Disparate dynamic viscoelastic responses of wheat flour doughs coated with different oils for preventing water evaporation during time sweeps and their mechanisms decoupled

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Abstract Various non-volatile oils are currently applied in order to prevent water evaporation from exposed surface of dough during oscillatory measurements. A systemic understanding of their effectiveness in controlling water loss and ensuring accuracy of rheological measurements is necessary. In this work, three kinds of coating oils (vaseline, dimethyl silicone oil and low viscosity silicone oil) were selected to minimize water evaporation from dough of 37%, 42% and 47% water content subjected to time sweep tests under oscillatory mode. Evolution patterns of the storage modulus, loss modulus and loss factor with time were followed, and the mechanisms responsible for the response patterns were decoupled. Disparate dynamic viscoelastic responses were found for the same dough coated with different oils. Spontaneous de-structuring of dough combined with thixotropic effect contributed to the decrease of dynamic modulus and increase of the loss factor with time. Dynamic vapor sorption tests showed that water evaporation did occur for the dough even coated with non-volatile oils including vaseline. Water evaporation led to an accelerated increase in dynamic modulus with time, while had a very limited impact on loss factor. Oil invasion only played a minor role in the decrease in dynamic modulus. The measured modulus was actually a sum of the

positive and negative contributions. Vaseline was observed as an effective coating oil for rheological measurements of dough, especially with high water content.

Keywords Dough · Linear viscoelasticity · Water evaporation · Coating oil · Mass transfer

Introduction

Dynamic oscillation methods are now intensively used for exploring rheological relations of wheat flour dough with its polymeric protein characteristics (Katyál et al. 2018; Singh et al. 2011), chemical compositions (Hardt et al. 2014; Watanabe et al. 2002), network structure (Davidou et al. 2008), mixing treatment (Kim et al. 2008; Meerts et al. 2017) and product quality (van Bockstaele et al. 2008). Before conducting an amplitude or frequency sweep measurement in linear viscoelastic range, the first consideration is to determine if the material is stable before data collection. A simple test for this purpose is an oscillatory time sweep. Time evolution of dynamic viscoelastic properties of dough in a rheometer is sparsely reported, and usually is not a major topic of one research. Even in these very few reports, the contradictory observation of dynamic modulus increase (Baltsavias et al. 1997; Edwards et al. 1999; Sofou et al. 2008), remaining constant (Schiedt et al. 2013) and decrease (van Bockstaele et al. 2008; Davidou et al. 2008) with time have been documented.

Water evaporation has a strong impact on the dynamic viscoelastic parameters of dough, and should be minimized during rheological measurements. Solvent-trap is a means for this purpose (van Bockstaele et al. 2008; Davidou et al. 2008). A solvent-trap can be home-made (Gabriele et al. 2001) or deliberately designed (Sato and Breedveld 2005).

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Another method commonly reported in the literature consists in applying a thin layer of a non-volatile oil to the exposed surface of the dough sample. Fluid-like oils such as mineral oil (e.g. Sofou et al. 2008; Kim et al. 2008) and silicon oil (e.g. Watanabe et al. 2002; Schiedt et al. 2013) are often applied. Low viscosity silicone oil was also used in some reports (e.g. Khatkar and Schofield 2002; Lopes-Da-Solva et al. 2007). Semi-solid oils such as vaseline (e.g. Masi et al. 1998; Moreira et al. 2015; Correa et al. 2017) are another group of often-used coating oils. Vegetable oil (Ducarci et al. 2017) and liquid paraffin (Tietze et al. 2017) are also options. In some reports, a coating oil was combined with a solvent trap for a better control of dough drying (Baltsavias et al. 1997; Gabriele et al. 2001).

Actually, water is soluble, despite sparingly, and diffusible in an oil (Zieverink et al. 2009), so an oil film is more or less permeable to water. In this sense, water loss can still be an issue with dough even coated with an oil before rheological testing. Szczesniak et al. (1983) found that the dough coated with 20 cS silicon oil presented lower dynamic modulus than that of bared dough. In an earlier report, Smith et al. (1970) found that coating wheat flour dough with mineral oil did not prevent drying out. In a recent report on agar gel (Mao et al. 2016), sunflower oil was verified to be effective for sample drying control, while its invasion into sample during oscillatory experiments hampered a precise measurement.

