten structure to form. Next, 4 mL of aqueous solution of *N*-ethylmaleimide (NEMI) (0.1 mol L^{-1}) was added to prevent chemical ageing of the gluten structure induced by sulfhydryl-disulfide interactions, as previously described [29, 30]. Rheological measurements were carried out at 20 °C using a Rheometric Scientific stress-controlled rheometer model SR 500. The cone-plate measurement geometry was used (cone diameter 25 mm, cone angle 0.1 rad). The samples were covered with 0.1 mol L^{-1} NEMI to avoid drying. After 1 h rest time, each sample was submitted to a frequency scan in dynamic mode and to a retardation test. Mechanical spectra were recorded over the frequency range 0.001– 200 rad/s; strain amplitude was kept within 3%. Retardation tests were performed with a creep stress value low enough to maintain the strain linearity range (σ_0 = 25, 20 and 2 Pa for samples of gluten "Begra", spelt SKO, and "Wilga", respectively). Creep was carried on during 10 h and creep recovery was recorded during 40 h.

Interpretation of rheological measurements

Mechanical spectra obtained from dynamic data were plotted as functions of storage and loss moduli (G', G''), or of storage and loss compliances (J', J'') versus the angular frequency ω. The compliances are defined as $J' = G'/\left(G'^2 + G''^2\right)$ and $J'' = G'/\left(G'^2 + G''^2\right)$ The Kronig–Kramers relation (Eq. 1) was used to verify the linearity of the gluten viscoelactic response over the experimental frequency window [31].

$$G''(\omega) = \frac{\pi}{2}\frac{\mathrm{d}G'(\omega)}{\mathrm{d}\ln(\omega)} \tag{1}$$

The J', $J'' = f(\omega)$ mechanical spectra were fitted with phenomenological Cole–Cole functions (Eqs. 2–4) yielding the plateau compliance J_N^0, plateau modulus $G_N^0 = 1/J_N^0$, loss peak characteristic frequency ω_0, and spread parameter n related to the peak broadness [31]. These parameters describe viscoelastic properties and provide information on the networking state of a polymer structure in the upper frequency limit of the viscoelastic plateau.

$$J' = J_N^0 \frac{\left[\left(\frac{\omega_0}{\omega}\right)^n + \cos\pi\frac{n}{2}\right]}{\left[\left(\frac{\omega_0}{\omega}\right)^n + 2\cos\pi\frac{n}{2} + \left(\frac{\omega}{\omega_0}\right)^n\right]} \tag{2}$$

$$J'' = J_N^0 \frac{\sin\pi\frac{n}{2}}{\left[\left(\frac{\omega_0}{\omega}\right)^n + 2\cos\pi\frac{n}{2} + \left(\frac{\omega}{\omega_0}\right)^n\right]} \tag{3}$$

$$J'' = \left(\frac{J_N^0}{2\tan\left(\pi\frac{n}{2}\right)}\right)\left[\left(1 + 4\frac{J'}{J_N^0}\left(1 - \frac{J'}{J_N^0}\right) \times \tan^2\left(\pi\frac{n}{2}\right)\right)^{1/2} - 1\right] \tag{4}$$

In the retardation test, assuming that the creep time t_0 was long enough to reach the steady state, the creep compliance $J(t)$ becomes a linear function of time ($t \le t_0$) as shown in Eq. 5 [32].

$$J(t) = J_e^0 + \frac{t}{\eta_0} \tag{5}$$

The steady-state viscosity η_0 and steady state compliance J_e^0 were determined by fitting Eq. 5 to the steady state part of the creep curves. These parameters relate to a polymer structure in a lower frequency limit of the viscoelastic plateau. The steady-state compliance J_e^0 was taken as a measure of overall total elastic deformation; note that J_e^0 is extremely sensitive to molecular mass distribution. The recoverable creep compliance $J_r(t)$ was determined from the creep recovery part ($t > t_0$) of the retardation test results as follows [32]:

$$J_r(t) = J(t_0) - J(t) \tag{7}$$

where t_0 is the total experimental creep time.

