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Non-linear Rheological Properties of Soft Wheat Flour Dough at Different Stages of Farinograph Mixing

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Abstract:
During mixing of wheat flour doughs, the distribution of the gluten network changes as a result of continuously applied large deformations. Especially gliadin, changes its distribution in the whole network during mixing. It is possible to fundamentally explain the role of molecular changes in more detail using large amplitude oscillatory measurements (LAOS) in the non-linear region. Therefore, the purpose of this study is to understand the effect of mixing on the non-linear fundamental rheological behavior of soft wheat flour dough using LAOS. Dough samples were obtained at 4 different phases of the Farinograph mixing and LAOS tests were done on each of them. LAOS tets give in depth intracycle understanding of rheology. All samples showed strain stiffening *S* and shear thinning *T* behavior at large strains previously not known in the cereal rheology community. Increasing mixing time (phase 1 to phase 4) and decreasing frequency resulted in retardation in the break of strain stiffening as strain increases. The strain stiffening behavior started to decrease for the dough samples at the 3rd and the 4th phases of mixing. LAOS data enabled us to describe the non-linear rheological changes occurring both in the viscous part largely attributed to the starch matrix and elastic part largely attributed to the gluten network components of the soft wheat flour dough under large deformations.

Key words:
Soft wheat flour dough, Farinograph mixing, non-linear rheological properties, LAOS

1 INTRODUCTION

Starch and gluten are known to be the main constituents of wheat flour; however it contains other components such as non-starch polysaccharides as well as lipids [1]. The viscoelasticity of wheat flour dough is due to gluten and its ability to interact with other components of wheat flour while hydrated with adequate amount of water during mixing. The quality and the quantity of gluten in wheat flour depends on the growth conditions and thus to the type of the wheat. Wheat (Triticum aestivum L.) is classified and traded as "hard or soft" and "winter or spring" based on the endosperm hardness or texture. Hard wheat flours are known to have more protein content compared to soft wheat flours [2–5]. Therefore, the type of wheat from which the flour is milled has a major effect on the rheological and technological properties of the wheat flour dough [6]. In order to understand the differences in the technological quality of the wheat flours, which usually arise due to the variety of wheat and the method used for milling, or sometimes to obtain better quality parameters in milling (i.e. optimizing the wheat blend for better technological properties in flour), several empirical rheological instruments are used. The Farinograph is one of these instruments which has become an industry standard where technological parameters for dough mixing such as water absorption, mixing tolerance, stability, softening value are recorded [7, 8]. These values are useful in optimizing formulations for baking quality especially in terms of determining the optimum water amount for a specific type of flour, optimizing the time of mixing to obtain a well-developed dough with optimal rheology and gas holding capacity and as a result obtaining baked products with excellent sensory and textural properties.

Wheat flour dough has been shown to be linear viscoelastic below the strains of approximately 0.2% depending on the type flour and become highly nonlinear beyond this strain level. Nonlinearity in wheat flour dough has been attributed to the breakdown of the elastic gluten protein network. The network is known to be held together by secondary bonding interactions which are susceptible to breakdown with increasing mechanical energy as strain increases [9, 10]. Non-linearity of wheat flour dough has been studied previously [11–15], however it has not been evaluated using Large Amplitude Oscillatory Shear (LAOS) technique concerning the change in the non-linear fundamental rheological properties throughout mixing for both hard and soft wheat flour doughs.

LAOS is a method based on Fourier transform rheology (FT-rheology), which characterizes materials in the non-linear region [16–21]. In LAOS experiments the stress response for an applied oscillatory strain wave loses its pure sinusoidal character (i.e. linearity) [22]. For a sinusoidal strain input $\gamma(t) = \gamma_o \sin(\omega t)$, the stress response can be represented completely by a Fourier series given in two alternate forms to emphasize either elastic or viscous scaling, respectively (Equation 1)

$$\sigma(t;\omega,\gamma_o)=\gamma_o\sum_{n\,odd}\{G'_n(\omega,\gamma_o)\sin n\omega t+G''_n(\omega,\gamma_o)\cos n\omega t\}$$
$$\sigma(t;\omega,\gamma_o)=\dot{\gamma}_o\sum_{n\,odd}\{\eta''_n(\omega,\gamma_o)\sin n\omega t+\eta'_n(\omega,\gamma_o)\cos n\omega t\} \tag{1}$$

Since the stress output is not purely sinusoidal, the behavior can no longer be accurately and correctly described in terms of a storage modulus G' and loss modulus G''. Ewoldt and McKinley and others [17] extended the method of orthogonal stress decomposition used previously by Cho et al [23] in order to interpret LAOS data and obtain fundamentally sound non-linear rheological properties. They used Chebyshev polynomials to be able to describe the strain dependence of material properties uniquely through LAOS data. Then they proposed $e_n(\omega,\gamma_o)$ as the elastic Chebyshev coefficients and $v_n(\omega,\gamma_o)$ as the viscous Chebyshev coefficients. They improved the equation provided by Reimers and Dealy [24], which is an expression of FT rheology in terms of amplitude and phase angle (Equation 2)

$$\sigma=\gamma_o\sum_{n:odd}|G_n{}^*|\sin(n\omega t+\delta_n) \tag{2}$$

where $|G_n{}^*| = \sqrt{G'_n + G''_n}$ is the scaled stress magnitude and δ_n is the phase angle with respect to the input strain signal $\gamma(t) = \gamma_o \sin\omega t$ of the imperfect wave. The variable δ_n was then interpreted in order to determine the initial conditions of the higher-harmonic contributions. At $\omega t = 0$, the third harmonic contribution is $|G_n{}^*|\sin(\delta_3)$ and thereafter oscillates with a frequency of $3\omega_1$ for $\omega t > 0$. The parameter δ_3 determines the initial value of the third harmonic contribution, and must range from $0 \le \delta_3 \le 2\pi$. And finally using these equations, Ewoldt et al. [14] related the Chebyshev coefficients for $n = 3$ phase angle with

$$e_3=-|G_3{}^*|\cos\delta_3 \quad \begin{matrix} >0 & \text{for} & \frac{\pi}{2}<\delta_3<3\pi/2 \\ =0 & \text{for} & \delta_3=\pi/2,3\pi/2 \\ <0 & \text{for} & -\pi/2<\delta_3<\pi/2 \end{matrix} \tag{3}$$

the intracycle stiffening/softening (Equation 3) and thickening/thinning (Equation 4) behaviors and proposed new measures for LAOS.

$$v_3=\frac{|G_3{}^*|}{\omega}\sin\delta_3 \quad \begin{matrix} >0 & \text{for} & 0<\delta_3<\pi \\ =0 & \text{for} & \delta_3=0,\pi \\ <0 & \text{for} & \pi<\delta_3<2\pi \end{matrix} \tag{4}$$