Although non-volatile oils such as vaseline and silicone oil are intensively used in rheological measurement of dough. Are these often-used oils really effective in preventing water evaporation, and controlling experimental errors within an acceptable range? In this work, dynamic viscoelastic responses of doughs of three water contents with each coated with one of three different oils were followed. Water loss and oil invasion were measured and their contributions to dynamic viscoelastic parameters were also evaluated. The major objective of this work is to judge the effectiveness of the three kinds of coating oils in stabilizing rheological measurements and to interpret their performances based on mass transport mechanisms.

Materials and methods

Materials

Tailored wheat flour (11.28% moisture, 12.83% protein) purchased from a local supermarket was used to prepare dough samples. Vaseline, dimethyl silicone oil (DMSO) and low viscosity silicone oil (LVSO) were applied as coating oils for water evaporation prevention. Their viscosity was measured using a DHR-1 rheometer at 25 °C. The LVSO and DMSO were found to be Newtonian fluids

with a viscosity of 0.097 Pa s and 1.025 Pa s, respectively. The vaseline exhibited a shear thinning behavior, with the viscosity decreasing from 89.367 Pa s at a shear rate of 1 s^{-1} to 1.651 Pa s at 100 s^{-1} .

Dough preparation

Three doughs with water contents of 37%, 42% and 47% were prepared in a ACA® bread baker using its mixing function. NaCl (2% (w/w) of dough weight) was dissolved in water, then the salt solution was added into wheat flour in the mixing bowl. Mass of each prepared dough was kept at $\sim 100 \text{ g}$. After mixing for $5 \text{ min} \times 2$, each dough was rested in a hermetical aluminum box for 1.5 h before rheological measurements. A resting period much longer than the duration in the literature was selected in order to let the doughs relax completely from the stress imparted by the mixing process. In order to study the effects of oil invasion on dough viscoelasticity, each coating oil of 5 g was added in the formulation of the dough with 42% water content to get three coating-oil-containing doughs.

Rheological measurements

Dynamic viscoelastic measurements of the doughs were conducted in a stress-controlled DHR-1 rheometer (TA Instruments, USA) at 25 °C. A parallel-plate geometry with a top plate of 20 mm diameter was employed for amplitude sweep and time sweep tests of the three plain doughs, and time sweep tests of the coating-oil-containing doughs. For all experiments using the parallel-plate geometry, a hand-made plastic cup was used as a solvent trap to minimize humidity fluctuation during measurements. The cup has an opening of about 40 mm diameter at bottom and a shallow peripheral groove around the opening. Its inner wall is lined with a piece of cotton pad soaked with saturated MgNO_3 solution. Air relative humidity equilibrated with this solution at 25 °C (53%) approximates to the average indoor humidity. About 2 g of dough was placed at the center of the Peltier plate. The plastic cup was placed on the Peltier plate with the dough centrally positioned within the bottom opening. The upper plate was then brought down to compress the sample to a gap size of 1550 μm using exponential close. The cup was raised very carefully, and excess dough was trimmed with a steel blade. For amplitude sweep tests, dough drying was minimized by painting its exposed surface with a thin layer of vaseline. While for time sweep tests, the three oils were separately applied for each dough. After oil coating, the cup was put down, the top opening of the plastic cup was covered with a two-piece split cover. Then the sample dough was further compressed to 1500 μm , and let to rest for 30 min. The amplitude sweep tests were performed

from 0.001 to 5% at 10 Hz. A test protocol called 3 interrupted time sweep (3ITS) was adopted in this work. In this protocol the dough was first subjected a time sweep for 20 min, followed by a rest in rheometer for 20 min, then another 20 min time sweep plus 20 min rest, finally a time sweep for 20 min. The 3ITS test protocol was proposed for verifying whether the measurement itself had disturbed the structure of a dough.