Kaschta and Schwarzl's [33] method was used to calculate the discrete retardation spectrum from the recoverable creep compliance $J_r(t)$, and $N = 8$ retardation modes were used (two spectral lines per decade) with a generalized Kelvin–Voigt model:

$$J_r(t) = \sum_{k=1}^{N} J_k\left(1 - \exp\left(-t/\tau_k\right)\right) \tag{8}$$

The discrete retardation spectrum was given by the set of $2N$ positive constants $\{J_k, \tau_k\}$ where J_k and τ_k are the intensity and the retardation time of the k^{th} spectral line, respectively. This spectrum was subsequently converted from time to frequency domain; storage (J'), loss (J''), and recoverable loss (J_r'') compliances were calculated from Eqs. 9–11 [31, 32].

$$J'(\omega) = \sum_{k=1}^{N} \frac{J_k}{1 + (\omega\tau_k)^2} \tag{9}$$

$$J''(\omega) = \frac{1}{\omega\eta_0} + \sum_{k=1}^{N} \frac{J_k(\omega\tau_k)}{1 + (\omega\tau_k)^2} \tag{10}$$

$$J_r''(\omega) = J''(\omega) - \frac{1}{\omega\eta_0} \tag{11}$$

This approach enabled the extension of the mechanical spectra frequency window to 10^{-6} rad/s. The glassy compliance J_g term was neglected in Eqs. 5, 8, and 9, since its order of magnitude for gluten (~10^{-9} Pa^{-1}) is much smaller than the compliance values measured in the experimental time window [29].

Results and discussion

General technological and chemical characteristics of studied samples

The protein content in spelt flour (14.7%) was significantly higher than in common wheat flours (see Table 1). Other studies report spelt flours protein contents ranging from 12.5 to 19.5% with a mean value ca. of 15% [1, 2, 5, 17].

As shown in Table 1, wet gluten yield was significantly higher for spelt (42%) than for common wheat, and spelt gluten spreadability was higher than technologically weak cv "Wilga". Other authors observe gluten yield ranging from 34.1 to 51.8% for spelt flour, with an average of nearly 40% for spelt cv. SKO [2, 5]. The spelt flour used in

Table 1 General characteristics of spelt and common wheat flours and gluten preparations (mean value ± SD)

Sample	Moisture (%)	Protein content ($N \times 5.7$) (% d.m.)	Wet gluten yield (%)	Gluten spread ability (mm)	Gluten value
Laboratory flours					
Spelt SKO	13.3 ± 0.02	14.7 ± 0.09	42.0 ± 0.1	10.5 ± 0.7	55.3 ± 1.9
"Begra"	14.0 ± 0.02	12.5 ± 0.24	32.9 ± 0.3	6.3 ± 1.1	52.5 ± 2.3
"Wilga"	13.6 ± 0.02	12.1 ± 0.17	30.1 ± 0.8	9.5 ± 0.7	41.6 ± 1.4
Freeze-dried gluten preparations					
Spelt SKO	2.80 ± 0.34	77.52 ± 0.88			
"Begra"	3.82 ± 0.57	82.55 ± 1.23			
"Wilga"	3.06 ± 0.11	80.72 ± 1.28			

the present study, despite its relatively high gluten spreadability, can be classified as good, like the common wheat "Begra" flour. "Wilga" wheat flour also can be classified as "good" but at the lower border of this quality class. The protein content ($N \times 5.7$) in the gluten preparations was the lowest in the spelt gluten (77.5%; most probably due to slightly higher content of fine fibrous particles) and exceeded 80% in common wheat glutens.

According to the Zeleny test, all flours represent sufficient baking quality (Table 2). Bojnanska and Francakova found higher sedimentation values for spelt cv. SKO (33–46, average 39.9 mL) [2]. Other authors have reported values ranging from 18 to 44.5 mL [1, 5, 17]. Farinographic analysis reveals that the water absorption capability for the spelt flour was slightly less (57.7%) than for common wheat (Table 2). All other farinographic parameters of spelt flour represent intermediate values as related to studied common wheat flours. Ceglinska [5] found slightly higher water absorption for spelt (62%) and a shorter spelt dough stability (1.7 min). Bonafaccia et al. [3] noted water absorption of 58% for spelt flour.