Ewoldt et al. [14] also plotted periodic stress response $\sigma(t, \omega, \gamma_o)$ at steady state parametrically against $\gamma(t)$. These parametric plots are commonly called Lissajous-Bowditch curves and they represent the raw data obtained from LAOS tests [15, 17, 19]. In order to define viscoelastic moduli for a nonlinear material response, Ewoldt et al. [17] proposed G'_M, the minimum-strain modulus or tangent modulus at $\gamma = 0$, and G'_L, the large-strain modulus or secant modulus evaluated at the maximum imposed strain, using the Lissajous-Bowditch curves. On the other hand, they proposed η'_M and η'_L, which indicate the instantaneous viscosity or coefficient at the smallest and largest shear-rates for the viscous response, respectively. Plots showing in detail how the new LAOS parameters are developed from a classical strain sweep that covers the non-linear region and how the Lissajous-Bowditch curves are obtained is illustrated in an excellent way elsewhere [17, 25]. We will not reproduce that graph here. These new parameters led to the calculations of other dimensionless non-linearity parameters S (stiffening ratio, Equation 5) and T (thickening ratio, Equation 6).

$$S\equiv\frac{G'_L-G'_M}{G'_L}=\frac{4e_3+\dots}{e_1+e_3+\dots} \tag{5}$$

$$T\equiv\frac{\eta'_L-\eta'_M}{\eta'_L}=\frac{4v_3+\dots}{v_1+v_3+\dots} \tag{6}$$

In this study, the non-linear rheological properties of soft wheat flour dough is characterized at 4 different

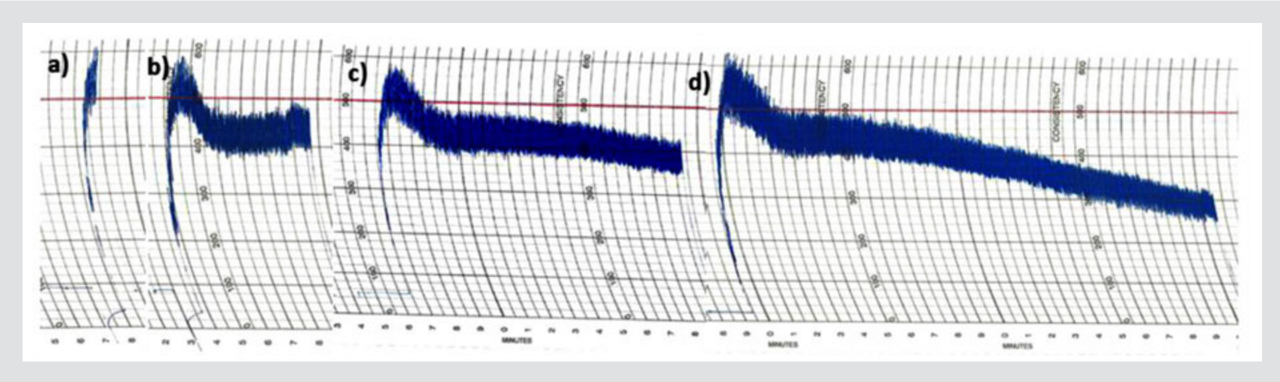

Figure 1: Different phases of Farinograph mixing: a) 1st phase, b) 2nd phase, c) 3rd phase, and d) 4th phase.

stages of Farinograph mixing using these LAOS parameters. During mixing of wheat flour doughs, the distribution of the gluten network changes as a result of the continuously applied large deformations. Moreover, recent studies using fluorescent quantum dot tags attached to gliadin showed that both main fractions of gluten (gliadins and glutenins) and especially the distribution of gliadin in the dough matrix changed during mixing [26, 27]. However, it is not possible to quantitatively explain these changes using a Farinograph, since it is an empirical method giving relative 101 torque information about the rheological behavior of dough. It may be possible to fundamentally explain such structural changes in dough using LAOS tests. Therefore, the purpose of this study is to understand the effect of mixing on the non-linear rheological behavior of soft wheat flour dough in more depth by using LAOS parameters and attempt to correlate them with structural changes during mixing. Previously, the effect of mixing on the non-linearity of hard wheat flour dough was evaluated [28]. The differences in the rheological properties of soft and hard wheat flour doughs, due to the different chemical compositions of hard and soft wheat varieties, are also emphasized through the characterization in the non-linear region with the LAOS parameters.

2 MATERIALS AND METHODS

2.1 MATERIALS

Soft red winter wheat flour (12.17 % moisture, 23.9 % wet gluten, 60.2 % water absorption) obtained from Siemer Milling Company (Hopkinsville, KY) was used to prepare the dough samples evaluated in this study.

2.2 METHODS

Dough samples were prepared using a Farinograph (Brabender, Germany) according to the AACC method 54-21 [29]. The Farinograph torque values were recorded as a function of time during mixing. The samples were obtained at 4 different stages of Farinograph mixing: At the peak point (1st phase), 5 minutes after the peak point (2nd phase), which shows the mixing tolerance index of the dough, 12 minutes after the peak point (3rd phase), which is an indicator of softening value, and 20 minutes after the peak point, which corresponds to the end of farinograph mixing measurement (4th phase). The non-linear rheological properties of the dough samples were measured with a DHR-3 Rheometer (TA Instruments, USA) using the LAOS mode. The measurements were carried out in triplicate at 25 °C using frequencies of 1, 10, and 20 rad/s and strain values of 0.01 and 200 % at nine values of strain. A 40 mm sand-blasted plate and a gap of 2 mm were used for all the measurements. The dough samples were rested until the axial normal force relaxed to 1 N. All the non-linear data were obtained through the use of TRIOS software provided by TA for LAOS analysis. The raw stress waves and Lissajous curves were drawn using the software OriginPro 8.6.

3 RESULTS AND DISCUSSION

3.1 RAW RHEOLOGICAL DATA FOR SOFT WHEAT FLOUR DOUGH

3.1.1 Dough development data during mixing

Figure 1 shows the Farinograms for the soft wheat flour dough at different stages of Farinograph mixing. The arrival time is 0.35 minutes, the peak time is 0.6 minutes, the departure time is 3.0 minutes and the stability of the dough is 2.65 minutes Samples were obtained at 4 different stages of the farinograph mixing: 1) at peak point, 2), 5 minutes after the peak point, which shows the mixing tolerance index of the dough, 3) 12 minutes after the peak point, which is a marker of softening value, 4) at 20 minutes, i.e. at the end of farinograph mixing. Hydration takes less time in soft wheat flour due to smaller particle size and it absorbs less water due to less amount of starch damage and protein content compared to hard wheat flour. Soft wheat flour is considerably softer in texture, therefore starch damage occurs less during milling. And it takes less time for soft wheat flour particles to hydrate and swell during mixing due to their smaller particles [7, 30]. For this reason, soft wheat flour dough showed less stability compared to hard wheat flour dough (16 minutes stability) studied before [28].