In order to judge oil invasion during oscillatory measurement, separate 3ITS tests were performed for the three plain doughs using coating oils containing 0.5% (w/w) food grade lemon yellow for evaporation prevention. Another group of tests were conducted for the dough of 42% water content to determine its dynamic modulus variation during rest outside the rheometer, where the dough from the same preparation was subjected to another 3ITS test after a 3ITS procedure and the same coating oil was used for both 3ITS. Aside the parallel-plate geometry, a concentric cylinder geometry (cup radius 15 mm and bob radius 14 mm) was employed to perform 3ITS tests for the dough with 47% water content. About 30 g dough was filled into the cup very carefully to ensure no air entrapped in the cup. Excess dough was trimmed, and the opening of the cup was covered with the split cover before measurement starting.

All time sweep tests were performed at a frequency of 10 Hz in linear viscoelastic range. A freshly prepared dough was used for each experiment unless otherwise specified. All tests were repeated at least once.

Water loss measurements

Dough discs for water loss rate measurements were prepared in the DHR-1 rheometer. The dough of 47% water content is difficult to form a disc. Only the doughs with water contents of 42% and 37% were used to prepare disc samples. A portion of dough of ~ 2 g was mounted on the Peltier plate, compressed to 0.5 mm thickness and trimmed. The upper plate was uplifted. The dough disc was removed very carefully from the Peltier plate to keep its surface undamaged, and was weighed before coated with vaseline, DMSO or LVSO separately. The coated dough discs were subjected to water loss measurement within 5 min using a dynamic vapor sorption apparatus (DVS, Surface Measurement Systems, UK). Operating temperature and relative humidity were fixed at 25 °C and 53%, respectively. All tests were conducted in duplicate.

Each experiment, no matter amplitude sweep, time sweep or DVS tests, yielded a unique set of values, then data points cannot be averaged. For clarity, only one set of values was presented. One way analysis of variance was used to determine the significance of difference. The significance threshold was $p < 0.05$. The Origin v8.5

(OriginLab Corporation, USA) was used for statistical analyses and plots.

Results and discussion

Dynamic viscoelastic responses during 3ITS

The linear viscoelastic range was defined as the value of strain, for which storage modulus (G') has dropped to 95% of the plateau value for small amplitudes (Schiedt et al. 2013). According to this definition, the linearity limits of the doughs of 37%, 42% and 47% water content were found to be 0.038%, 0.035% and 0.031%, respectively, which were quite similar to others from 0.01 to 0.08% (Hardt et al. 2014; Meerts et al. 2017). Subsequently, all time sweep tests were performed at a strain amplitude of 0.02%.

Figure 1 shows representative response curves of the various dough in 3ITS tests using different coating oils for evaporation prevention. When LVSO and DMSO were used as coating oils, both storage modulus and loss modulus (G'') increased with time for all dough except the sweep 1 for the dough of 37% water content coated with DMSO. On the contrary, both G'' and G' decreased with time when vaseline was applied. Although the variation of modulus with time for each sweep can be approximated by a straight line, almost all the curves were actually concave in the whole duration of 3ITS.

For the dough with same water content, when coated with different oils, the measured dynamic moduli changed in opposite directions (Fig. 1), which was unacceptable for rheological measurement. This paradoxical observation indicated that coating oil selection had a pronounced effect on the measured modulus values.

The modulus versus time data in the first sweep of each 3ITS test were fitted to a linear equation G' or $G'' = at + b$, where t is time, a and b are slope and intercept of the line, respectively. The obtained values of a , b were collected in Table 1. All the slopes for vaseline coating are negative regardless water content.

Theoretically speaking, the three curves for the doughs with same water content should cross at the same point at -30 min. Our results were not the case because of experimental errors. A fresh prepared dough was used for each 3ITS test, which had inevitably led to a relatively higher error. Relative error levels of up to $\sim 20\%$ or more were reported for the dynamic modulus of dough (Lopes-Da-Solva et al. 2007; Sofou et al. 2008). Now, let us conduct a “theoretical” evaluation of the errors caused by different coating oils for a dough just after 30 min of rest plus 5 min of time sweep. Here, the modulus in the 30 min of resting period was assumed to change at the same speeds

