Extensional Rheology of Bread Dough

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December 19th, 2005

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Chairman, Department Committee on Graduate Students
Abstract

We investigated the extensional properties of wheat flour dough on the Filament Stretching Rheometer (FISER), in which the sample approaches uniform uni-axial extension flow at a constant strain rate over a large portion of the experiment, thereby allowing us to directly probe the transient material function characterizing the behavior of dough in extension. The large dynamic range of this Rheometer permitted us to investigate the visco-elastic nature of the dough well into the baking/proofing range. Special experimental protocols and modifications to the rheometer fixtures were designed and built to overcome problems in sample preparation. Parameters such as water content, base flour type and mixing conditions were varied to determine their respective effects on the extensional properties.
Ultimately we would like to develop a constitutive equation describing the evolution of stress during extension and arrive at a model for the stability against rupture in these doughs. This will form the basis for developing protocols to map results from the true uni-axial extension experiments onto empirical measurements obtained from existing and widely utilized industrial standard testing devices. As an example in this first stage, we focused on the Mixograph, which is a widely accepted method of testing dough in the food industry, and considered how its output can be related to the true material functions generated in filament stretching rheometry.

Thesis Supervisor: Gareth H. McKinley

Title: Professor of Mechanical Engineering
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<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHEOLOGICAL INVARIANCE</td>
<td>43</td>
</tr>
<tr>
<td>DEFORMATION Tensors</td>
<td>44</td>
</tr>
<tr>
<td>UPPER CONVEXED MAXWELL AND OLDROYD-B MODEL</td>
<td>44</td>
</tr>
<tr>
<td>PHAN-THEIN MODEL</td>
<td>46</td>
</tr>
<tr>
<td>POM-POM MODEL</td>
<td>49</td>
</tr>
<tr>
<td>POWER LAW MODEL</td>
<td>50</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>51</td>
</tr>
<tr>
<td>FILAMENT STRETCHING RHEOMETRY</td>
<td>52</td>
</tr>
<tr>
<td>KINEMATICS</td>
<td>53</td>
</tr>
<tr>
<td>DYNAMICS</td>
<td>55</td>
</tr>
<tr>
<td>FIXTURES AND PROTOCOLS</td>
<td>58</td>
</tr>
<tr>
<td>FILAMENT STRETCHING EXPERIMENT</td>
<td>61</td>
</tr>
<tr>
<td>RESULTS</td>
<td>61</td>
</tr>
<tr>
<td>STRAIN RATE - VISCO-ELASTICITY OF DOUGH</td>
<td>63</td>
</tr>
<tr>
<td>CONSTITUTIVE EQUATION AND CHARACTERISTIC TIME-SCALE</td>
<td>67</td>
</tr>
<tr>
<td>CONSIDÈRE CRITERION</td>
<td>70</td>
</tr>
<tr>
<td>NON-DIMENSIONAL REPRESENTATION OF RESULTS</td>
<td>76</td>
</tr>
<tr>
<td>Different Flour Types</td>
<td>80</td>
</tr>
<tr>
<td>MIXING</td>
<td>85</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>85</td>
</tr>
<tr>
<td>DEFORMATION OF DOUGH IN THE MIXOGRAPH</td>
<td>85</td>
</tr>
<tr>
<td>SEPARATING THE TWO COMPONENTS</td>
<td>91</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>95</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>96</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>99</td>
</tr>
</tbody>
</table>
Introduction

Wheat flour dough has the unique ability to form cohesive elastic doughs when mixed with water under the certain conditions. Because of this characteristic, such doughs has the ability to retain leavening gas during the bread-making process to yield a light, fine cell structure and a soft yet resilient response to chewing. Doughs formed from other flours are significantly less elastic and extensible, and yield products which are coarser and denser. We begin by first discussing the various components which go into forming the dough.

Ingredients

Wheat Flour

The species of wheat commonly milled for baking flours are of the species *Triticum Vulgare* and can be divided into the following types [1]:

1. Hard Red Spring Wheat (HRS) – produced in the Northern Great Plains states. The flours are high in protein and have strong gluten. Suitable for rolls and specialty breads, they can also be blended to improve baking quality of weaker flours.

2. Hard Red Winter Wheat (HRW) – grown in the Southern Great Plains states. These flours are of intermediate protein percentage and strength. They are the all-purpose flour commonly found in pan white bread.
3. Soft Red Winter (SRW) Wheat – Mostly grown east of the Missouri and Mississippi rivers and South of the Great Lakes. Has low protein content and relatively weak gluten. These flours are suitable for cakes, cookies and pastries.

![Diagram of a grain of wheat with annotations](http://www.dovesfarm-organic.co.uk/composition-grain-of-wheat.htm)

The harvested wheat is cleaned and conditioned. Conditioning involves dampening and heating to make the outer bran layer less susceptible to break up during the grinding stages. Milling separates the endosperm from the bran and germ. The endosperm is then grounded into a fine powder.

**Composition**

Typical composition of both wheat and flours are presented in Table 1 and Table 2 respectively, they vary according to the year and area of production.

We are primarily interested in the properties directly related to rheology,
therefore little attention will be given to chemical make-up of these constituents.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Protein</td>
<td>7.0</td>
</tr>
<tr>
<td>Mineral (Ash)</td>
<td>1.5</td>
</tr>
<tr>
<td>Lipids</td>
<td>1.5</td>
</tr>
<tr>
<td>Starch</td>
<td>60.0</td>
</tr>
<tr>
<td>Cellulose</td>
<td>2.0</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 1 Composition of Wheat [2]

<table>
<thead>
<tr>
<th>Type of Wheat at 14% moisture</th>
<th>Mineral Ash (%)</th>
<th>Protein (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard Red Spring</td>
<td>0.47</td>
<td>12.9</td>
</tr>
<tr>
<td>Hard Red Winter</td>
<td>0.47</td>
<td>12.1</td>
</tr>
<tr>
<td>Soft Red Winter</td>
<td>0.38</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 2 Composition of flours [3]

**Starch**

Starch is the most abundant constituent within the wheat and flour, representing over 70% of the total weight. They appear in the form of granules in two distinct size ranges: small spherical granules of 5-15 μm in diameter and lenticular particles of about 30 μm [4, 5].

During dough preparation, starch will absorb water. It will swell and increase its mass by up to 50% of its dry weight. A significant fraction of starch can be
damaged in the milling process and mixing. The damaged starch has higher water absorption capability [6] and can reduce the water available to other components. By and large, starch granules can be considered as an inert filler in the network of proteins [7]. However its influence on rheology is complex because the protein denaturation temperature range overlaps with the starch gelatinization range. [8, 9].

In the oven, starch granules gelatinize. The gelatinization process is irreversible. At a critical temperature, swollen starch granules and some soluble macromolecules forms a starch paste. There will be interaction between the soluble macromolecules in the form of overlaps. Upon cooling, entanglements form resulting in a gel. Without going into the detailed chemistry of the process, we summarize the gelation states in Figure 2.

Figure 2 Schematic representation of gelatinisation process of starch granules [10]. (I) Starch granules, (IIa) Starch granules swollen with water, (IIb) Granules and soluble macromolecules, forming a paste under heating, (IIIa and IIIb) Formation of network (gelling).
Protein

Proteins are commonly classified by their solubility by a system introduced by Osborne [11]. The proteins are extracted sequentially with a series of solvents. This classification does not necessarily divide the proteins according to its biochemical properties or physical functionality, however, due to its convenience it is still widely used to separate the constituents into broad functional groups such as gliadin and glutenin. The non-gluten proteins (typically 15 – 20% of total proteins content) play only a minor role in bread-making, they occur mostly in the outer layers of the wheat kernel. While the gluten proteins (80 – 85%), mostly from the endosperm, has significant contribution to the properties relevant to the bread-making process. In view this functionality, more attention will be paid to the gluten proteins in this article.

<table>
<thead>
<tr>
<th>Osborne fraction</th>
<th>Solubility behavior</th>
<th>Composition</th>
<th>Biological role</th>
<th>Functional role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albumin</td>
<td>Water</td>
<td>Non-gluten proteins (mainly monomeric)</td>
<td>Metabolic and structural proteins</td>
<td>Variable/insignificant</td>
</tr>
<tr>
<td>Globulin</td>
<td>Dilute salt solution</td>
<td>Non-gluten proteins (mainly monomeric)</td>
<td>Metabolic and structural proteins</td>
<td>Variable/insignificant</td>
</tr>
<tr>
<td>Gliadin</td>
<td>Aqueous alcohol</td>
<td>Gluten proteins</td>
<td>Prolamin-type seed storage proteins</td>
<td>Dough viscosity/plasticity</td>
</tr>
<tr>
<td>Glutenin</td>
<td>Dilute acetic acid</td>
<td>Gluten proteins</td>
<td>Prolamin-type seed storage proteins</td>
<td>Dough elasticity/strength</td>
</tr>
<tr>
<td>Residue</td>
<td>Unextractable</td>
<td>Gluten proteins</td>
<td>Prolamin-type seed storage proteins</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3 Different groups of protein, as defined by Osborne (1924)
Gluten can be further sub-divided into glutenin and gliadin, which are present in roughly equal amounts.