Albumins and globulins represented about 20% of the protein content for spelt and common wheat cv. "Begra" flours (Table 3). Common wheat cv. "Wilga" flour contained ca. 30% of albumins and globulins. The values found for common wheat are typical for these cultivars [30, 34]. There were substantial differences in the total gluten protein (TGP) composition between spelt and common wheat. AAS prolamins represented 94.1% of TGP in spelt flour, making them much more than in wheat flours (85–87% TGP). Spelt flour contained half as much NaOH-soluble glutenins (5.1% TGP) as common wheat flours (~10% TGP). Moreover, NaOH-insoluble nitrogen compounds represented only 0.8% TGP in spelt flour but 3.0–4.4% in common wheat. According to Wieser [14], gluten proteins from spelt cv. SKO contain 75.3% of total gliadins, 17.7% of LMW-GS, and 6.6% of HMW-GS; total gliadins and LMW-GS represent 93% of TGP. The amount of AAS prolamins found in our work remains very close to the last value. Therefore, it seems possible that most of the LMW-GS of spelt cv. SKO are acetic acid soluble.

Rheological properties of spelt and common wheat gluten

The fundamental rheological methods used to study wheat gluten properties combined with the physicochemical characteristics of gluten proteins explain the molecular and supramolecular background of the gluten structure and its viscoelastic behaviour [35–43]. Most commonly, the small strain in simple oscillatory shear (dynamic experiments) and retardation tests (creep and creep recovery) are used. In dynamic experiments, the mechanical spectrum of gluten, represented as storage and loss moduli (G', G'') versus frequency ω, encompasses only a part of the viscoelastic plateau [29, 39, 40, 44]. In this part of the plateau, gluten reveals a transient viscoelastic network structure [29, 35–37, 39, 44]. Viscoelastic properties of the material mani-

Table 2 Comparison of sedimentation test and farinographic parameters of spelt and common wheat flours

Sample	Zeleny sedimentation value[a] (mean ± SD) (mL)	Water absorption recalculated for 14% flour moisture (%)	Dough development time (min)	Dough stability time (min)	Dough softening after 10 min (B.u.)
Spelt SKO	27.0 ± 0.4	57.7	3.5	3.9	53
"Begra"	32.0 ± 0.7	59.1	5.2	9.0	22
"Wilga"	21.0 ± 0.4	58.1	3.2	2.4	98

[a] Baking quality: >50 very good, 35–50 good, 20–34 sufficient, <20 insufficient quality

B.u. Brabender unit

Table 3 Protein fractional composition of spelt and common wheat flours according to the three-step extraction procedure (mean value ± SD)

Sample	TNP					AAS/(NaOH sol + ins) ratio
	Pyrophosphate buffer 0.01 mol L^{-1}, pH 7.0	Acetic acid 0.05 mol L^{-1}	NaOH 0.1 mol L^{-1}	Insoluble residue	Total gluten proteins (TGP)	
Spelt SKO	19.1 ± 0.5	76.1 ± 1.4	4.1 ± 0.3	0.7	80.9	
% of TGP		94.1	5.1	0.8		15.9
"Begra"	19.9 ± 0.6	68.1 ± 2.6	8.5 ± 1.3	3.4	80.1	
% of TGP		85.0	10.6	4.4		5.7
"Wilga"	29.1 ± 0.4	61.4 ± 0.4	7.4 ± 0.9	2.1	70.9	
% of TGP		86.6	10.4	3.0		6.5

TNP, total nitrogen percent; *AAS*, acetic acid soluble nitrogen; (*NaOH sol + ins*), sum of NaOH-soluble and NaOH-insoluble nitrogen

fested in the upper frequency region of the plateau can be quantified using Cole–Cole functions; this has been demonstrated for synthetic polymers and some biopolymers, including wheat gluten [29–31].

In retardation tests, time-dependent creep or creep recovery compliance $J(t)$ is calculated as the ratio of the corresponding strain to imposed stress [31, 32]. Rheological properties of the material manifested in the lower frequency region of the viscoelastic plateau can be quantified using steady state compliance J_e^0 and steady state viscosity η_0 quantities.