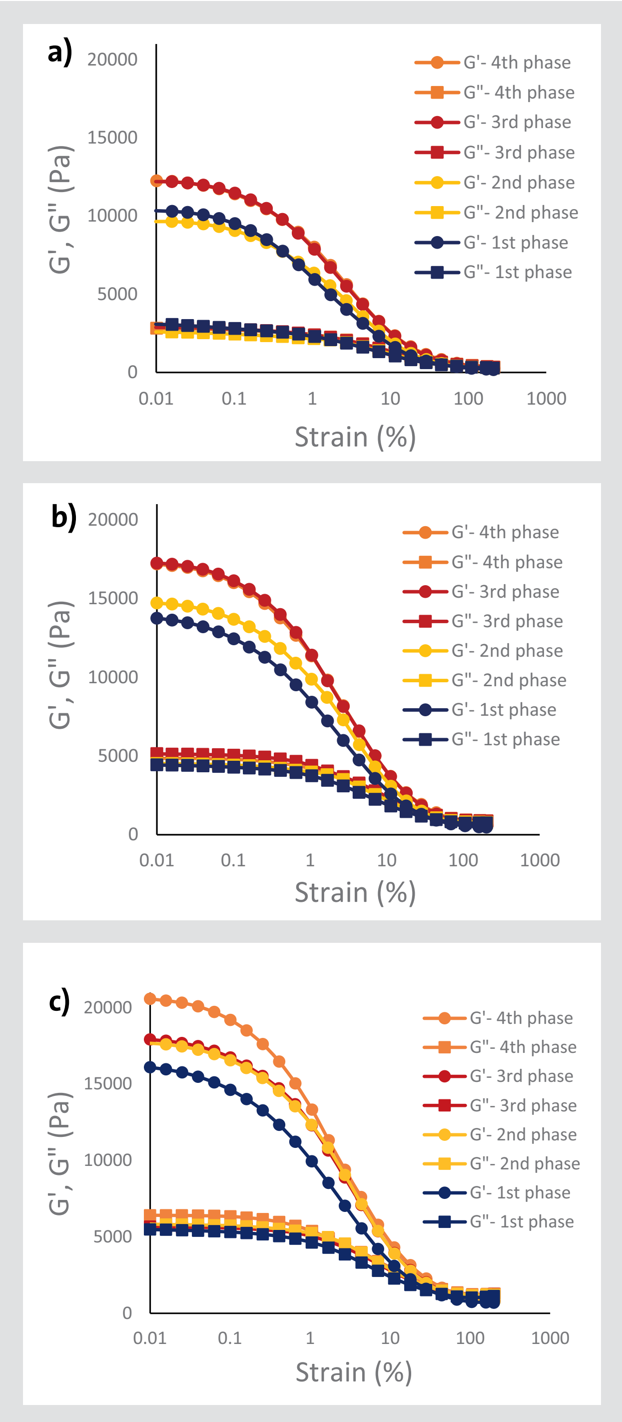

Figure 2: G' and G'' values of soft dough samples: a) 1 rad/s, b) 10 rad/s, and c) 20 rad/s.

3.1.2 Analysis of the rheological behavior in the linear and non-linear region

Strain sweeps for soft wheat flour at different mixing times are shown in Figure 2. In this figure, both the linear and the non-linear regions are clearly observed and the transition from linear to non-linear behavior is slightly affected by the mixing time of the dough. As the mixing time increases, at the shorter mixing time, the onset of non-linear behavior first occurs at low strains (0.015 % at 0.1 rad/s) at the 1st phase of mixing since the gluten network just starts to form; but then at the longer mixing times, in the 2nd and the 3rd phases, the onset occurs at higher strains (0.06 % for 20 rad/s). At the 4th phase of mixing, since the gluten network weakens due to the mechanical effect applied during mixing, the onset of non-linearity decreases to lower strain again (0.039 % at 20 rad/s) and this information reflects how the rheological behavior of soft dough changes throughout the phases of mixing. The onset of non-linear behavior occurs at lower strains as the frequency increases, especially at mixing times beyond the departure time of the dough (Figure 2). Clearly, this onset is also a function of the frequency selected for the particular strain sweep. At the shorter frequencies, the onset is larger, while at the larger frequencies, the onset is at lower values of strain. In Figure 2, the linear behavior of the soft wheat flour is shown in all phases of mixing. The storage modulus *G'* and the loss modulus *G''* values both increased as the frequency increased, and the dough sample obtained at the last phase of mixing always showed higher *G* values at all frequencies studied. *G* values increased gradually as the mixing proceeded from the 1st phase to the 3rd phase. *G'* values of the samples at the 3rd and the 4th phase are nearly the same, which suggest that the dough development was completed at the 3rd phase and remained stable into the 4th phase demonstrating that there is not any significant breakdown in the gluten network once the equilibrium breakdown region has been reached in phase 3. Dough development still continued for hard wheat flour dough samples even at the 4th phase of mixing [28]. Farinograms are consistent with small amplitude behavior. As expected, the stability for the soft wheat flour dough is 2.65 minutes, whereas the stability of hard wheat flour dough was 16 minutes.

Specific analysis of the linear and the non-linear behavior was carried out at different values of strain (0.01, 0.06, 1.6, 11, 28, 44, 70, 105, and 200 %). Examples of raw stress waves in the non-linear region (200 %) are shown for 2 selected relatively high (20 rad/s) and relatively low (1 rad/s) frequencies, for the samples obtained at the peak point of Farinograph mixing (1st phase) and at the end of Farinograph mixing (4th phase) (Figure 3). The stress waves show progressively slight deviations from pure oscillatory behavior, a characteristic behavior of non-linearity, at the frequency of 20 rad/s and they become triangular waves rather than oscillatory waves, a clear indication of the increased non-linearity at the higher frequency. These triangular waves require usually higher harmonics in order to fit the distorted curve. At the lower frequency, the curves have a different kind of non-linearity with the bell-shaped sinusoidal curve distorted to the left. These distortions are getting slightly worse with mixing time at the relatively low frequency, but they be-