Glutenin – a heterogeneous mix of high molecular weight polymers (Mw – 8 x $10^4$ to $10^6$). They are one of the largest proteins found in nature [12]. Due to its insolubility, the structure of glutenin remains largely unknown until recent years where new techniques such as light, X-ray and electron scattering, NMR, AFM etc... [13-21] were made available. During mixing glutenin forms a continuous network throughout the dough, giving it the distinct elastic property.

Gliadin – a highly polymorphic group of monomeric polymers. (Mw – 3 x $10^4$ to $10^6$).

Gluten functionality arise largely from glutenin. Gliadin are thought to act as plasticizers on the glutenin network, increasing its viscous (liquid-like) behavior. The quality and quantity of the gluten is critical to the overall quality of the flour. We shall discuss in detail the mechanism of how these proteins give wheat flour dough its unique visco-elastic property.

**Water**

Water performs two functions in bread-making. Firstly it hydrates the constituents allowing them to interact to give dough its chemical and physical properties. Flour mixed with insufficient water will not form a lumpy discontinuous mess rather than a cohesive dough. Secondly, a portion of water is retained in the bread after baking and will play a major role in determining its texture.

Typical flour has a moisture content of 10 – 15%, additional water is introduced
during mixing so that it constitute 40 – 60% of the dough mass. If water is added gradually, the first 30 – 35% will be bounded to the flour forming a single-phase system. Water added after this will form a separate phase of "free" water. This aqueous phase dissolves water soluble components and is the medium for chemical reactions [22].

The rheological properties can be extremely sensitive to water content [23, 24]. The most significant effect is on the modulus, this "free" water can act as a plasticizer by swelling the gluten network thus reducing its stiffness [25]. Otherwise, the "free water" does not seem to change the structure of the dough significantly [26].

Impurities in water can have significant result. Compared to hard water, if soft water is used to form a dough, less water will be needed to form a dough of same stiffness. The resulting dough will also be "stickier".

**Others**

We include a brief discussion of some other components which have a functional purpose in the process.

**Leavening Agents** – The purpose of leavening agents is to make the dough rise and produce a porous product. This is achieved through the release of carbon-dioxide and ethanol into gas cells trapped by the gluten phase. The most common leavening agent is the bakers yeast (*Saccharomyces cerevisae*), other than causing rise, the chemical process also contributes to the flavor and texture. Other chemical leavening agents can also be used.

**Salts** – The presence of salt affects the water ionic properties, starch structure and
hydration. The effect on rheology can be significant [27].

Pentosans – pentosans can modify the rheological properties of dough because of its large molecular weight and gel forming ability.

Added gluten – Improves and increases the gluten already present in the flour

Fats – Improves the crumb structure and sometimes the loaf volume

Anti-oxidants – Preservation purposes

**The Structure of Dough**

On the macro-scale, dough can be approximated as an isotropic, homogeneous continuum, however upon closer inspection, the composite nature is revealed. Through the microscope lens capable of seeing features on the micron scale, different phases are visible [28, 29]. Distinct starch granules, swollen by water, can be discerned. A protein phase surrounds these starch granules binding them together. Voids can be seen too, which represents air bubbles or gas cells entrained into the dough during mixing.
Molecular structure of Glutenin Network

The distinctive feature which makes wheat flour dough uniquely suitable for bread-making is its ability to resist rupture of the gas cells during proofing and baking. Air is included into the dough during mixing in tiny pockets (∼10⁻⁵ to 10⁻⁴ in diameter) dispersed throughout the dough, constituting approximately 10-15% of total dough volume. Leavening agents release gas into these cells further increasing the size. They undergo yet another expansion during baking through heating and release of dissolved alcohol/CO2 previously dissolved in the dough [7, 30]. The dough walls surrounding the gas cells are stretched and becomes thinner. It is believed that a “weak” dough with insufficient elasticity/strain-hardening will form dough walls which will rupture under these conditions. Van Vliet et al [31] provides a qualitative theory on how elasticity and strain-
hardening can lead to a more stable dough wall under stretching. Their argument is essentially a linear stability analysis considering the effect of a small defect on a uniform sheet of dough under extension. Through this analysis they arrive at criterion which is equivalent to the Considère criterion, stating that rupture will occur when the rate of increase of stress with respect to strain falls below a certain value. A number of studies have been performed and seem to provide experimental justification for this hypothesis [28, 32-36].

Having recognized the property relevant to good dough quality to be elasticity and strain-hardening, we can next ask the question of what distinct feature of wheat flour gives rise to these properties? Experimental evidence point towards the gluten fraction of wheat proteins. Various researchers have come to the consensus that the glutenin macropolymer forms a three-dimensional network throughout the dough. The initially distinct glutenin molecules in the flour swells in size due to hydration and begin to interact with neighbouring glutenin molecules in the process of mixing/working. The large molecular weight of the glutenin macroplymers is essential to form a critical number of interactions in order to achieve a sample spanning structure which gives elasticity. The exact nature of this network is still unclear. We shall briefly discuss some of the models which have been proposed to describe this network.

**Elastic network**

In the early years of dough research, some scientists believed glutenin forms a disulfide cross-linked structure. These cross-links are covalent bonds and the overall structure is like that of vulcanized rubber. This model is also known as
the “giant protein molecule” model [37]. Though this model can explain the elastic properties of dough (through rubber elasticity [38]), since the “life-time” of a covalent bond will be significantly longer than the experiment and bread-making time-scales, this model fails to explain the visco-elastic (time dependent) rheology of dough.

![Diagram of giant protein molecule model](image)

**Figure 4 Giant protein molecule model. Glutelin macropolymers are covalently cross-linked to form a sample spanning structure.**

**Alignment**

Ewart proposed a model of network formation where working of the dough is modeled as a predominantly shearing deformation [39]. Shearing causes the glutelin molecules to align themselves. The overlap between neighbouring molecules gives them increased overall strength.
Figure 5 A stylized sketch of the Ewart's shear/cohesion model. Initially cohesion is weak, strength is limited by end to end forces of polymers. Shearing increases overlap between neighbouring molecules, interaction between molecules along the length greatly increases strength.

**Entanglement**

Rather than the cohesiveness of the glutenin macropolymers, another model considers the molecular extension during dough working through both tensile and shear forces [40]. During the initial stages of mixing, the large molecular weight of glutenin means that it will form a random coil in its equilibrium state. The mixer blades or action of kneading imparts a strong extensional flow on these molecules causing them to stretch. Simultaneously the molecules will retract itself into its equilibrium/coiled state like an entropic spring. If the rate of extension is greater than that of recoiling, there will be a net extension and vice versa for extension rates that are slower than recoiling. During mixing, the rate of
extension varies significantly, and the characteristic length of these macropolymers will be changing continuously too. Above a critical average rate of mixing, the polymers will have increased their characteristic length to a point where it will be in contact with neighbouring glutenin molecule. During recoil, the glutenin polymers can become entwined with each other. We refer to the points where these interactions occur as entanglements. As mixing progresses, the number of entanglements will increase and eventually a sample spanning structure will be formed.

Indirect evidence of this model comes from situation where the critical average rate of mixing is not reached. Under these circumstances, the extensional flow is insufficient to increase the characteristic size of glutenin molecules to a state where it begins to interacts with its neighbour. Instead, the action of mixing serves to increase the random entropic motion of retraction, the molecules will disentangle from each other, and the dough will lose its elasticity. This effect has been termed “unmixing” and has been observed in the laboratory [41, 42].
1. Undisturbed glutenin polymers takes the form of random coils.

2. Hydration leads to swelling, extensional flow causes polymer to stretch. They begin to interact.

3. Entanglements form throughout dough leading to a sample spanning network.

Figure 6 Stylized schematic of the entanglement model.

The structure of the molecule is unspecified in an entanglement model. The only requirement is that the polymers are of substantial length for entanglements to be likely and to provide entropic elasticity. This is why wheat flour which has an abundance of high molecular weight glutenin is suitable for bread-making.