Fig. 1 Temporal evolution of elastic and viscous moduli and loss factors of the three doughs coated with three kinds of oils during 3ITS tests. **a** and **b** 37% water; **c** and **d** 42% water; **e** and **f** 47% water. **a**, **c** and **e** dynamic modulus; **b**, **d** and **f** loss factor

as that we calculated based on the data from the first sweep (Table 1). Our preliminary tests showed that when a time sweep started immediately after dough loading, only the data of the initial period of 200 s at most were not on the trend curve obtained from the following period. The G' and G'' values just 5 min after test starting were calculated using the regression equations with parameters presented in Table 1. According to the discussions in the following “Dynamic viscoelastic responses during 3ITS without a coating oil” section, the measured modulus values for the vaseline as coating oil were most close to their true values, and were specified as the true values for relative error calculation. Estimated errors are also presented in Table 1. If a relative error of $> 10\%$ is unacceptable for a dynamic viscoelastic measurement, DMSO

and LVSO are not recommended for a dough of $\geq 42\%$ water content.

Apart from the analyses of G' and G'' , interesting information about the nature of the dough also comes from the loss factor $\tan \delta$. The loss factor increased slightly as moisture content increasing from 37 to 47% (Fig. 1), in line with the results of Masi et al. (1998). Although the dynamic modulus can increase or decrease with time, the variation trends of loss factor were independent of oil type for the dough samples with same water content, indicating that an identical event had occurred no matter which type of oil was used.

Temporal decrease of dynamic modulus accompanied with increase of $\tan \delta$ has been observed for wheat flour dough during (Schiedt et al. 2013) and after (Kim et al.

Table 1 Line regression results of G' and G'' to time for sweep 1 in each 3 ITS test of the three doughs and estimated errors of G' and G'' after 30 min resting plus 5 min measurement

Doughs	Coating oil	G'		$\Delta G' (\Delta G'/G' - \text{vaseline})$	G''		$\Delta G'' (\Delta G''/G'' - \text{vaseline})$
		a (Pa/s)	b (kPa)		a (Pa/s)	b (kPa)	
37%	Vaseline	-13.04 ± 1.38	410.23 ± 15.31	0 (0%)	-5.05 ± 0.08	157.17 ± 1.24	0 (0%)
	DMSO	-4.21 ± 0.44	412.57 ± 13.80	18.54 (4.84%)	-0.23 ± 0.07	159.70 ± 3.32	10.12 (6.90%)
	LVSO	3.12 ± 0.72	429.95 ± 17.99	33.94 (8.86%)	2.09 ± 0.34	164.67 ± 8.79	14.99 (10.23%)
42%	Vaseline	-3.51 ± 0.73	66.95 ± 11.35	0 (0%)	-0.88 ± 0.42	26.54 ± 3.48	0 (0%)
	DMSO	1.93 ± 0.14	64.83 ± 3.46	11.42 (19.17%)	1.10 ± 0.04	26.27 ± 1.18	4.19 (16.84%)
	LVSO	2.71 ± 0.52	59.78 ± 11.04	13.06 (21.92%)	1.47 ± 0.27	24.74 ± 3.93	4.94 (19.99%)
47%	Vaseline	-0.22 ± 0.18	17.66 ± 1.89	0 (0%)	-0.13 ± 0.04	6.82 ± 0.56	0 (0%)
	DMSO	1.92 ± 0.09	15.75 ± 0.22	4.49 (26.13%)	0.81 ± 0.02	6.63 ± 0.03	1.97 (30.15%)
	LVSO	2.80 ± 0.46	16.91 ± 1.60	6.34 (36.88%)	1.16 ± 0.19	6.87 ± 0.65	2.71 (41.38%)

2008) mixing, and in rheometer (Edwards et al. 1999). Different from the results in these reports, for the dough of 37% and 42% water content coated with DMSO and LVSO, dynamic moduli did not decrease but increase with time. Increase of $\tan \delta$ was interpreted as a reduction in network extension (Gabriele et al. 2001), because of depolymerization of gluten or breakup of starch granule aggregates in a dough system (Kim et al. 2008). The modulus increase observed in our work may be indicative of water loss occurrence. For the dough of 47% water content, the $\tan \delta$ decreased very slowly with time, which was probably due to fact that the water loss effect (increasing $\tan \delta$) had predominated the network softening effect. Singh and Singh (2013) found viscoelastic modulus increase for the dough from stronger varieties after under-optimally- or over- mixing. Baltsavias et al. (1997) also reported modulus increase accompanied with slight $\tan \delta$ decrease. Both observations were in line with our results about the doughs of 47% water content coated with DMSO or LVSO. Baltsavias et al. (1997) did not give an explanation for their observation. In this research, the author applied a humidity chamber of $a_w = 0.83$ for dough drying control. According to the isotherm data of Lind and Rask (1991), the dough should have lost water in the chamber. Therefore, the similar variation trend as that of the dough of 47% water content in our work was observed.