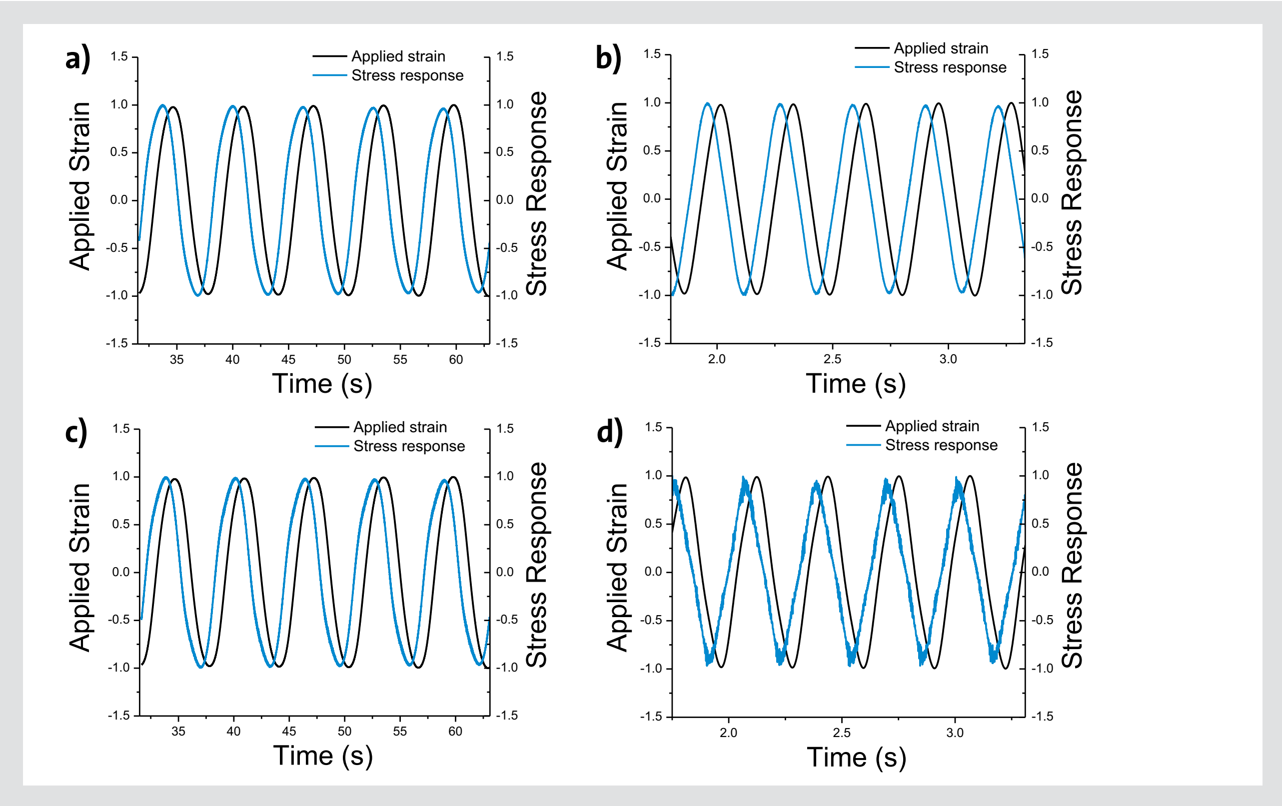

Figure 3: The difference in stress responses of soft dough through mixing at high and low frequencies in the non-linear region at 200 % strain: a) 1st phase of mixing (1 rad/s), b) 1st phase of mixing (20 rad/s), c) 4th phase of mixing (1 rad/s), and d) 4th phase of mixing (20 rad/s).

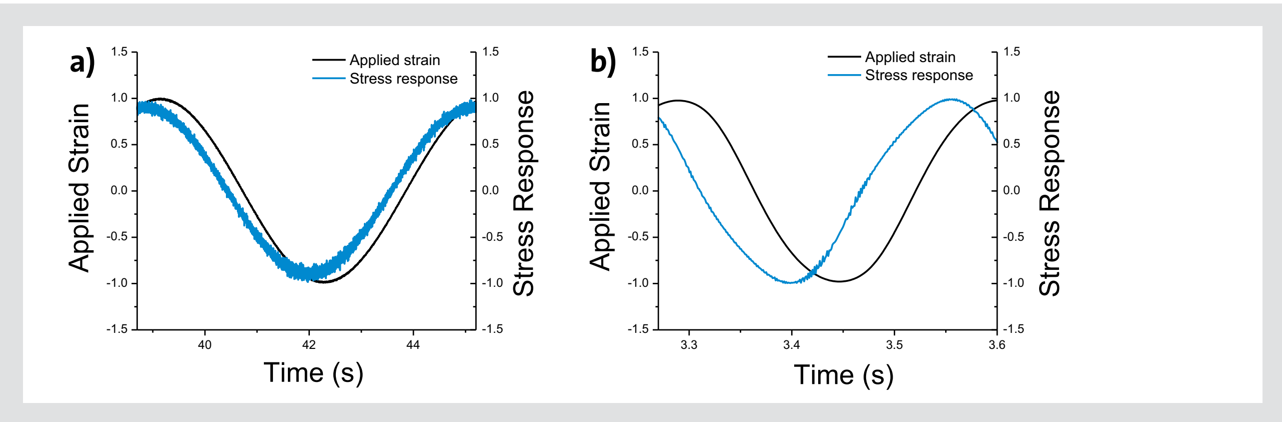

Figure 4: The difference in stress responses of soft dough at minimum and maximum frequency-strain combinations applied: a) 1 rad/s and 0.01 % and b) 20 rad/s and 200 %.

come visibly and obviously more triangular with mixing time in the case of the frequency of 20 rad/s.

In order to magnify the shape and behavior of the oscillatory curves, we have expanded them at one mixing time and two different strains to gain a better and clearer appreciation of non-linearity. Stress waves for the lowest frequency and strain combination (1 rad/s and 0.01 %) and for the highest frequency and strain combination (20 rad/s and 200 %) are plotted in Figure 4 for the 1st phase of mixing. We can see that the non-linearities are much more pronounced as the strain increases and are now quite obvious since the waves have been expanded.

3.2 ANALYSIS OF THE BEHAVIOR OF LISSAJOUS CURVES

The Lissajous-Bowditch curves are plotted in the form of normalized total stress and normalized elastic/viscous stress versus normalized strain for each frequency and for the four phases of dough mixing. These plots enable understanding of the intracycle rheological behavior of soft wheat flour dough. In these curves, the amplitude of strain increases up to the amplitude of the strains studied (0.01, 0.06, 1.6, 11, 28, 44, 70, 105, and 200 %) where the stress data were obtained. The plots obtained for each selected strain amplitude at all intracycle strains were superimposed for each applied fre-