Recent microscopy has revealed glutenin to possess a highly branched secondary structure. The entanglement model can also be applied to branched polymers where rather than entwinements, branch points serve to pin the molecules against each other. Such a model is known as the Pom-Pom model [43, 44] and has been used by polymer scientist to describe the rheology of branched polymer melts such as LDPE, a mathematical constitutive model has been developed for it.
Literature Review – Mechanical Testing and Functionality of Dough

In the previous chapter, we introduced the idea that the rheology of dough is intimately linked to its quality. In this chapter we will discuss the equipment used to experimentally establish and quantify their relationship.

The ultimate goal of dough rheology is to directly measure or otherwise indirectly obtain its material function which can then be used to describe the functional properties of the dough.

Bagely [45] outlined the range of difficulties encountered by rheologist attempting to characterize the mechanical response of dough. Firstly, there is the difficulty in obtaining repeatable data. He found that samples were so
heterogeneous that even those from the same mixing batch displayed significant variations. He also noted that these heterogeneity can be eliminated by over-mixing the dough, but over-mixed dough are of little practical interest. Short of over-mixing, the only solution is really to be extra careful and consistent in preparing the sample, and to perform a large number of experiments to obtain a statistical mean.

Since very few experiments allow us to directly measure the material functions, after performing the tests, how should the rheologist interpret the raw data (force/pressure/displacement/Brabender Units etc...), and is it possible to form a basis for comparing different doughs? How do we compare the results from say the extensigraph test to the Alveograph or dynamic shear test? These are questions which we will consider in this chapter.

**Shear Rheology**

Shear rheology is a convenient and well developed method of exploring the response of the dough. The most commonly encountered problem is slip. The large viscosity of dough generates large shear stresses at the interface between the sample and end-plates, which often leads to slip. Slip is usually eliminated by introducing a roughened surface (usually sandpaper) at the end-plates.

**Steady shear experiment**

The shear rate dependent viscosity \(\eta(\dot{\gamma})\) is defined as:

\[
\tau_{xy}^{\text{steady state}} = \eta(\dot{\gamma})\dot{\gamma}_{xy}
\]  
(1)
Attempts to measure $\eta(\dot{\gamma})$ has not been successful because the shear stress does not reach a steady state. For experiments conducted at relatively high rates, the sample tend to roll-out of the geometry. While at very slow strain rates, the stress can appear to approach a steady value and therefore extrapolated to give an estimate of the viscosity.

**Start-up of steady shear**

The material function obtained from this test is the transient shear viscosity:

$$\tau_{xy}^+ = \eta^+(\dot{\gamma},t)\dot{\gamma}_{xy}$$  \hspace{1cm} (2)

At very low rates, when the transient shear viscosity becomes independent of the strain rate, one can use the Gleissle’s mirror [46] relationship to obtain an estimate of the steady shear viscosity:

$$\eta(\dot{\gamma}) = \eta^+(t)\big|_{\dot{\gamma} = \dot{\gamma}}$$  \hspace{1cm} (3)

**Small Amplitude Oscillatory Shear test**

Doughs are composite materials that show a high degree of polydispersity and we expect its response to depend on a large range of time scales. Dynamic shear rheology can probe the behavior over this wide spectrum.

The first step towards dynamic shear rheology is to identify the linear range. The linear range of dough is surprisingly small (strains $\gamma \sim 10^{-3}$).
Figure 8 Strain sweep of HRS dough. Both moduli drop dramatically at strain of $5 \times 10^{-3}$ which we define as the limit of linear range.
Figure 9 Dynamic oscillatory shear data for wheat flour dough at various water concentrations

Phan-Thein et al [24] had reasonable success in using the oscillatory shear technique for characterizing dough behavior and obtained a relaxation spectrum for dough. The relaxation spectrum $H(\lambda)$ is defined as:

$$G' = \int_{0}^{\lambda} \frac{\lambda^2 \omega^2}{1 + \lambda^2 \omega^2} H(\lambda) d\lambda = G'_{\infty} + \int_{\alpha}^{\beta} \frac{\lambda^2 \omega^2}{1 + \lambda^2 \omega^2} H(\lambda) d\lambda$$  \hspace{1cm} (4)

or equivalently:

$$G'' = \int_{0}^{\lambda} \frac{\lambda \omega}{1 + \lambda^2 \omega^2} H(\lambda) d\lambda = \int_{\alpha}^{\beta} \frac{\lambda \omega}{1 + \lambda^2 \omega^2} H(\lambda) d\lambda$$  \hspace{1cm} (5)

where $\alpha$ and $\beta$ are the range of the experiments. These functions are inverted [47, 48] to give the relaxation spectrum.
Figure 10 Linear relaxation spectrum of a strong Australian flour-water dough at different water concentration [24].

A typical relaxation spectrum is shown in Figure 10. The data span from $10^3$ to $10^5$ s with increasing error/uncertainty at very large and low time-scales. An averaged relaxation time is defined by the first moment of the relaxation spectrum:

$$\bar{\lambda} = \frac{\int \lambda H(s) ds}{\int H(s) ds}$$  \hspace{1cm} (6)$$

Phan-Thein et al found the averaged relaxation time to be of the order of 500s for a strong Australian wheat flour dough system.

To increase the accuracy of the spectrum, we need data from a wider range of
frequencies. Time-temperature superposition is usually used to extend the range but is difficult to apply in this case, because change in temperature can alter the molecular/chemical structure significantly (gelling, drying etc…)

We also note that an estimate of the steady shear viscosity can be obtained through the Cox-Merz rule:

$$\eta(\dot{\gamma}) = \left. \eta^*(\omega) \right|_{\omega=\dot{\gamma}} = \eta'(\omega) \left[ 1 + \left( \frac{\eta''}{\eta'} \right)^2 \right]^{1/2}$$

(7)

**Capillary Rheometry**

As an alternative to the typical rotational rheometer, a capillary rheometer is sometimes used. Samples are extruded through a tube driven by a pressure difference $\Delta p$. We approximate the flow to be fully developed and therefore the pressure drops linearly and velocity profile does not change along the length of the tube.

![Figure 11 Fully developed flow in a capillary rheometer.](image)
Shear stress in a fully developed flow is given by:

\[ \tau = \frac{\Delta \rho R}{2(L + eR)} \]  

(8)

Where \( e \) is an end correction factor. This end correction factor can be significantly large for dough, values of up to 200 are typical. It is therefore critical to have a large \( L/R \) ratio to mask the effect. We estimate an apparent strain rate at the wall by considering fully developed flow of a Newtonian fluid with parabolic velocity profile:

\[ \dot{\gamma}_{\text{apparent}} = -\frac{\partial v_r}{\partial r} = \frac{4Q}{\pi R^3} \]  

(9)

Where \( Q \) is the volume flow rate. An apparent viscosity can then be computed:

\[ \eta_{\text{apparent}} = \frac{\Delta \rho \pi R^4}{8Q(L + eR)} \]  

(10)

**Comparison between different methods of rheometry**

Relatively few attempts have been made to compare the results obtained from different shear rheometry measurements. Bagley et al [45] presented results from capillary rheometer and start-up of steady shear in a cone and plate set-up. The two sets of data did not overlap each other, but it seems plausible that the shear-thinning behavior can be extrapolated from the cone and plate data to the capillary data.
Figure 12 Apparent viscosity from a LEN 89 wheat flour. Values from start-up of steady shear in the cone and plate geometry was computed from the Gleissle rule. Capillary data was obtained through a pressure driven capillary rheometer. [45]

Phan-Thein et al computed the relaxation spectrum from dynamic oscillatory data and step strain relaxation and found them to be in good agreement.
Figure 13 Comparison between relaxation spectra computed from dynamic oscillatory data and step-strain relaxation.

Such results are encouraging for they confirm the ability of the well-developed shear rheometry methods in measuring material functions accurately. But shear rheometry alone is insufficient to characterize the functional properties relevant to bread-making. Since the deformations are in shear and usually of small amplitude, the results cannot be readily translated into properties relevant to the large extensional flows relevant to baking.

**Extensional Rheology**

**Uni-axial Compression**

Uni-axial compression can be performed on instruments such as INSTRON and texture analyzer. A typically disc shaped sample is compressed along its axis of
symmetry. To generate a shear free flow, the end plates must be lubricated to allow perfect slip and the resulting deformation will be equivalent to bi-axial stretching. Unfortunately, maintaining perfect slip motion is perhaps more difficult than ensuring no-slip in a shear experiment. Consider the case where no-slip is occurring. The small aspect ratio ($\Lambda = L/R \ll 1$) suggests that a lubrication approximation should be appropriate. Performing the analysis will show that the pressure arising from extension scales like:

$$\tau_{ext} \sim \eta \frac{V}{L}$$

while pressure arising from shear:

$$p_{\text{shear}} \sim \eta \frac{V}{\Lambda L} \gg \tau_{ext}$$

We see that the lubrication pressure can overwhelm the force measured at the endplates; extracting extensional properties can be difficult. Furthermore, stick-slip situations are often observed, therefore generating a steady flow can be tricky.
Figure 14 Two approximations of uni-axial compression streamlines.