Dynamic tests along with retardation experimental methods can provide data over a particular overlapping frequency or time range. A number of methods have been developed in synthetic polymers rheology to transform the results from one type of experiment to another, usually from time to frequency domain [32, 33]. These methods of data conversion have been successfully implemented in common wheat gluten rheology, to provide a set of factors quantifying its viscoelastic properties [29, 44, 45]. However, only a few works address spelt gluten fundamental rheology. These studies concentrate on correlating the spelt gluten protein fractional composition derived from SE-HPLC with basic technological quality parameters and some rheological parameters [7, 8].

Rheological behaviour of gluten in dynamic tests

The mechanical spectra obtained in the dynamic experiments, represented as $G',G'' = f(\omega)$, are practically superimposed for the spelt and "Begra" gluten samples (Fig. 1a). Under the same conditions, the mechanical spectrum of "Wilga" gluten shifts down and shows a crossover point at the frequency of ~ 5 rad/s. The dynamic measurements were linear over the frequency window as demonstrated by the Kronig–Kramers test (Fig. 2).

When the mechanical spectra are presented as compliance functions, the fast dissipative peak on the $J''(\omega)$ curve appears at the upper frequency window (Fig. 1b). This peak is the most striking manifestation of a transient network structure in viscoelastic polymers and biopolymers [31, 32]. Over the frequency region, where behaviour of a material is dominated by the dissipative peak, J' and J'' can be fitted by Cole–Cole functions.

Fitting the Cole–Cole arcs to the experimental data plotted in the complex plane J'' versus J' reveals sound differences between the viscoelastic properties of spelt gluten and common wheat "Begra" gluten (Fig. 3a, b), and particularly "Wilga" gluten (Fig. 3a). The positioning of experimental points along the Cole–Cole arc of spelt gluten indicates that no long-range dissipative processes occurred in the dynamic experiment frequency window [31, 34, 39]. Therefore, the mechanism of the dissipative effects in spelt gluten differs from those in the studied common wheat gluten in this frequency zone.

Table 4 presents the Cole–Cole parameters J_N^0, G_N^0, ω_0, and n calculated for the gluten samples. The viscoelastic plateau modulus G_N^0 of common wheat gluten samples varied significantly from 96.4 Pa for "Wilga" to 967 Pa for gluten "Begra". Spelt SKO gluten shows an intermediate G_N^0 value of 425.7 Pa.

For comparison, similar values of G_N^0 were found for gluten samples of "Begra" wheat harvested in 1998 (1,014 Pa) and 2000 (837 Pa), originating from the same plant breeding station [29, 30, 34, 45]. Among common wheat gluten of acceptable bread making quality, "Wilga" gluten represents one of the weakest materials and strongly varied in its viscoelastic properties depending on the harvest year. The G_N^0 values for this cultivar span from 26 Pa for 1998 to 225 Pa for 2000 [30, 45]. Moreover, the mechanical spectra of gluten for cv. "Wilga" frequently show upper crossover and transition zone in the experimental frequency window [34]. Lefebvre et al. [39, 40, 46] demonstrate the extent of the variability of the G_N^0 values depending on gluten HMW-GS composition. For gluten originating from the near-isogenic lines of common wheat

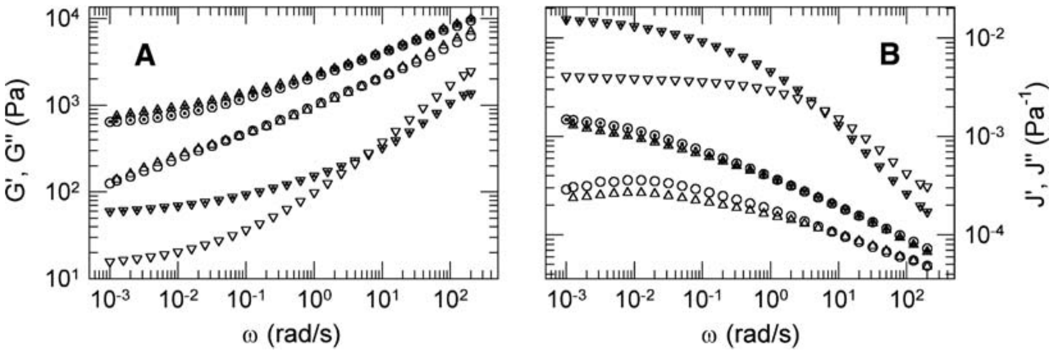

Fig. 1 Mechanical spectra of spelt and common wheat gluten. **a** $G',G'' = f(\omega)$; **b** $J',J'' = f(\omega)$. Symbols: G' and J' (*dotted*), G'' and J'' (*empty*); spelt cv. SKO (*circles*), common wheat cv “Begra” (*triangles*), common wheat cv “Wilga” (*inverted triangles*)