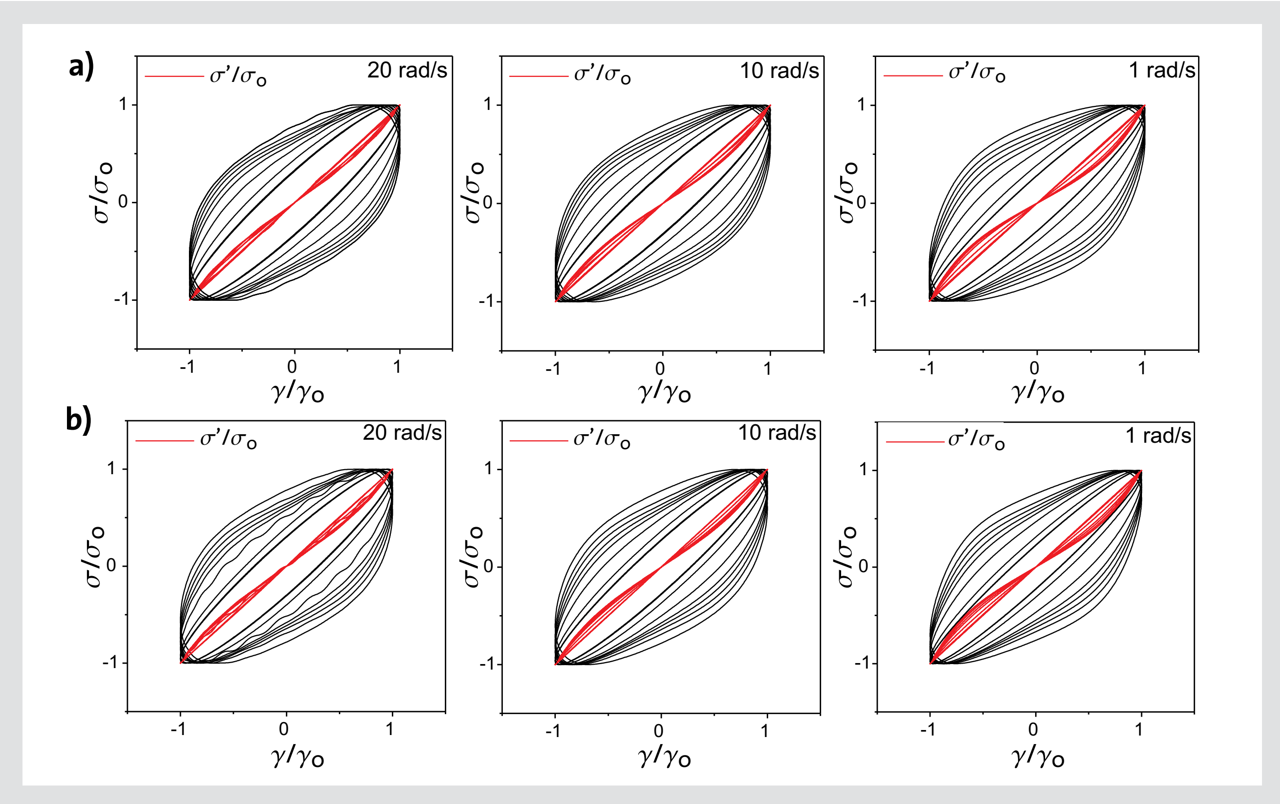

Figure 5: Lissajous curves for the elastic component of soft wheat flour dough: a) obtained at the 1st phase of Farinograph mixing (peak time) and b) obtained at the 4th phase (where the protein network starts to breakdown) of Farinograph mixing.

quency. The stress response is evaluated as two components: Elastic stress and viscous stress, to investigate separately how these two components of the dough samples behave in the non-linear region and to be able to characterize the non-linear viscoelastic behavior of the soft wheat flour dough samples in detail.

A linear viscoelastic response appears as a narrow ellipse, which contains two mirror planes defined by the major and minor axes of the ellipse. In the linear region, the major axis is much larger than the minor axis and the ellipse is completely symmetric. A steady nonlinear viscoelastic response loses the mirror planes [17] and the ellipse becomes progressively distorted as the amplitude of strain increases into the non-linear region. The ellipses lose their symmetry and they progressively acquire a rhomboid shape. When the stress data is plotted versus the amplitude of strain rate and as a function of intracycle strain rate, a perfectly linear viscous material shows a spherical trajectory and as the material becomes progressively non-linear, the sphere becomes distorted and the degree of distortion increases with increasing strain amplitude in the non-linear region.

3.2.1 Analysis of the elastic Lissajous curves (plots of normalized stress versus normalized strain)

Elliptical trajectories are the indication of dominant elastic behavior and linear viscoelasticity, while circular trajectories are an indication of viscous dominated linear viscoelastic fluid behavior in the Lissajous-Bowditch curves [17]. In our data, we plot the intracycle stress versus the intracycle strain for each strain amplitude and the first observation is that the curves started to get wider and progressively distorted as the frequency decreased. As we increase the frequency, the material shows a progressively elastic behavior as expected. And in the linear region, this is manifested by the increase in *G'* with frequency. The Lissajous curves are consistent with the overall viscoelastic behavior observed with wheat flour dough. Figure 5 shows the elastic analysis as a function of mixing time. In these figures, the dough sample obtained at the 4th phase showed more elastically dominated behavior compared to the samples obtained from the 1st phase of mixing at all frequencies studied. Dough samples showed elliptical trajectories, which shows soft wheat flour dough remained elastically controlled viscoelastic material in the non-linear region. At low strains, in the linear region, the Lissajous curves are narrow ellipses with a very high major to minor axis ratio consistent with a highly elastic material in the linear region. As the strain increased, the Lissajous curves started to become wider and distorted. It is noteworthy to observe that in the 1st phase of mixing the Lissajous curves deviate from ellipticity faster at 1 rad/s as the strain amplitude increases. There are two contrarian events at low frequency as is well known from linear viscoelastic measurements, the material behaves less elastic than at high frequency. However, as the strain decreases, the material structure decays and the dough becomes progressively more viscous because of structure breakdown at the higher strain amplitude. This causes the progressive change in the Lissajous curves going from 1 to 20 rad/s where the increasing strain amplitude creates a feature that we would refer