Despite these difficulties, uni-axial compression has been performed on doughs and the response was found to approximate an upper convected Maxwell model with relaxation time in the range of 10 to 50s [49].

Extensigraph

The extensigraph was developed by Brabender. Dough is rolled into a cylindrical sample and clamped at its two ends. A hook is moved perpendicularly across the sample stretching it to a V-shape (Figure 15).
Brabender extensigraph outputs the resistance $R(t)$ that the hook experiences and the distance which the hook has moved through $E(t)$. Resistance is measured in Brabender Units (BU), a typically arcane measurement favored by Brabender company, though it is not difficult to calibrate it to the more common S.I. units. From these, a number of empirical value which supposedly reflect the rheological properties can be computed:

\[
\text{Ratio number} = R_n = \frac{R(t)}{E(t)}
\]  

A more useful measure is the extensibility $E_{\text{max}}$, which is simply the maximum length the dough can be stretched through before rupturing. The common
belief is that extensibility will have some direct relation to the final loaf volume. An idealized analysis can be performed on the extensigraph to convert resistance and extension to stresses and strains:

![Figure 16 Idealized kinematics of extensigraph.](image)

We assume the sample remains symmetrical during the experiment. The length \( L \) is given by the Pythagoras theorem:

\[
L = \left( L_0^2 + 4E^2 \right)^{\frac{1}{2}}
\]  

(14)

We can calculate the longitudinal strain:

\[
\varepsilon_i = \ln \frac{L}{L_0}
\]

(15)

If we assume the sample remains uniform along its length and is incompressible, the cross-sectional area is given by:
A = \frac{A_0 L_0}{L} \quad (16)

and the tension T within the sample:

\[ T = \frac{R \sin \theta}{2} = \frac{R E}{L} \quad (17) \]

and finally the stress:

\[ \tau_x - \tau_y = \frac{T}{A} \quad (18) \]

Despite the bold assumptions it requires, such an analysis can be extremely insightful. Because stress and strain are fundamental quantities independent of the set-up. These should be treated as the starting point in mapping results from different equipments and developing relevant material functions.

**Bubble inflation technique**

The bubble inflation technique is perhaps the most widely adopted method for performing extensional tests on doughs. Its popularity is due to the similarity in kinematics to the actual deformation during baking and proofing which is predominantly bi-axial. Furthermore, a set of accompanying equipment has been developed to form the initial sample conveniently and consistently with minimal handling. The Chopin Alveograph was one of the earliest development. Subsequent improvements and adaptations were made [33], but the underlying principle remains the same (Figure 17). A flat round disc of dough is clamped around its edges. A driven piston supplies a controlled flow of air, inflating the dough sheet into a bubble. Usually, only the volume and pressure of air are
measured as raw data.

Figure 17 Schematic of bubble inflation set-up [50].
The interpretation of pressure and volume profiles have been the subject of many studies. An early analysis performed by Hlynka [51] arrived at a quantity termed Alveograph resistance. He first assumed that the pressure within the bubble is a function of two factors: some dough property related to its tensile strength and the thickness of the bubble wall. He concluded that to single out the dough property one can simply divide pressure by wall thickness:

$$\text{Alveograph Resistance} = \frac{\text{Pressure}}{\text{Thickness}}$$  \hspace{1cm} (19)

The wall thickness can calculated from the volume data by assuming the dough forms a spherical shell of uniform thickness:
\[ t = \frac{\pi a^2 t_0}{S} \]  
\[ S = 2\pi R^2 \pm 2\pi R(R^2 - a^2)^{\frac{1}{2}} \]  

Where \( a \) is the initial sample diameter, \( t_0 \) the initial thickness, \( S \), the surface area and \( R \) the radius of curvature.

However, the Alveograph resistance was not adopted as a basis for comparison between doughs; Hlynka did not include a third factor, the radius of curvature, which has a large influence on the pressure. We can take into account of the curvature by applying the "thin walled pressure vessel theory" to calculate the stress within the dough wall:

\[ \sigma = \frac{PR}{2t} \]  

Where \( P \) is the pressure within the shell. This stress is much more fundamental and meaningful measure in this context.

The corresponding measure of deformation should be the true strain, given by:

\[ \varepsilon = -\frac{1}{2} \ln \frac{t}{t_0} \]  

In calculating the thickness, we again made the assumption of a uniform spherical shell. How valid is this assumption? Bloksma [52] wrote a very influential paper on this subject and the result is widely used today for calculating the thickness. Instead of the uniform thickness assumption, he considered the kinematics under the conditions below:

1. Dough forms a spherical shell.
2. Volume flow rate of air is constant.

3. The dough is incompressible.

4. The motion of any point on the dough sheet is normal to its surface.

The expression he arrived at for the wall thickness was:

$$ t = t_0 \left( \frac{a^2 + s^2 h^2}{a^2 (a^2 + h^2)} \right)^2 $$

(23)

Where $h$ is the height of the bubble and $s$ is the particles initial distance from centre of sheet. The thickness distribution described by this equation decreases from $t_0$ at where it is clamped to $t_0 \left( a^2 / (a^2 + h^2) \right)^2$ at the pole.

A more recent study was performed to investigate the kinematics of dough inflation through experimental techniques [50] and numerical computation of plausible constitutive equations [53]. This yielded a number of interesting observations:

1. Neither uniform thickness (equation (20)) nor Bloksma assumptions (equation (23)) give good predictions for the actual wall thickness. At the pole, equation (20) over-predicts the thickness (under-predicts the strain) while equation (23) under-predicts it (Figure 19).

2. The shape of the sheet approximates a spherical shell until some point after the radius of curvature has reached a minimum (hemi-spherical shell), after which it becomes an ellipsoid with major to minor axis ratio $k$ of 1.1. This result can affect the calculation of stress. At the pole of the ellipsoid, the radius of curvature is less than that of the corresponding...
sphere. From equation (21), using the assumed spherical radius of curvature will give a stress which is smaller than its true value.

3. Compressibility can have a large effect. Relaxing the Poisson ratio from 0.5 to 0.46, gives stresses up to 100% larger at a given stage of inflation.

![Graph showing comparison between Bloksma Assumption, Uniform thickness, and Experimental data.](image)

**Figure 19** Comparison of dough wall thickness between data obtained experimentally and calculated values.

**Conclusion**

The test methods discussed in the last section suffer from a lack of control and information concerning the actual deformation of the dough. Furthermore, these experiments are usually performed at a constant inflation rate/cross-hair speed, rather than constant strain-rate. Achieving a constant strain-rate through a
specific profile of inflation/cross-hair movement is not possible either, because the actual strains are not known. Controlling and understanding the kinematics of these tests is important; it allows us to translate the results to fundamental rheological quantities such as stress and strain; by controlling the rate of deformation so that the strain rate is constant, we can obtain true material functions such as transient extensional viscosities. Material functions serve to classify fluids, they are used to determine constants in non-Newtonian constitutive equations. An idealized mode of deformation for probing elongational properties is a steady homogeneous shear free flow, included under this class of kinematics is uni-axial extension.

It is well known that dough is a visco-elastic material. Therefore it is surprising that most studies on its extensional rheology have been confined to a single or a limited range of strain rates. And of these strain rates, most of them are far larger than those associated with bread making, the reason being that it is extremely difficult to maintain regular extensional deformation at these slow rates. Baking has strain rates of the order $\dot{\varepsilon} = 10^{-3} \text{s}^{-1}$, while proofing is of the order $\dot{\varepsilon} = 10^{-4} \text{s}^{-1}$. 
In the chapter 4, we present results obtained from the Filament Stretching Rheometer, where the sample approaches uniform uni-axial extension flow at a constant strain rate over a large portion of the experiment. The large dynamic range of this Rheometer will allow us to probe the visco-elastic nature of the dough well into the baking/proofing range. Special experimental protocols and modifications to the rheometer fixtures were introduced to overcome problems in sample preparation.

**Constitutive Equations**

A constitutive equation relates the state of stress $\tau$ in a fluid element in terms of its deformation history $\dot{\gamma}(t,t')$. It is a framework for relating the two typical raw data of forces and deformation obtained in dough rheology. Such equations provides us with a quantitative method in evaluating and comparing quality
of the dough. Provided a suitable form of material function is selected, the effects of each ingredient and additive should become apparent through changes in the parameters such as relaxation time and modulus. Knowledge of the appropriate material functions can also improve accuracy for calculations in process engineering leading to better efficiency.