Fig. 2 Verification of linearity of viscoelastic response of spelt and common wheat gluten. G' (*solid circles*), G'' (*empty circles*), G'' (*solid line*) recalculated according to the Kronig–Kramers method (Eq. 1). *Left*: spelt cv. SKO. *Right*: common wheat cv “Begra”

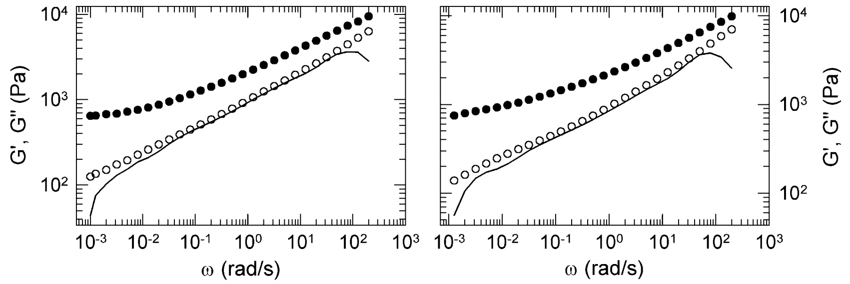

Fig. 3 Mechanical spectra of spelt and common wheat gluten in the complex plane. **a** All samples. Spelt SKO (*circle*), “Begra” (*triangle*), “Wilga” (*inverted triangle*), Cole–Cole arcs (*solid lines*) fitted to the experimental data (Eq. 4). **b** Enlarged plot for spelt SKO and “Begra” gluten

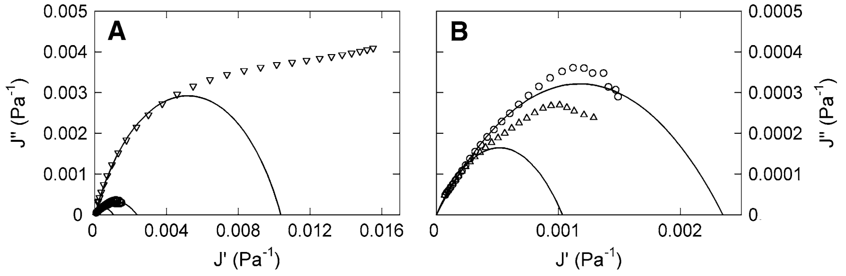

Table 4 Cole–Cole parameters calculated for spelt and common wheat gluten

Sample	J_N^0 (Pa^{-1})	G_N^0 (Pa)	ω_0 (rad/s)	n	r[a]
Spelt SKO	2.35×10^{-3}	425.7	0.01	0.340	0.999
“Begra”	1.03×10^{-3}	967.2	0.31	0.393	0.997
“Wilga”	1.04×10^{-2}	96.4	0.88	0.653	0.999

[a] r correlation coefficient

cvs “Olympic” and “Gabo” crosses, the values of G_N^0 range from 14 Pa (near-isogenic line “triple null”, i.e. all HMW-GS removed) to 3,330 Pa (control line: 1/17 + 18/5 + 10) [39, 46].

The characteristic frequency ω_0 of examined systems shifts significantly between spelt gluten (0.01 rad/s) and common wheat glutens (0.3 and 0.9 rad/s for “Begra” and “Wilga”, respectively). In synthetic cross-linked polymers chains, a decrease in ω_0 value means a lower average molecular mass for the network segments [32]. In gluten, the increase of ω_0 was observed when native gluten was rich in strong network of glutenin subunits (1D × 5) or gluten proteins were submitted to networking via isopeptide bonds with the use of transglutaminase [41, 47]. The effect of the strong decrease of ω_0 was observed when HMW-GS-coding genes were removed from the common wheat genome [38]. In our study, a low ω_0 value for spelt gluten seems to be associated with the abundance of gliadins.