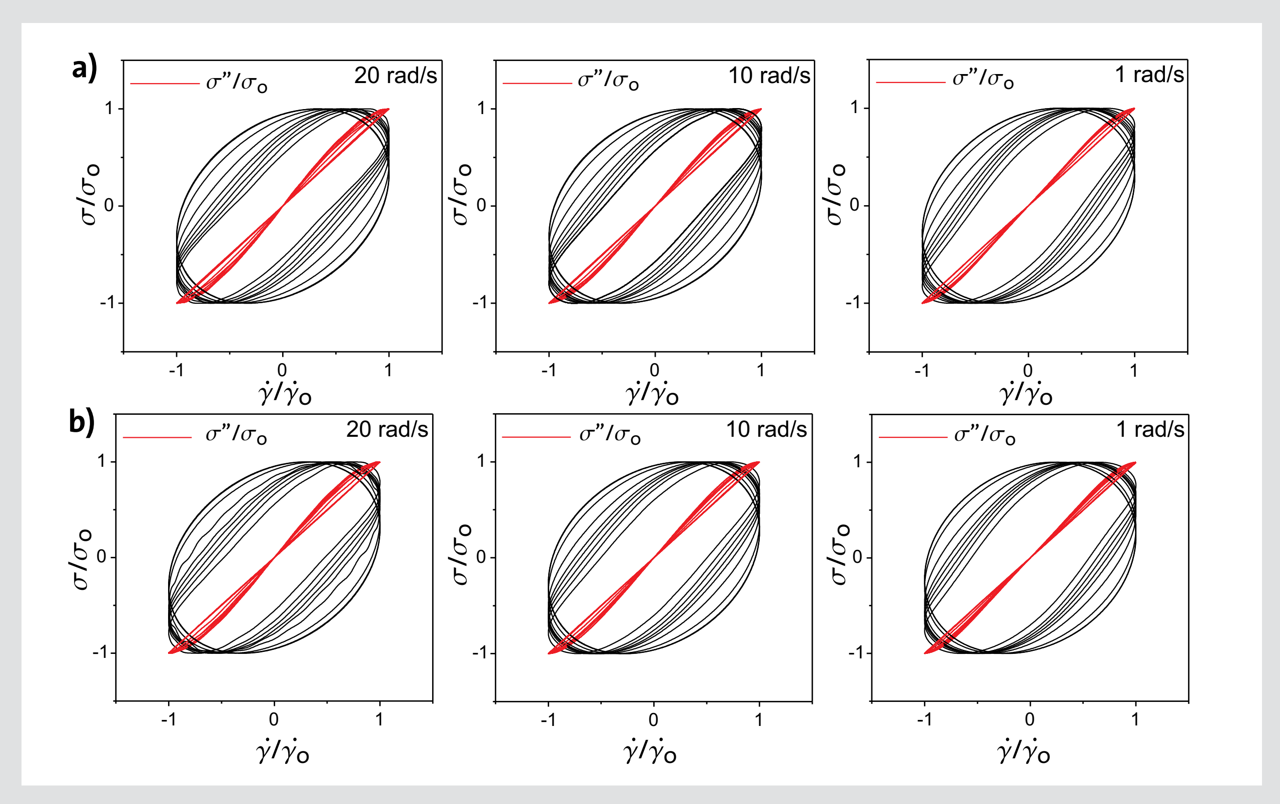

Figure 6: Lissajous curves for the viscous component of soft wheat flour dough: a) obtained at the 1st phase of Farinograph mixing (peak time) and b) obtained at the 4th phase of mixing.

to as a sagging balloon at 20 rad/s. These are the two conflicting events. At the high frequency, the decay in elasticity is facilitated because the increase in the combination of strain and frequency produces higher strain rates compared to the low frequency resulting in the sagging balloon behavior that we observe in the high strain rates. This is very new and detailed information about the intracycle viscoelastic rheology of soft wheat flour dough never reported before.

We present similar data for the 4th phase of mixing to compare the behavior of the Lissajous curves with the 1st phase of mixing. In the 4th phase of mixing, the behavior with respect to frequency mirrors that which we observed in the 1st phase of mixing. The ellipses become distorted faster at 20 rad/s as the strain amplitude increases. This is also consistent with the degradation that occurs in soft wheat flour dough as the departure time is reached and exceeded that we observe in the Farinograph. The degree of distortion is sharper in the 4th phase of mixing compared to the 1st phase of mixing in general, suggesting that the viscoelastic character progressively changes from an elastically dominated behavior to growing viscous behavior. The rate at which this transition occurs is faster in the 4th phase of mixing. This too is consistent with the breakdown observed in the Farinograph curves.

3.2.2 Analysis of the viscous Lissajous curves

We plot normalized stress versus normalized strain rate in the form of viscous Lissajous curves as a function of frequency and mixing time in Figure 6. These plots are shown in order to study the evolution of the viscous character of soft wheat flour dough and are meant to be complementary to the Lissajous plots where normalized stress is plotted versus normalized strain. In essence, they are mirror images of the previous plots that examine the viscous component in detail. As indicated earlier, at the lowest strain studied, the curves are approximated by a circle and appear to be ellipses with a small major to minor axis ratio, because the y-axis is more expanded compared to the x-axis and wheat flour dough is not a purely viscous material but a viscoelastic material. Also it must be noted that the two axes are normalized. And therefore, the curves are concentric in nature because of that normalization. Comparison of the evolution of the shape of the viscous component for the soft dough sample at the 1st phase of mixing (Figure 6a) shows that at 1 rad/s the dough becomes more viscous faster and progressively. The evolution of viscosity slows down from 10 to 20 rad/s as indicated by the close concentricity of the curves at 20 rad/s slowly distancing themselves from one another as the frequency reduces to 10 and 1 rad/s. When we study Figure 6b carefully, we also observe that at the 4th phase of mixing, the curves are somewhat more deviating from circular behavior at a faster rate consistent with the breakdown that we observe in the Farinograms and mirroring the discussion in relation to the elastic component in Figure 5.

As Figure 6 is evaluated, it is observed that the trajectories did not show a remarkable change as the mixing proceeds from the 1st phase to the 4th phase. This means that the elastic component is more dominant in