Rheological modeling of dough borrows heavily from the related field of polymer science. Most studies have focused on dynamic oscillatory response using the dynamic moduli as a starting point for building a spectrum of modes. Relatively little work has been done on the mathematical description of extensional behavior. Under such strong flows, many phenomena that cannot be probed by shearing will become apparent. These includes finite extensibility and strain-hardening which are both important in the context of functionality.

**Rheological Invariance**

An important concept for building a rheological constitutive equation is admissibility. The admissible (rheologically invariant) equations must be [54-59]:

1. Form invariant under a change of co-ordinate system.

2. Value invariant under a change of translational and rotational motion of the fluid element as it goes through space.

3. Value invariant under a change of rheological history of neighboring fluid elements.

To satisfy these conditions, the deformations need to be described by appropriate tensors.
**Deformation Tensors**

Under shear free extensional flow, the velocity gradient and strain rate tensors are:

\[
\begin{pmatrix}
-1/2(1+b) & 0 & 0 \\
0 & -1/2(1-b) & 0 \\
0 & 0 & 1
\end{pmatrix} \dot{\varepsilon}(t)
\] (24)

and

\[
\begin{pmatrix}
-(1+b) & 0 & 0 \\
0 & -(1-b) & 0 \\
0 & 0 & 2
\end{pmatrix} \dot{\varepsilon}(t)
\] (25)

respectively.

**Upper Convected Maxwell and Oldroyd-B model**

One of the simplest visco-elastic model used to describe behavior of dough in extension is the upper-convected Maxwell model which contains only two variables.

\[
\tau + \lambda \tau_{(1)} = \eta \dot{\gamma}_{(1)}
\] (26)

Where \( \eta \) is a polymeric viscosity, \( \lambda \) is the relaxation time and the subscript \( (1) \) is the upper-convected derivative operator:

\[
\tau_{(1)} = \frac{D\tau}{Dt} - [(\nabla \tau)^T \cdot \tau + \tau \cdot (\nabla \tau)]
\] (27)

The equation can be thought of as a description of a polymer modeled as a
Hookean spring with a particular relaxation response. We take the filament stretching as an example, where the flow is nominally un-axial extension (i.e. $b=1$), assuming the strain rate to be constant, we insert the strain rate tensor into the U.C.M. constitutive equation and integrate, we find the normal stress difference to be:

$$\tau_{zz} - \tau_{rr} = \frac{2\eta \dot{\varepsilon}}{2\dot{\varepsilon} \lambda - 1} e^{\frac{2\dot{\varepsilon} \lambda - 1}{\lambda}} \frac{\eta \dot{\varepsilon}}{1 + \dot{\varepsilon} \lambda} e^{-\frac{2\dot{\varepsilon} \lambda - 1}{\lambda}} + \frac{3\eta \dot{\varepsilon}}{(1 + \dot{\varepsilon} \lambda)(1 - 2\dot{\varepsilon} \lambda)}$$  \hspace{1cm} (28)

To further understand the behavior of the model we non-dimensionalize the equation:

$$Tr = \frac{\tau_{zz} - \tau_{rr}}{\eta \dot{\varepsilon}} = \frac{2}{2De - 1} e^{2De - 1} - \frac{1}{1 + De} e^{1 + De} + \frac{3}{(1 + De)(1 - 2De)}$$  \hspace{1cm} (29)

Where the Deborah number is defined as $De = \dot{\varepsilon} \lambda$. The Deborah number represents a ratio comparing the time-scale of the polymer against that of the experiment. At extremely low rates of stretching $De \rightarrow 0$, the flow is not strong enough to stretch out the polymer and it remains in its equilibrium coiled shape, the response will be like that of a Newtonian liquid:

$$\lim_{De \rightarrow 0} Tr = 3$$  \hspace{1cm} (30)

At the rapid stretching limit, where $De \gg 1$:

$$\lim_{De \rightarrow \infty} Tr = \frac{1}{De} \left( e^{2\varepsilon} - e^{-\varepsilon} \right)$$  \hspace{1cm} (31)

which is also known as the Neo-Hookean limit. The rate of deformation is so large that the polymer has not relaxed significantly during the time-scale of the
experiment and instead is deformed affinely, like a cross-linked rubber system.

A simple extension to the U.C.M. is to add a solvent contribution to the stress. Such a model is known as the upper-convected Jeffrey's or Oldroyd-B model:

\[
\begin{align*}
\tau_{\ell} &= \tau_{p} + \tau_{s} \\
\tau_{p} + \lambda \tau_{p}(1) &= \eta_{p} \dot{\gamma}(1) \\
\tau_{s} &= \eta_{s} \dot{\gamma}(1)
\end{align*}
\] (32)

For both of these models, steady state will not be reached if \( De \geq 0.5 \). Above this critical Deborah number, the stress increases without bounds. From a physical point of view, this is unrealistic because a finite extensibility limit will be reached where the polymer has reached its maximum extension.

Another short-coming of these models is that they are single modes. Published data on the dynamic oscillation response show a wide relaxation spectrum, indicating the highly poly-disperse nature of dough, a mode generalized form containing multiple modes will be required to fully describe this behavior.

Despite their simplicity, these models are useful starting point in understanding polymer behavior and building more realistic constitutive models.

**Phan-Thein Model**

The Phan-Thein model [24] is able to address many of the features which are not well described by the simple models in the previous section. It is a phenomenological model which describes the stress tensor \( \tau_{\ell} \) as a combination of a hyper-elastic term \( \tau_{E} \) representing the glutenin/cross-linked network and a
visco-elastic contribution ($\tau_v$, representing the suspension of starch globules and gliadin components).

\[
\tau = \tau_E + \tau_v
\]  

(33)

\[
\tau_E = \frac{G_E}{1 + a} f(\gamma) \left( B - a B^{-1} \right)
\]  

(34)

$G_E$ is the elastic modulus, $B$ is the relative Cauchy strain tensor.

The visco-elastic contribution is expressed as a summation of distinct modes with constant relaxation times $\lambda_j$ and viscosities $\eta_j$.

\[
\tau_v = f(\gamma) \sum_{j=1}^{N} t^{(j)}
\]  

(35)

\[
\tau^{(j)} + \lambda_j \tau^{(j)} = \eta_j \dot{\gamma}
\]

$G_E, \lambda_j$ and $\eta_j$ are not arbitrary constants. They are determined from the oscillatory data:

\[
G^*(\omega) = G_E + \sum_j \frac{i\omega \eta_j}{1 + i\lambda_j \omega}
\]  

(36)

\[
\eta^*(\omega) = \frac{G_E}{i\omega} + \sum_j \frac{\eta_j}{1 + i\lambda_j \omega}
\]

The remaining parameters $a$ and $f(\gamma)$ are determined from start-up of steady shear flow experiments. Phan-Thien et al observed the shear stress to increase with time to a peak value and then decrease continuously afterwards with a "conspicuous" absence of steady state response. They believed that the peak value corresponds to a "rupture" or partial "breakdown" of the elastic network.
This behavior is modeled through the strain-softening function \( f(\gamma) \):

\[
f(\gamma) = \frac{1}{(1 + \gamma/\gamma_s)^{(1-m)/2}} \exp\left\{-\left(\frac{\gamma}{\gamma_p}\right)^4\right\}
\]

(37)

where \( \gamma \) is the equivalent strain \( \gamma = (\text{Tr}B - 3)^{1/2} \), \( \gamma_s \) represents the strain at which shear-thinning occurs in the manner of the Carreau viscosity model with exponent \( m \), and \( \gamma_p \) is the strain at which “rupture” occurs.

The predicted stress for a range of strain rates was compared to experimental data on start-up of steady shear flow and dynamic oscillation. They showed reasonable agreement, which is not at all surprising, since the constants are fitted from these data. This illustrates an important point in evaluating a constitutive equation: how will the predictions fair when compared to data obtained under different kinematic conditions? Since in the case of doughs, extensional behavior seems to be of most practical interest, so the natural question to pose is whether a model can predict extensional rheological response. Rock [60] performed a numerical study on the predicted response of the model under bi-axial extension, but unfortunately no attempt has been made to compare the predictions with extensional data yet.

The greatest drawback for the Phan-Thein model is that it requires an unusually large number of parameters, making it unwieldy in performing qualitative analysis such as kinematic failure. It also makes it difficult to compare relative functionality of different doughs. Fitting the strain-softening function is also extremely empirical, it is difficult to relate stress development to the molecular
structure of the gluten network.

**Pom-Pom model**

The Pom-Pom model [43, 61] has a feature particularly appealing to rheologist studying dough: it describes the effect of branching on large deformation rheology. Micrographs of the glutenin network showed the molecules to have a highly branched structure [28].