Dynamic viscoelastic responses during 3ITS without a coating oil

In order to specify the role of the vaseline coating in the modulus shown in Fig. 1, separate 3ITS tests were performed for the dough of 47% water content using a cup-and-bob geometry, which makes oil coating unnecessary and prevents water evaporation almost completely. In this case, the measured dynamic modulus was not disturbed by

extrinsic factors such as sample drying, and very close to its true value. The variation of G' , G'' and $\tan \delta$ with time is shown in Fig. 2a. The average decrease speeds (the negative slopes of the modulus vs. time regression lines over the 3ITS duration) of both G' and G'' measured using the concentric cylinder probe (0.3249 Pa/s and 0.0981 Pa/s, respectively) were higher than their corresponding speeds using the parallel plate geometry (0.1165 Pa/s and 0.0751 Pa/s, respectively). The difference was significant for G' ($p < 0.05$). This indicated that even the vaseline coating could not completely prevent water loss from the dough of 47% water content. With the assumptions proposed in “Dynamic viscoelastic responses during 3ITS” section for error evaluation, the G' variation because of geometry difference just 5 min after sweep starting was calculated to be $(0.3249 - 0.1165) \times 2100 = 438$ Pa, which was only $\sim 3\%$ of the initial G' measured using the concentric cylinder geometry. This variation is judged to be acceptable in consideration of the time-dependent nature of dough. Considering that the dynamic modulus values from the parallel plate geometry were higher than those from the concentric cylinder geometry, the relative errors presented in Table 1 should have been underestimated.

Dough with 47% water content, showed a decrease in $\tan \delta$ during 3ITS using the parallel plate geometry (Fig. 1), where water loss can occur. While for the same dough, its $\tan \delta$ increased when the concentric-cylinder probe was used (Fig. 2a), where almost no water was lost. This discrepancy further affirmed our supposition that water loss should be responsible for the slight decrease of $\tan \delta$ during the 3ITS tests presented in Fig. 1.

Dynamic modulus decrease with time in a rheometer was also observed for dough (van Bockstaele et al. 2008; Davidou et al. 2008). In these two papers, oscillatory tests started immediately or 5 min after sample loading. So, the authors attributed the modulus decrease to the relaxation of

Fig. 2 Viscoelastic responses of the dough with 47% water content during 3ITS test using a concentric cylinder geometry (**a**), and of the dough of 42% water content coated with three kinds of oils during the double-3ITS tests using parallel-plate geometry (**b** G' and G'' , **c** $\tan\delta$)

stress imposed during sample loading. For the case of ours, the dough was rested in the rheometer for 30 min before test starting. Also considering the prolonged resting of 1.5 h before sample loading, the stress generated by sample loading should have been relaxed almost completely.

Evolution of viscoelastic responses during rest outside rheometer

After loading the dough of 42% water content for a 3ITS test, the residual dough was rested in a hermetical aluminum box at 25 °C. When the 3ITS test was over, the residual dough was subjected to another 3ITS test. The same coating oil was applied for each pair of 3ITS tests. The results are shown in Fig. 2b and c. No matter which type of coating oil was applied, both G' and G'' decreased, while $\tan\delta$ increased, during the resting period outside the rheometer. The $\tan\delta$ increase suggested that the doughs became more liquid-like. Obviously, the modulus decrease can not be attributed to stress relaxation from sample loading. The changes of dynamic properties observed in

this period were not triggered by any extrinsic factor including testing process. In other words, the doughs had experienced a spontaneous de-structuring process during resting outside the rheometer. Similar observation was also reported by Kim et al. (Kim et al. 2008), who attributed their observation to the stress relaxation of the extended and unfolded protein molecules.