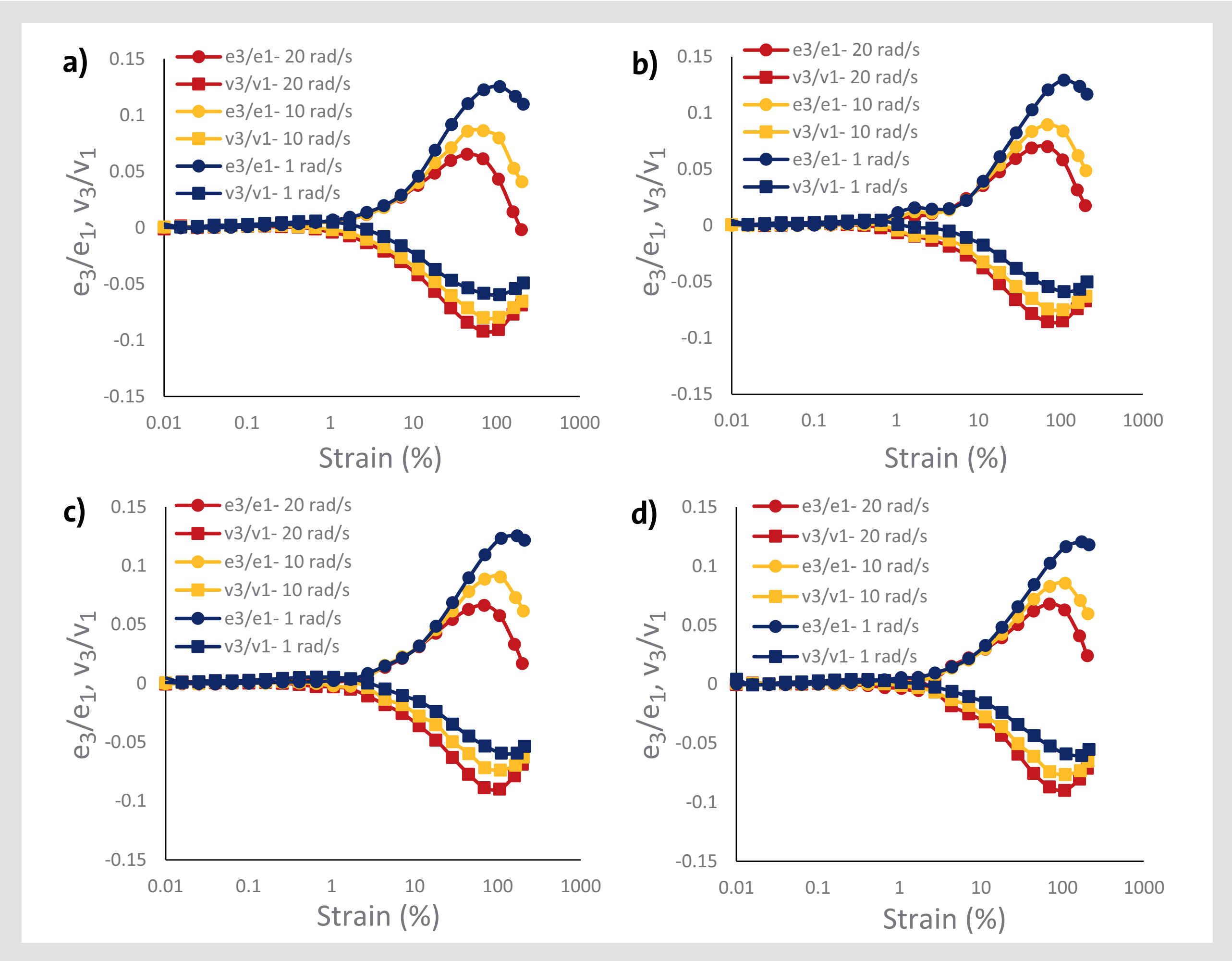

Figure 7: The changes in e_3/e_1 and v_3/v_1 values of soft dough samples at different frequency values: a) 1^{st} phase, b) 2^{nd} phase, c) 3^{rd} phase, and d) 4^{th} phase of mixing.

the non-linear region compared to the viscous component of the soft dough samples. The elastic component is affected by mixing more than the viscous component, because the changes occurring in the elastic component are more pronounced as the mixing proceeds as is well known in the literature [7, 31]. The increase in the viscous behavior of the viscous component is observed as progressively increasing stickiness in the dough at the end of Farinograph mixing. In the 1^{st} phase of mixing, on the other hand, the gluten network just starts to form and for this reason the dough is not as strong as in the next phase of mixing. Therefore, the elastic component becomes more dominant in the proceeding phases of mixing. Because mixing and dough development is all about gluten network formation and gluten constitutes the elastic component of the dough sample. The changes in the elastic gluten structure are the ones that are reflected in the intracycle rheology in a more pronounced way.

3.3 NON-LINEAR RHEOLOGICAL ELASTIC PROPERTIES OF DOUGH AS A FUNCTION OF MIXING PHASE

Figure 7 shows the ratio of the 3^{rd} order elastic Chebyshev coefficient to the 1^{st} order e_3/e_1 and the ratio of 3^{rd} order viscous Chebyshev coefficient to the 1^{st} order v_3/v_1 for the all dough samples obtained at different stages of mixing at all frequency values. The soft dough samples showed strain stiffening and shear thinning behavior at all phases of mixing and applied frequencies in the non-linear region. However, the intensity of the strain stiffening and shear thinning behavior started to decrease at around 44 – 70 % strain value, where the applied frequency is 20 rad/s (at 44 % strain for the sample obtained at the beginning of mixing and 70 % strain for the dough obtained at the end of mixing). As a result, in soft wheat flour dough exposed to increasing strain, the gluten network starts to breakdown at lower strains than the hard wheat flour dough [28]. e_3/e_1 values showed increase gradually in the non-linear region as the mixing proceeded from the 1^{st} phase to the 4^{th} phase. It was also observed that the decrease in the strain stiffening behavior was retarded as the frequency decreased. Amemiya and Menjivar [10] states that at small strains, short interactions are affected, however at high strains, protein phase starts to dominate the wheat flour dough behavior and strain stiffening is observed. At strains above that, protein fibrills start to break down; so strain softening occurs. Therefore, 44 – 70 % strain value might be the critical strain where the gluten network started to weaken for the soft dough samples. And this critical strain value increased as the frequency decreased. It occurred at 44, 70, and 109 % at the 1st phase of mixing for 20, 10, and 1 rad/s frequency values, respectively. This is because the protein fibrills in the gluten network can find more time to recover and align themselves against the applied strain when the frequency is low. For this reason, the strain value where the intensity of strain stiffening behavior start to decrease increases as the frequency decreased.

G_L (large strain modulus) values indicated in the Figure 8 showed the same trend with the *G* values. G_L values increased for all the dough samples obtained at different phases of mixing, as the frequency increased. At 20 rad/sec, dough sample at the 4th phase showed the highest G_L value, while the dough sample from the 1st phase showed the lowest. And the samples from the 2nd and the 3rd phase showed almost the same G_L values. At 10 and 1 rad/s, the dough samples from the 3rd and the 4th phase showed the same G_L values while the samples from the 1st and the 2nd phase showed close and lower G_L values.

In Figure 9a, the values related to the elastic behavior of the samples were plotted against the strain to be able to get supportive explanation about the nonlinearity of the soft wheat flour dough samples. The stiffening ratio *S* values showed correlation with the e_3/e_1 values. As the frequency increase, *S* values started to decrease after a certain strain value. This behavior is described as the decrease in the intensity of the strain stiffening behavior. Because as long as $S > 0$, it means that the material shows strain stiffening behavior [17]. *S* values also supported that the soft dough samples obtained at different phases of mixing showed strain stiffening behavior in the non-linear region. As the frequency increased, *S* values slightly decreased due to the fact that protein fibrills in the gluten network are affected more by the applied strain in the high frequencies.