The exponent n of spelt SKO gluten (0.34) was similar to that of good common wheat “Begra” gluten (0.39). For gluten “Wilga”, n was considerably higher (0.653) and close to the values found for very weak glutens, e.g. “Wilga” 1998 (0.745) [34, 45] and ‘triple null’ gluten (0.639) [46].

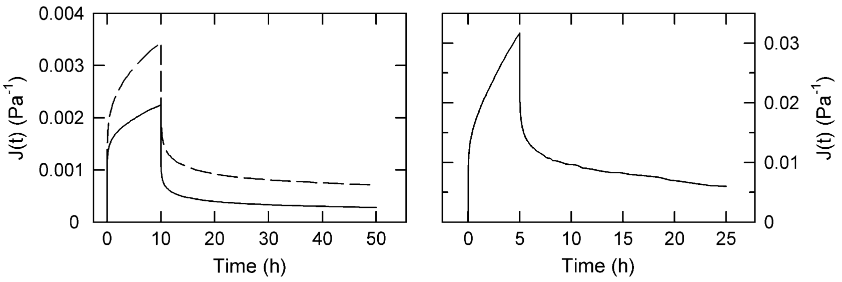

Fig. 4 Creep and creep recovery test of spelt and common wheat gluten. *Left* spelt SKO (*dashed line*) and common wheat "Begra" (*solid line*). *Right* common wheat 'Wilga.'

Table 5 Creep parameters and width of elastic plateau τ_m^0/τ_0 for spelt and common wheat gluten

Sample	J_e^0 (Pa^{-1})	η_0 (Pa s)	r^a	τ_m^0/τ_0
Spelt SKO	2.56×10^{-3}	4.03×10^7	0.998	1,159
"Begra"	1.77×10^{-3}	7.52×10^7	0.999	41,738
"Wilga"	1.72×10^{-2}	1.24×10^6	0.999	18,834

[a] *r* correlation coefficient

Rheological behaviour of gluten in retardation tests

Figure 4 shows the behaviour of gluten samples in retardation tests. Creep and creep recovery curves differ significantly depending on the gluten sample. The value of steady state compliance J_e^0 ranges from 2.56×10^{-3} Pa^{-1} for spelt to 1.77×10^{-3} Pa^{-1} for "Begra" and 1.72×10^{-2} for "Wilga" (see Table 5). Generally, J_e^0 reveals significantly higher values as compared to the corresponding value of J_N^0 for "Begra" and "Wilga" glutens, which agrees with observations for synthetic polymers and biopolymers [29, 32, 39]. In the case of spelt, the difference between J_e^0 and J_N^0 was practically insignificant (~8%). The steady state viscosity η_0 values ranged within the order of magnitude of 10^6 Pa s for "Wilga" gluten and 10^7 Pa s for "Begra" and spelt glutens.