The first five G' data of each 3ITS test were averaged to calculate G' decrease speeds during the rest outside the rheometer. The results for vaseline, DMSO and LVSO coating were 0.72 Pa/s, 1.09 Pa/s and 0.95 Pa/s, respectively. Their average 0.92 Pa/s was significantly ($p < 0.05$) lower than the average decrease speed of the same dough coated with vaseline in the former 3ITS (1.40 Pa/s). So, it can be postulated that the oscillatory measurement had softened the dough. In fact, the softening is indicative of thixotropic characteristic of the dough. Considering that water evaporation can increase storage modulus, the modulus decrease with time for the case of vaseline as coating oil (Fig. 2b) suggests that the thixotropic effect plus spontaneous de-structuring had offset the water loss

effect and gave a reduced modulus. For the cases of DMSO and LVSO as coating oils, the water loss effect predominated the thixotropic effect plus spontaneous de-structuring. If our reasoning holds, the G' decrease probed by the concentric cylinder geometry (Fig. 2a) should be a combined result from thixotropic effect and spontaneous de-structuring.

Water loss and oil invasion visually observed

The above discussion suggests that the dynamic modulus of an undisturbed dough should decrease with time as a result of thixotropic effect plus spontaneous de-structuring. While Fig. 1 indicates that when DMSO or LVSO was selected as a coating oil, the measured G' and G'' continuously increased. After the 3ITS tests, the dough samples were removed from the Peltier plate and stretched. Fissures were formed at the edge of the dough samples coated with LVSO and DMSO (Fig. 3). Fissuring was more serious for the LVSO coated sample. These observations suggest that water loss had occurred at least for the cases of LVSO and DMSO coating. For the dough of 42% water content, similar results were observed (data not shown).

In another group of 3ITS tests, lemon yellow was added to the three coating oils. After 3ITS measurements, the dough discs were cut along their diameter. Their photographs were presented in the right three columns of Fig. 3. Because of being very soft and sticky, the dough discs of 47% water content coated with LVO and MSO were seriously deformed when the upper plate was lifted, and were absent from Fig. 3. For the dough of 37% water content coated with vaseline, almost no oil invasion was observed. With water content increasing and oil viscosity decreasing, more and more amount of coating oils was transported into the dough.

Water loss probed by DVS and its contribution to modulus evolution

In order to get quantitative data about water loss of the doughs during time sweeps. Each dough disc of 0.5 mm thickness, after coated with different oils, was continuously weighted using a DVS system. Results are presented in Fig. 4. Water loss really occurred no matter which kind of oil was applied. The water loss rate of the dough coated with LVSO was the highest, followed by that with DMSO, then with vaseline. Coincidentally, the modulus magnitude of the doughs coated with different oils also followed the same sequence (Fig. 1). For the dough with a higher moisture content, water evaporation was faster. It is worthwhile to note that the evaporation rate measured using the DVS can not completely reflect the situation met in the rheometer. One major difference is that in the later case the water is transferred along the radius, which has a relatively much longer dimension than that of the thickness. While in the former case, water is mainly transferred along the thickness direction. This difference contributed, at least partly, to the gradually slowing water evaporation shown in Fig. 4. For the case of water loss during oscillatory measurements, water transfer can be approximated as a quasi-steady state, and its rate can be approximated by the initial water loss speed from the DVS measurement.

Dynamic modulus increase with time has been reported in some earlier researches for the dough just after mixing (Baltas et al. 1997; Sofou et al. 2008) or a large deformation (Berland and Launay 1995; Meerts et al. 2017). The increase was mainly attributed to the gluten cross-linking (Sofou et al. 2008). As for our cases, Fig. 2a suggests that structural formation did not occur. The dynamic modulus increase with time (Fig. 1) and its accompanying water loss (Fig. 4) suggest that it was water loss that contributed to the increasing dynamic modulus.

Fig. 3 Photographs of stretched and cut dough disc samples after 3ITS tests

Fig. 4 DVS results of the doughs (37% and 42% water content) coated with LVSO, DMSO and vaseline

For the cases of DMSO and LVSO as coating oils, after offsetting the spontaneous de-structuring and thixotropic effect, the drying effect still gave a increase in modulus.