3.4 NON-LINEAR VISCOUS PROPERTIES OF DOUGH AS A FUNCTION OF MIXING PHASE

The thickening ratio *T* values plotted in Figure 9b for the data obtained at 10 rad/s frequency. The highest values for *T* were obtained at the highest frequency applied and they decreased gradually for all the dough samples as the frequency decreased. As the frequency increased, *T* values belonging to the dough sample obtained at the 1st and the 2nd phase of mixing were the ones affected the most. All soft dough samples showed shear thinning behavior since *T* values were smaller than 0 [17]. Large strain rate values η_L obtained at 10 rad/sec frequency are showed in Figure 10. At 20 and 10 rad/s frequency values, η_L values increased as the mixing proceeds from the 1st phase to the 4th phase. η_L values showed a significantly decreasing trend as the frequency applied increased. η_L and η_M (minimum strain rate) values were almost the same for the soft dough

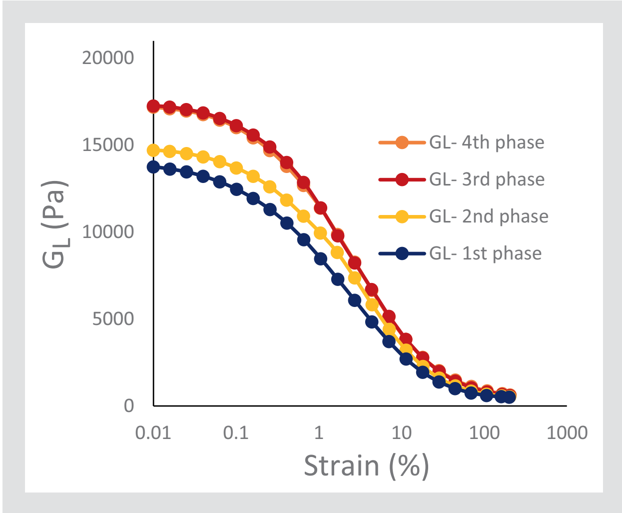

Figure 8: Large strain modulus G_L values for soft dough sample at 10 rad/s.

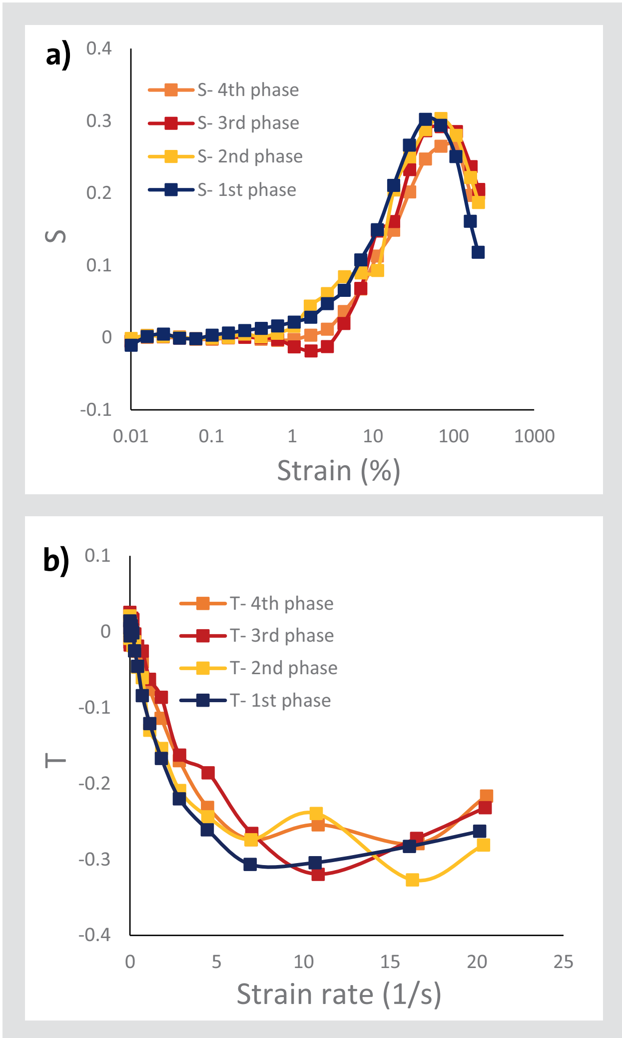

Figure 9: S (a) and T (b) values of soft dough sample at 10 rad/s.

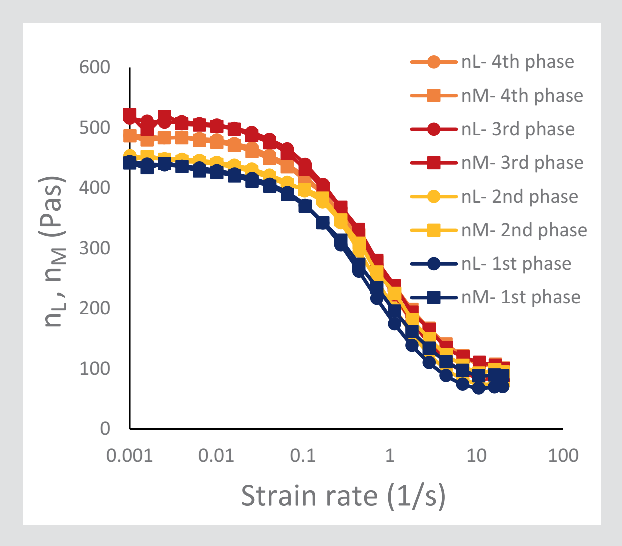

Figure 10: Large η_L and minimum strain rate viscosity η_M change versus strain rate values for soft dough sample at 10 rad/s.

samples at all phases of mixing and at all frequencies studied. And generally, these values seemed not to be affected by mixing for the soft dough samples.

4 CONCLUSIONS

Soft wheat flour dough samples obtained at different phases of Farinograph mixing showed non-linear behavior at strains larger than 0.015 – 0.06 %. As the frequency increased from 1 to 20 rad/s, soft flour dough samples started to behave more elastically as shown in Lissajous curves. On the other hand, as the strain increases from 0.01 to 200 % gradually, soft dough samples started to display more viscously dominated viscoelastic character due to the structural breakdown in the gluten network at high strains and the increasingly dominant role that starch played because the gluten network started to break down. The elastic component of the soft wheat flour dough was affected by mixing more compared to the viscous component. When Lissajous curves were evaluated at the beginning and at the end of Farinograph mixing at different frequencies, more remarkable changes were observed in the elastic component. Clearly the elastic component of the soft dough samples influenced the non-linear region more. This may be attributed to the changes occurring in the protein fibrils in gluten network at large strains [10].

The dough samples obtained at the four phases of mixing showed strain stiffening ($S > 0$) and shear thinning ($T < 0$) behavior at all frequencies studied up to the strain value of 200 %. e_3/e_1 values showed an increase supporting the strain stiffening behavior as the strain increased gradually. However, a decrease in the intensity of e_3/e_1 values were observed when the strain reached 44 – 70 %. This strain range may be the critical strain for the soft wheat flour dough where the gluten network starts to weaken with increasing strain and the resulting mechanical energy introduced in the sample. This critical strain value increased as the frequency decreased from 20 to 1 rad/s. When the applied frequency of oscillation was lower the critical strain values were higher and the protein fibrils in the gluten network could recover and align themselves up to these critical strain levels. The large strain modulus G_L increased with increasing mixing time. Except for the highest frequency applied, G_L values at the 3rd and the 4th phase of Farinograph mixing were close in magnitude which showed that the gluten network development stopped when the sample reached to the 3rd phase of mixing. On the other hand, the decreasing strain stiffening behavior occurred in the gluten network after the strain values of 44 – 70 % and the shear thinning behavior observed in the starch matrix as the strain increased can be regarded as the explanation for the decreasing trend observed in the Farinograms as the mixing continued.

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