The Pom-Pom model is an extension to reptation theory, where polymers are modeled as composing a backbone with branched ends (Figure 21).

![Figure 21 The Pom-Pom model](image)

Branch point acts as a constraint “pinning” the ends of the polymer backbone to define affinely with the flow. However, this “pinning” effect is not permanent and will release allowing the branched points to retract into the reptation tube if the backbone is stretched to a certain limit. The resulting constitutive equations are:
\[ \tau = G\phi^2 S \]
\[ A_{\text{eq}(1)} = \frac{1}{\lambda_b} \left( A - \frac{1}{3} I \right) \]
\[ S = \frac{A}{\text{Tr}(A)} \]
\[ \frac{D\phi}{Dt} = \phi (\nabla \cdot S) - \frac{1}{\lambda_s} (\phi - 1) \quad \text{for } \phi < q \]

(38)

Where \( G \) is the modulus, \( S \) is the orientation tensor and \( \phi \) is a measure of backbone stretching. The backbone relaxation occurs at a characteristic stretch relaxation time-scale \( \lambda_s \) while the orientation can also relax separately at a time-scale of \( \lambda_b \). Branched point retraction bounds the stress growth providing a mechanism of finite extensibility to the model.

A natural extension to the Pom-Pom model is to include a spectrum of mode shapes to capture the dynamic shear response, however this will again increase its complexity because we will need to specify a \( q \) value for every single mode.

**Power Law Model**

In this thesis, we use a simple power-law model to characterize certain features of the stress strain curves under uniform uni-axial extension.

\[ \tau = Ge^n + H \]

(39)

It is important to note that this equation is not frame invariant and is only applicable to the specified deformation. However, this equation is able to describe the strain-hardening behavior of dough with reasonable accuracy using a manageable number of parameters. A detailed discussion is included in the
following chapter.

**Conclusion**

The equations discussed here are by no means a comprehensive study of the different approaches in building a constitutive equation for dough. Other examples include K-BKZ [62], Bird Carreau [63] model etc... Most models require a large number of constants reflecting the complex composition of the dough. An important question to ask when selecting one is whether it can describe the functionality we are interested in. In this work, we are most interested in the response under extensional deformation and will be willing to sacrifice some accuracy in order to capture the important physics behind mechanism of strain-hardening and rupture discussed in the introduction.
Filament Stretching Rheometry
The Filament Stretching Rheometer, FiSER III, allows a large dynamic range (strain rates up to $0.001 \leq \dot{\epsilon} \leq 5s^{-1}$ are possible), produces good accuracy in force measurements and is able to monitor in real-time the evolution of the mid-plane diameter during the experiment. The last item is particularly important because under large strains the axial profile of the stretched filament is often not uniform. This extra piece of information gives us more accuracy in calculating rheological parameters such as true tensile stress and true Hencky strain. It also allows us to study the growth of non-uniformity that ultimately leads to rupture.

Figure 22 shows a schematic of the FiSER set-up.
Kinematics

A sample of dough was attached between the top- and bottom-plates by means of sandpaper disks punched from a sheet of self-adhesive sandpaper. At the beginning of the test, the top-plate moved away from the stationary bottom plate at an exponential rate, stretching the dough at a nominally constant strain rate:

$$L = L_0 e^{Et}$$

(40)

From this relationship, we define the nominal strain:

$$E = \dot{E}t = \ln \frac{L(t)}{L_0}$$

(41)

Mounted on the middle plate is a laser micrometer. This plate travels at half the velocity of the top-plate allowing the laser micrometer to monitor the evolution of the diameter at the mid-plane during the experiment. The laser micrometer was manufactured by OMRON (Z4LA), which measures diameters in the range of 50μm to 9mm with an accuracy of ±10μm.

$\dot{E}$, the axially-imposed or ‘nominal’ strain rate is based on the total length of the sample. In an ideal experiment for an incompressible material involving a fictional end-plate clamp which deforms accordingly so that the entire sample remain cylindrical, $E$ will be the true strain everywhere in the sample. In practice, as a result of the no-slip condition at the end-plates, the filament shape is concave, and the true strain will vary along the axial length of the sample. The
true strain experienced by the fluid elements near the axial mid-plane can also be calculated from the diameter measurements from the laser micrometer through the relationship

$$
\varepsilon(t) = \int \dot{\varepsilon}(t) dt = -2 \ln \frac{D_{\text{mid}}(t)}{D_0}
$$

(42)

Where $D_{\text{mid}}(t)$ is the measured diameter from the laser micrometer and $D_0$ is the initial sample diameter. The local or effective strain rate can also be found from differentiation of this expression

$$
\dot{\varepsilon}_{\text{mid}}(t) = \frac{d\varepsilon(t)}{dt} = -\frac{2}{D_{\text{mid}}(t)} \frac{dD_{\text{mid}}(t)}{dt}
$$

(43)

In general, the relationship between the two strains has to be computed numerically. However, it is insightful to obtain these relationships under two idealizations (Figure 23).

First of all we consider the period near the beginning of an experiment, when the aspect ratio $\Lambda = \frac{L(t)}{R(t)}$ is small. With this idealization, the Navier Stokes equation can be linearized to form the “lubrication” approximation. Solving the Navier Stokes equation together with continuity will yield the relationship:

$$
\dot{\varepsilon}(t) = \frac{3}{2} \dot{\varepsilon}
$$

(44)

On the other hand, as the experiment progresses, the aspect ratio $\Lambda$ increases, a large portion of the sample is cylindrical in shape. Under these conditions, the sample approaches the ideal filament stretching limit, where:
\[ \dot{\epsilon}(t) = \dot{\epsilon} \] (45)

\[ \Lambda \gg 1 \]

\[ \Lambda \ll 1 \]

Figure 23 Lubrication and uni-axial approximation

**Dynamics**

A force transducer was mounted on the stationary bottom plate to monitor the tension within the dough filament. The force transducer was manufactured by Futek (L2338) and can measure forces up to 10N with an accuracy of ±0.05N. The force transducer has a characteristic time constant of 50 ms.
Figure 24 Force balance on a sample undergoing filament stretching

The stress within the sample can be found by performing a force balance at the mid-plane of the sample \([64, 65]\).

\[
p = \tau_{zz} + \frac{\sigma_s}{R}
\]  
\[
F_p = (\tau_{zz} - p)\pi R_{mid}^2 + \sigma_s(2\pi R_{mid}) + \rho g \frac{V_0}{2} - \rho \pi \int_0^{L(t)/2} R^2(z,t) \frac{\partial v_z(z,t)}{\partial t} dz
\]

Before writing out the explicit expression for computing stress evolution from FISER data, a few simplifications can be obtained by considering the relative contribution from each of the terms. We make an estimate of each of the terms:
Extensional Stress difference $= \tau \pi R_{\text{mid}}^2 \sim \eta \dot{\epsilon} R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}$

Surface tension $= \sigma_r (2\pi R_{\text{mid}}) \sim \sigma_r R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}$

Gravitational force $= \rho g \frac{V_0}{2} \sim \rho g \frac{R_0^2}{2} L_0 \pi$

Inertia $= \rho \pi \int_0^{L(t)/2} R^2(z,t) \frac{\partial^2 v}{\partial t^2} \, dz \sim \frac{\rho \pi R_0^2 L_0^2 \dot{\epsilon} e^{2 \dot{\epsilon} t}}{4}$

The characteristic size of experimental parameters:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Typical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>$10^4 \text{ Pa s}^{-1}$</td>
</tr>
<tr>
<td>$\dot{\epsilon}$</td>
<td>$10^{-3}$ to $10^4 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\dot{\epsilon} t$</td>
<td>0 to 3</td>
</tr>
<tr>
<td>$R_0$</td>
<td>$10^{-3} \text{ m}$</td>
</tr>
<tr>
<td>$L_0$</td>
<td>$10^{-3} \text{ m}$</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>$10^{-2} \text{ N m}^{-1}$</td>
</tr>
<tr>
<td>$g$</td>
<td>$10^1 \text{ ms}^{-2}$</td>
</tr>
</tbody>
</table>

We can show that for the case of filament stretching of dough, all other terms can be considered negligible to the stress difference by evaluating their ratios:

$$\frac{\text{Surface tension}}{\text{Stress difference}} = \frac{\sigma_r R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}}{\eta \dot{\epsilon} R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}} = \frac{\sigma_r e^{\frac{1}{2} \dot{\epsilon} t}}{\eta \dot{\epsilon} R_0} \sim 10^{-4} = Ca^{-1}$$

$$\frac{\text{Gravitational force}}{\text{Stress difference}} = \frac{\rho g R_0^2 L_0 \pi}{2 \eta \dot{\epsilon} R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}} = \frac{\rho g L_0 e^{\dot{\epsilon} t}}{2 \eta \dot{\epsilon} R_0} \sim 10^{-2} = Bo \frac{Ca}{Ca}$$

$$\frac{\text{Inertia}}{\text{Stress difference}} = \frac{\rho \pi R_0^2 L_0^2 \dot{\epsilon} e^{2 \dot{\epsilon} t}}{4 \eta \dot{\epsilon} R_0^2 e^{-\frac{1}{2} \dot{\epsilon} t}} = \frac{\rho L_0^2 \dot{\epsilon} e^{3 \dot{\epsilon} t}}{4 \eta} \sim 10^{-4} = \text{Re}$$