Composite mechanical spectra

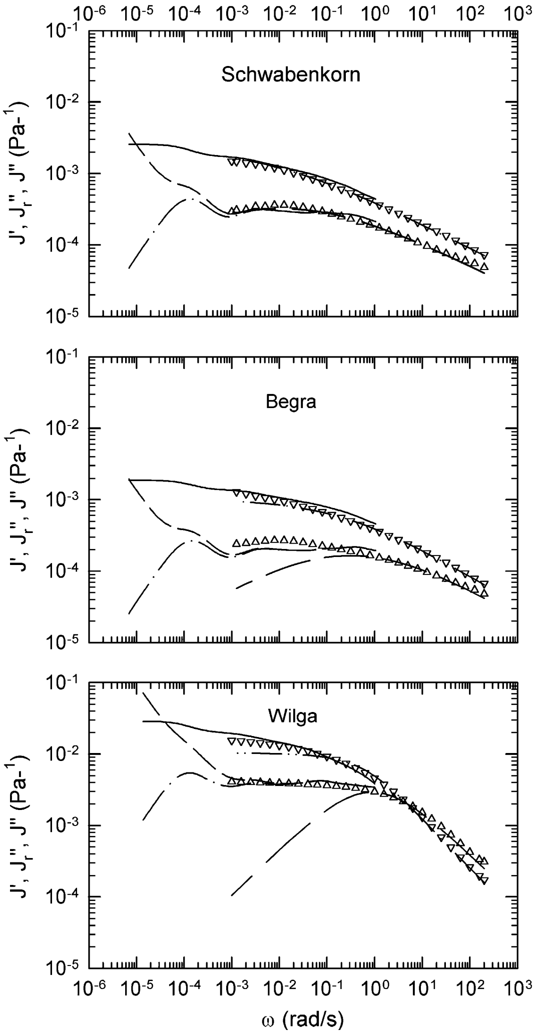

Fig. 5 Composite mechanical spectra of spelt and common wheat gluten. Data from dynamic measurements: J' (*inverted triangle*), J'' (*triangle*). Data calculated according to the Cole–Cole method: *dash-dot-dot line* J' (Eq. 2), *long-dashed line* J'' (Eq. 3). Data calculated from retardation tests according to the Kaschta method: *solid line* J' (Eq. 9), *short-dashed line* J'' (Eq. 10), *dash-dotted line* J_r'' (Eq. 11)

Figure 5 presents the composite mechanical spectra of studied gluten, obtained by combining J' and J'' data from the dynamic measurements and calculated from the Cole–Cole fit, as well as the J', J'' and J_r'' values calculated from the retardation tests according to Kaschta and Schwartzl's method. The $J'(\omega)$ and J'' (ω) curves exhibit lower crossover in the 10^{-6} to 10^{-5} rad/s frequency range, proving that the viscoelastic plateau has a limited extension for common wheat and spelt glutens. Because of the high viscosity η_0 of gluten at frequencies $\omega > 10^{-2}$, J_r'' and J'' become practically superimposed. Bimodal nature of dissipative processes, occurring in the gluten network, manifests at the J_r'' curve as two peaks corresponding to fast (right peak) and slow (left peak) dissipative processes. The fast dissipative peak would be related to the small-scale motions inside the building blocks of the network structure. The slow dissipative peak would be linked to the structure at the macroscopic level, i.e. to the network connectivity [10, 29, 39]. These peaks delimit the viscoelastic plateau and are typical

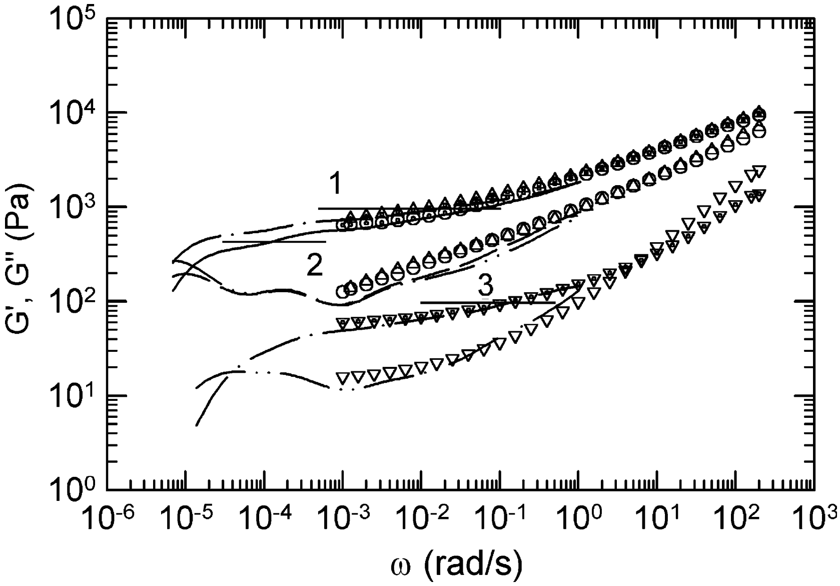

Fig. 6 Composite mechanical spectra of spelt and common wheat gluten. Data from dynamic measurements: G' (*dotted symbols*), G'' (*empty symbols*). Spelt cv. SKO (*circles*), common wheat cv. "Begra" (*triangles*), common wheat cv. "Wilga" (*inverted triangles*). Data calculated from retardation test according to the Kaschta method: SKO: *solid line* G'', *dashed line* G''', "Begra" and "Wilga": *dash-dotted line* G', *dash-dot-dot line* G''. Location of G_N^0 value on the G' curves (*horizontal solid line*): "Begra" (*1*), SKO (*2*), "Wilga" (*3*)

for entanglement polymer systems and physical gels [29, 32, 39, 44].