As shown in Fig. 1, water content of a dough became unknown except at starting time because of its continuous decrease. So, the initial water content (M) and its corresponding storage modulus of each dough coated with vaseline (b value in Table 1) were adopted for establishing an experiential relation. A power-law model [Eq. (1), $R^2 = 0.9971$] was found to give better fitness than an exponential model ($R^2 = 0.9923$) does.

$$G'(M) = 0.000804M^{-13.172} \quad (1)$$

Theoretical analysis of water evaporation and its contribution to dynamic modulus

Total resistance to the water transfer from dough coated with an oil to ambient air includes three parts: diffusion resistance in dough, permeation resistance through the oil film and convective resistance between oil film surface and ambient air. Water permeation resistance (PR) in a film can be estimated as (Olsson et al. 2013):

$$PR = \frac{L}{Dk} \quad (2)$$

where D is the water diffusion coefficient in oil, k is the water solubility in oil, L is the thickness of the oil film.

The D value of water in vaseline ($0.85 \times 10^{-9} \text{ m}^2/\text{s}$, Hilder and van den Tempel 1971) is even higher than that of water in dough at 25°C ($\sim 0.15 \times 10^{-9} \text{ m}^2/\text{s}$, Karathanos and Kostaropoulos 1995). While water solubility in edible oils and fats is of the order 10^{-2} (mole fraction) under the condition of 60°C and saturation water vapor pressure (Hilder and van den Tempel 1971). Then for the dough coated with vaseline, the water permeation

resistance through the vaseline film should be much higher than that in the dough. In this case, water content gradient of the dough after a time sweep should be very small, which is supported by the photograph of the stretched dough coated with vaseline (Fig. 3).

If the PR is small enough, water evaporation will become an internal diffusion-controlled process. In this case, the dough disc will become a radically inhomogeneous material after a time sweep, and the measured dynamic modulus is actually an apparent value. For an inhomogeneous material probed using a parallel plate geometry, its storage modulus ($\bar{G}'$) is the sum of the contributions of all the volume elements with different rheological properties, and can be calculated using Eq. (3) (Joubert et al. 2001; Liotier et al. 2010).

$$\bar{G}' = \frac{4}{R^4} \int_0^R G'(r) r^3 dr \quad (3)$$

where R is the radius of the plate, $G'(r)$ is the local modulus at radius r . Theoretically speaking, a quantitative relationship between water content and r can be established with the help of water transfer analysis of the dough disc. The storage modulus as a function of water content has been established as shown in Eq. (1). Then the apparent storage modulus can be predicated using Eq. (3). In fact, the values of the parameters such as water diffusivity, solubility and convective mass transfer coefficient are scarce in the literature, which makes it very difficult to calculate the water content at r .

Compared with the vaseline coating, the LVSO film should have a much higher water diffusion coefficient because of its much lower viscosity (Wilke and Chang 1955). In addition, water solubility in the LVSO may be higher than that in the vaseline. Finally, it is possible that the resistance of water permeating through the LVSO film would be lower even than the diffusion resistance in the dough. Also considering the very slow diffusion of water in dough, water loss should occur mainly in a very narrow region next to the inner surface of the oil film (Crank 1975), which is supported by our observation shown in Fig. 3. If both the inner and the outer regions are assumed to have a uniform water content, Eq. (3) becomes integrable, and Eq. (4) is obtained.

$$\bar{G}' = \frac{R_1^4 G'_1 + (R^4 - R_1^4) G'_2}{R^4} \quad (4)$$

where R_1 is the radius of the inner region, G'_1 and G'_2 are the storage modulus of the inner and outer regions, respectively. For our case, $R = 10 \text{ mm}$, assuming $R_1 = 9 \text{ mm}$ (see Fig. 3), Eq. (4) is reduced to Eq. (5).

$$\bar{G}' = 0.66G'_1 + 0.34G'_2 \quad (5)$$

It can be found that even for a homogeneous material ($G'_1 = G'_2$), the outer domain with a thickness of only 1 mm contributes 34 percentage of the average modulus. When $R = 20$ mm, the contribution factor of the outer domain reduces to 0.186. So, using a parallel plate geometry of larger diameter will attenuate the impact of water evaporation on dynamic modulus. Equation (5) combined with Eq. (1) explains the accelerated increase of the dynamic modulus during time sweep testing (Fig. 1). On the contrary, structure-forming such as cross-linking of gluten molecules leads to decelerated dynamic modulus increase (Baltasvias et al. 1997; Edwards et al. 1999; Meerts et al. 2017).