We conclude that capillary, gravitational and inertia effects are insignificant.
compared to the visco-elastic forces within the dough under filament stretching for strain rates investigated in these experiments. Thus the force balance simply results in the following relationship:

\[ \tau_z(t) - \tau_r(t) = \frac{F_p(t)}{\pi R_{mid}^2(t)} = \frac{4F_p(t)}{\pi D_{mid}^2(t)} \]  

(50)

**Fixtures and Protocols**

Initially, some crude filament stretching experiments were performed on the Texture Analyzer TA.XT2, we identified the need to improve on the systematic handling and loading of samples, especially during the mounting procedures. For this purpose, we designed and built a specialized end-plate assembly. Using this assembly, the sample could be mounted, pressed to the required thickness and cut into the required diameter, then allowed to relax without further deformation before mounting onto the FISER for testing. The design is illustrated below.
Figure 25 Procedures for preparing dough samples

Self-adhesive sandpaper was attached onto each end of the custom built end-plates. A sample of dough was then placed between them and pressed to the required thickness. The cookie cutter was then used to cut the sample into a cylindrical shape of the same diameter as the lower end-plate.

Dough sample of approximately 5g were mounted on to the customized end-plates. They are compressed to a thickness of 2.5mm then cut into a disc shape with radius 19.05mm. Next, a pre-stretch was performed so that the disc of dough was elongated to a cylinder of height 7.5mm and diameter of approximately 7.5mm, which is an initial aspect ratio $\Lambda_0$ of 2. The sample was
painted with a thin film of silicone oil and left to relax for 30 mins before testing.

![Figure 26 Pre-stretch of sample](image)

The purpose of the pre-stretch is two-fold. Firstly, it increases the aspect ratio, by-passing the initial “lubrication” flow regime. The filament can be considered as almost cylindrical through most of the experiment. This greatly simplify the kinematics as discussed in the previous section. Secondly, the cross-sectional area is reduced, thus reducing the adhesive load required at the end-plates.

The thin film of silicone oil prevents excessive drying of sample. Vegetable oil and glycerol is not used because we found that the dough can absorb some of this coating fluid. The silicone oil used has viscosity 100 Pa s. This viscosity was selected so that it the oil is thick enough to resist draining by gravity yet not provide any significant contribution to the force balance in equation (47).

During the 30 minutes of relaxation, the force drops from $10^1$ to $10^2$ N. The length of relaxation was established through trial and error; experiments with shorter period of relaxation showed poor repeatability.
Figure 27 Typical Force/Diameter vs time data from FISER

Presented in Figure 27 are typical results obtained from filament stretching experiments. The diameter decreases exponentially (straight line on a log-linear scale), corresponding to a linear increase of strain in time. The profile of the stretched sample strongly resembles a cylinder because of reasons discussed in the previous section and the extreme care in ensuring a uniform initial condition. We note that over most of the experiment, $\epsilon = E$, i.e. uniform uni-axial extension.

Results
In the first part of the results, dough mixed from Hard Red Spring was studied. For each batch of test, 30g of flour was mixed with 20g of water (66% weight ratio) in a National Mfg Mixograph. We recorded the extensional response under two conditions:

**Fixed mixing time.** It is widely believed that dough at the point of mixed peak provides the best baking qualities, therefore we shall begin by studying the response of peak-mixed dough (360s), and varying strain rate (0.03 to 3.0 s⁻¹). These experiments allowed us to develop a constitutive equation, from which we can infer a parameter to quantify the dough’s strain-hardening capability and stability in extension.

**Varying mixing time.** From the framework developed from the above-mentioned experiments, we investigate the change in extensional properties during mixing. Dough mixed for 120s to 600s were tested on the filament stretching rheometer.

In the second part of the experiment, we looked at the extensional properties of doughs mixed from different flour types: Hard Red Spring (HRS), Soft Red Winter (SRW), Durum (DF).
**Strain rate - Visco-elasticity of dough**

The change in stress-strain behavior for a range of strain rates are presented in Figure 28. The visco-elasticity of dough is apparent; stress is a function of both strain and strain rate. At high strain rates, the increase in stress is more rapid than proportional to strain, we refer to this phenomenon as strain-hardening. On the other hand, at low rates, the shape of the curve is “convex”, or “strain-softening”. At this point, we need a constitutive equation to describe this phenomenon quantitatively. Various constitutive equation have been suggested to incorporate the complex response of dough, but they tend to be complex and unwieldy requiring a relatively large number of constants which have to be
determined experimentally. Here we introduce an empirical constitutive equation which provides a reasonable description of the visco-elastic response:

\[
\sigma = H + GE^c
\]  \hspace{1cm} (51)

where \( H = H(\dot{E}) \) is a viscous offset, a modulus \( G = G(\dot{E}) \) and \( c = c(\dot{E}) \) a strain-hardening index. It is important to note that this constitutive equation is not frame invariant and should only be applied to true uni-axial extension. For a more detailed discussion of frame invariance and admissible constitutive equations, the reader is should consult the appropriate references [38, 58, 59].

The relationship between \( HG \) and \( c \) to the strain rate can be approximated by a power law relationship:

\[
\begin{align*}
H(\dot{E}) &= 2935\dot{E}^{1.46} \\
G(\dot{E}) &= 27277\dot{E}^{0.29} \\
c(\dot{E}) &= 1.3277\dot{E}^{0.28}
\end{align*}
\]  \hspace{1cm} (52)

Finally we note that the failure strain also increase with increasing strain rate.
Figure 29 Effect of mixing on stress-strain behavior for HRS dough (66% water weight ratio) at strain rate of 0.3 s\(^{-1}\).

The change in extensional rheological response during mixing is truly dramatic. Presented on Figure 29 are the stress-strain curves recorded at a strain-rate of 0.3 s\(^{-1}\) of doughs with the same constituents but mixed for various amount of time. The strain-hardening exponent is large (\(c > 1\)) for dough mixed for less than 400s, while dough mixed for more than 400s show strain-softening (\(c < 1\)). The strain at failure also decrease as the doughs are mixed for longer times. The significance of our results showing higher strain-hardening and extensibility for relatively short mixing times (well before peak-mixed condition) is unclear. A possible explanation is that gluten network breakdown occurs well before the peak-mixed
condition, the increase of torque is merely a result of increasing hydration of the constituents resulting in a swelling of starch and glutenin without forming additional cross-links.

![Graph showing stress and torque](image)

**Figure 30** Maximum stress, stress at strain =1 and mixograph torque for HRS 30g, water 20g.

Another theory is that the formation of glutenin network structure might not be always desirable if stability in extension is to be maximized. A very elastic network can undergo brittle like fracture resulting in reduced extensibility illustrated by region IV on the master curve [66] in Figure 31.
** Constitutive Equation and Characteristic Time-scale **

The rheological characterization of dough through constitutive equation has been the subject of many studies [45]. Beginning with Scholfield and Scott-Blair in 1932, these mathematical equations gradually evolved to be increasingly sophisticated and effective in describing the complex behavior of dough. Other than the ability to accurately predict the rheological response, a true constitutive model must also satisfy the criteria of admissibility laid down by Oldroyd [54-59]. Equations are admissible if “they are (a) form invariant under a change of co-ordinate system, (b) value invariant under a change of translational
or rotational motion of the fluid element as it goes through space, and (c) value invariant under a change of rheological history of neighbouring fluid elements” [38]. The measure of deformation $E$ in equation (51) has to be replaced by the infinitesimal strain tensor $\varepsilon$ if the equation is to describe the full three-dimensional deformation.

\[ E = \nabla u + (\nabla u)^T \]  

or

\[ E_{ij} = \frac{\partial}{\partial x_i} u_j + \frac{\partial}{\partial x_j} u_i \]  

This infinitesimal strain tensor is not frame invariant (criterion (b)). This can be seen if we consider an experiment performed on a turntable, and compare the resulting tensors obtained by a set of axis fixed in space and an a set rotating with the table. Despite not satisfying Oldroyd’s criteria, equation (51) is still useful in comparing results from uniform uni-axial deformations.