The broadness of the fast dissipative peak visualised as $J''(\omega)$ calculated from the Cole–Cole fit (Fig. 5), was strongly diversified for the gluten samples. For spelt gluten, the peak was enormously broad, spanning nearly five frequency decades. For "Begra" gluten, the fast dissipative peak was typical for the strong common wheat. The fast dissipative peak for "Wilga" gluten was very narrow. Observed differences in the broadness of the fast dissipative peaks suggest existence of differences in the width of viscoelastic plateau. To estimate true width of viscoelastic plateau, the location of the lower and the upper $G'(\omega)$ and $G''(\omega)$ crossover points should be known. In our experiment, the upper crossover point is not visible for spelt and common wheat "Begra" gluten (see Figs. 5, 6).

Figure 6 presents the composite mechanical spectra of studied gluten as the functions G' and G'' versus angular frequency ω revealing the differences in viscoelastic properties of spelt and common wheat "Begra" gluten that are not seen in Fig. 1a. Note that the G_N^0 position on the frequency scale for spelt gluten shifts considerably toward lower values and is located out of the lowest frequency of the dynamic measurements window. This was not observed for gluten from common wheat of acceptable baking quality [39, 40, 45, 46].

Width of viscoelastic plateau

The width of the plateau zone on the logarithmic time or frequency scale can be arbitrarily taken as τ_m^0/τ_0 where $\tau_m^0 = \eta_0 J_e^0$ is the longest and $\tau_0 = 1/\omega_0$ is the shortest objectively assigned retardation time of the viscoelastic plateau [32]. Defined in this way, the dimensionless width of the plateau is a parameter that connects the characteristic parameters of the fast and the slow dissipative processes.

As seen in Table 5, the width of the viscoelastic plateau τ_m^0/τ_0 of spelt gluten appears very short (1.16×10^3) compared to those of common wheat "Begra" and "Wilga" (41.7×10^3 and 18.8×10^3, respectively). To compare, τ_m^0/τ_0 of gluten originating from wheat "Begra" and "Wilga" harvested in 1998 correspond to 200×10^3 and 7.8×10^3, respectively [45]. According to Lefebvre (personal communication), τ_m^0/τ_0 for 'triple null' wheat gluten (no HMW-GS) equals 0.83×10^3; therefore, the width of the viscoelastic plateau of spelt gluten observed in the present study was only slightly higher. The observed difference τ_m^0/τ_0 between spelt and common wheat gluten is perhaps the most sound rheological evidence of the prevailing impact of monomeric gliadins that hide the elastic contribution of polymeric glutenins in the overall viscoelastic properties of spelt gluten.

Conclusions

A set of fundamental rheological parameters calculated from dynamic measurements (G_N^0, J_N^0, ω_0, n) and the retardation test (J_e^0, η_0) enables multi-parameter quantification of the elastic and viscous parts of overall viscoelastic properties of gluten. Considering the results of the present study, the existence of a transient network structure in spelt and common wheat gluten, proven by the shape of the composite mechanical spectra, is evident. The elastic part of the overall viscoelastic properties of the studied gluten samples follows the presence of HMW-GS dublets involved in determining the technological quality of wheat, i.e. 5 + 10 for good baking quality ("Begra") and 2 + 12 for lower baking quality ("Wilga" and spelt SKO). Generally, the rheological properties of spelt gluten are predominated by gliadins as a very sticky monomeric plasticizer, while those of common wheat gluten by glutenins as a networking polymeric factor.

Indeed, spelt and common wheat gluten appear to be a convenient model for fundamental rheological studies of the networked systems, naturally predominated by the physicochemical properties of different groups of gluten proteins. Future studies might examine gluten preparations originating from a larger group of spelt and common wheat cultivars, clearly differentiated in their technological quality and protein fractional composition, to find a critical Glia/Glu ratio separating gluten types dominated in their rheological properties by gliadins or glutenins, respectively.

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