Contributions of oil invasion

We appraised the effect of oil invasion on the dynamic moduli with the help of experimental observation of the modulus change when different oils were added into the dough of 42% water content. The results are presented in Fig. 5. Both storage and loss moduli were reduced no matter which kind of coating oil was formulated into the dough. Because the vaseline was used as coating oil, the dynamic moduli unsurprisingly decreased very slowly during time sweeps regardless of oil type added.

Here we roughly evaluate the contribution of oil invasion to the G' decrease observed for the dough of 42% water content coated with vaseline (Fig. 1), where the G' reduced from 55,500 Pa at the beginning of the 3ITS test to 46,500 Pa at the end of the test. The reduction magnitude was 9000 Pa. If the oil penetrating into the dough disc reaches the level of 4.76% and is homogeneously distributed, the lowest G' value should be 38600 Pa, the initial G' value for DMSO as coating oil (Fig. 5). Then the largest

reduction magnitude of G' would be $55,500 - 38,600 = 16,900$ Pa, much higher than the measured value of 9000 Pa. Actually, the following considerations will make the estimated reduction magnitude become smaller and smaller. First, the DMSO invasion can not reach a level of 4.76%. We assume that the DMSO penetrating into the dough disc all locates in the outer domain with a thickness of 1 mm (see Fig. 3), and that the amount of the penetrated oil is equal to the amount of water evaporated. Water evaporation rate of the dough disc coated with the DMSO is 0.17 mg/min (Fig. 4). After some mathematics, water content in the outer domain was found to be 39.95%. Then, oil content in the outer domain would be $42 - 39.95\% = 2.05\%$. Assuming that the G' is a liner function of oil content, and that the contribution factor of the outer domain to the measured G' of the dough disc is still 0.34 as shown in Eq. (5), the G' reduction magnitude would be $16,900 \times (2.05/4.76) \times 0.34 = 2475$ Pa. Second, as we all know that oil solubility in water is much lower than water solubility in oil. Because of its large molecular weight, the oil should diffuse much slowly in dough than water in oil film. According to Eq. (2), the amount of DMSO penetrating into the dough will be much less than the amount of water evaporating from the dough disc. The estimated G' reduction of 2475 Pa should be seriously discounted, and become much smaller than the measured G' reduction of 9000 Pa. So, oil invasion should only play a very minor role in the G' from the 3ITS tests. This is why we discuss oil invasion at the end of this paper and did not consider it while interpreting G' change.

Fig. 5 Dynamic moduli (a) and loss factors (b) of the dough (water content 42%, coating oil content 4.76%) coated with vaseline during 2ITS tests

Conclusion

In summary, while conducting a time sweep test, the measured storage and loss moduli of a dough can increase or decrease depending on the coating oil applied. Water loss can occur for a dough even coated with non-volatile oils including vaseline. Compared with the DMSO and the LVSO, the vaseline coating resulted in a much slower water loss especially for the dough of low water content. Small diffusivity and solubility of water in oil are crucial for an oil film to prevent water evaporation effectively. During a time sweep, dough can experience water loss, oil invasion, spontaneous de-structuring, and thixotropic process simultaneously. The measured dynamic modulus was actually the combine of these positive and negative contributions. Water evaporation was the major contributor to modulus increase, and responsible for the disparate dynamic viscoelastic responses of the doughs coated with different oils. Moreover, the power-law dependence of dynamic modulus on water content and volume-averaged contribution of local modulus to apparent modulus contributed to the accelerated increase of the dynamic modulus with time. While, the spontaneous de-structuring plus the thixotropic effect led to the reduction in dynamic moduli and the increase in loss factor during a time sweep. Oil invasion had very limited effect on the modulus. It was shown that the use of DMSO and LVSO is of special attention for rheological properties determination of dough especially of high water content.

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