More recently, Nhan et al [67] presented a constitutive model which includes the contribution from gluten as a hyper-elastic network, and the suspension of starch globules and other long chain components are represented by a multi-mode Maxwell model. The model was able to predict with reasonable accuracy behavior in oscillatory and shear flows. Other approaches include a 24 parameter Wagner formulation [68], Bird Carreau model [63] and Upper Convected Maxwell models [49] etc...

However, together with accuracy in describing the deformation and stress, these
constitutive equations also became increasingly complex, requiring an unwieldy number of constants to be fitted from experimental results.

In this article, we presented the constitutive equation (51). This equation was able to describe the stress strain behavior with reasonable accuracy using a manageable number of parameters. The index $c$ captures the capability of the dough to strain-harden at different strain rates. A material with $c = 1$ behaves like a Bingham plastic with yield stress $H$ and stress increasing proportional to strain. Dough changes from a strain-softening to hardening behavior as $c$ increases through 1 as the strain-rate is increased. The rate at which $c = 1$ can be extrapolated from equation (52) to form a characteristic time scale $\tau$.

$$\tau = \left. \frac{1}{E} \right|_{c=1}$$  \hfill (55)

Since this time-scale arise from the strain-hardening behavior, we also expect it to be closely related to the relaxation time. The change in this characteristic time-scale and thus strain-hardening capability as mixing progresses is illustrated on Figure 32.
Figure 32 Change in characteristic time-scale through mixing. Red curve - HRS, blue- OSRW and black -DF.

Considère Criterion

The strain-hardening index can be related to extensibility in uni-axial deformation through the Considère criterion [69, 70]. The criterion was originally developed for true solids where viscous effects are negligible, but is useful for gaining a first estimate of the failure strain. We can derive the criterion by considering the increment in energy of a cylinder of length $l$ at time $t$ through an increment in length of $\delta l$. 
\[ \Delta U = F\delta l + \Delta F \frac{\delta l}{2} + O(3) \]

**Figure 33 Possible deformations at each time step**

Consider two "choices" it can make when it is at time \( t \) and length \( l \).

1. Continue uniform uni-axial extension of extension \( \delta l \).

2. A portion of the cylinder of length \( \lambda l \) undergoes extension of \( \delta l \), while the remaining length \( (1 - \lambda)l \) remain at the same length.

Since both of these scenarios will satisfy the controlled strain requirement in a FISER test, the option which requires less increment in energy will be favoured.

For an elastic solid (no viscous effect) undergoing a constant strain rate \( \dot{E} \) uni-axial extension test, energy increment of choice 1:
\[ \Delta U_1 = F \delta l + \left( \frac{\partial F}{\partial E} \right) \frac{\delta l^2}{2l} \]

For small increments \( \delta l \), \( \Delta E = \frac{\delta l}{l} \)

\[ = F \delta l + \left( \frac{\partial F}{\partial E} \right) \frac{\delta l^2}{2l} \]

Similarly, for choice 2:

\[ \Delta U_2 = F \delta l + \left( \frac{\partial F}{\partial E} \right) \frac{\delta l^2}{2\lambda l} \]

Option 2 is preferred if \( \Delta U_2 \geq \Delta U_1 \), i.e. instability,

\[ F \delta l + \left( \frac{\partial F}{\partial E} \right) \frac{\delta l^2}{2\lambda l} \leq F \delta l + \left( \frac{\partial F}{\partial E} \right) \frac{\delta l^2}{2l} \]

\[ \left( \frac{\partial F}{\partial E} \right) \frac{1}{\lambda} \geq \left( \frac{\partial F}{\partial E} \right) \]

Since \( 0 < \lambda < 1 \), instability will occur if:

\[ \frac{\partial F}{\partial E} \leq 0 \]

For a material with the constitutive equation (51):

\[ F = \sigma A \]

\[ = (H + GE^\alpha) A \delta e^{-E} \]  

(56)

Instability will occur when:
\[
\frac{dF}{dE} = \frac{G\epsilon E_{\text{c}1}}{H + GE_{\text{cri}}^c} = 0
\]

The effect of strain-hardening is more clearly demonstrated if we assume viscous offset is small, \( H \ll GE^c \)

\[
F \approx GE^c A_0 e^{-E}
\]

Force reaches a maximum when

\[
\frac{dF}{dE} = G(cE_{\text{cri}}^{-1} - 1)E_{\text{cri}}^c A_0 e^{-E_{\text{cri}}} = 0
\]

\[
E_{\text{cri}} = c
\]

In other words, greater stability in extension can be achieved in materials exhibiting a larger degree of strain-hardening.

The solution for \( E_{\text{cri}} \) for a range of strain rates are plotted and compared to the actual failure strain in the experiments. The criterion consistently under-predicts the failure strain. This is attributed to the fact that (a) the Considère criterion does not consider the change in energy increment due to the change in strain rate and (b) a finite amount of additional time after the critical strain is needed for an instability to grow through the specimen causing rupture. The criterion can be improved by including the effects of (a). There is a further increase in force due to the larger local strain rate of the non-uniform specimen (choice 2):

\[
\Delta U_2 = F\delta l + \left( \frac{\partial F}{\partial E} \Delta E + \frac{\partial F}{\partial \dot{E}} \Delta \dot{E} \right) \frac{\delta l}{2}
\]

The small change in strain rate can be linearized:
\[ \Delta \dot{E} = \frac{1}{\lambda} \frac{\partial l}{\partial t} - \frac{1}{l} \frac{\partial l}{\partial t} = \left( \frac{1}{\lambda} - 1 \right) \dot{E} \]

The inequality denoting condition of instability becomes:

\[ \frac{\partial F}{\partial E} \frac{1}{\lambda} + \left( \frac{1}{\lambda} - 1 \right) \dot{E} \frac{\partial F}{\partial E} \leq \frac{\partial F}{\partial E} \]

\[ \left( \frac{1}{\lambda} - 1 \right) \dot{E} \frac{\partial F}{\partial E} + \left( \frac{1}{\lambda} - 1 \right) \frac{\partial F}{\partial E} \leq 0 \]  

\[ \dot{E} \frac{\partial F}{\partial E} + \frac{\partial F}{\partial E} \leq 0 \]  

(61)

By substituting the equations (51) and (52) into the improved criterion, the predicted \( E_{\text{crit}} \) are plotted on Figure 34. The prediction are significantly improved for experiments conducted at high strain rates. At low rates, the growth of the instability is slow, the failure strain is still under-predicted. To put into perspective, our experiments span region III and IV on the master curve (Figure 31), in region III increasing rates give rise to enhanced elasticity and stability. However at very high rates (region IV), the stabilizing effect of viscosity by retarding the growth of neck is not present, the strain at failure begins to plateau out.

We believe further improvements can still be made to these predicted failure strains if the rate of growth of instabilities are included into the analysis. A starting point was suggested by Hutchinson et al [71], where the growth of a small perturbation in diameter of a cylinder under elongation is linearized. This leads to a first order evolution equation:
\[
\frac{d\delta \hat{A}}{dE} = \frac{(1-m-\gamma)}{m} \delta \hat{A} + \frac{\gamma}{m} \delta \hat{A}_0^{E=0} e^{-E} \\
A(t) = A_0(t) + \delta A(t), \quad \hat{A}_0 = \frac{A(t)}{A_0^{E=0}} \\
m = \frac{\dot{E}}{\sigma_0} \frac{\partial \sigma}{\partial \dot{E}}, \gamma = \frac{1}{\sigma_0} \frac{\partial \sigma_0}{\partial E}, \delta \hat{A}_0^{E=0}
\]

Where \(A\) is the area, \(\delta A\) is the defect in area, \(E\) is the strain, and \(\sigma\) is the stress. The subscript 0 denotes conditions for the unperturbed state. The terms \(m\) and \(\gamma\) represent influence of strain rate softening and strain hardening respectively.

From this equation, one can see that the front factor:

\[
\frac{(1-m-\gamma)}{m}
\]

is equivalent to the stability condition described by equation (61). This term also determines the rate at which the instability grows. This equation should only be valid when the defect is small, but integrating it till the point of failure can be instructive. We see that an increased viscous influence will indeed retard the growth rate. This is in agreement to the observed result and the suggested mechanism for region III of the master curve, where a large amount of additional strain occurs before actual rupture occurs for low rate tests where viscous effect dominates. For high rates where elastic effects dominate, rupture occurs almost immediately after instability.
Failure Strains
- Experiment
- Strain at first instability
- Considere $E_{\text{crit}}$
- Improved Considere $E_{\text{crit}}$

Figure 34 Comparison between experimental failure strain and prediction of instability through energy analysis.

**Non-dimensional representation of results**

With experiments performed for strain rates spanning over four decades and a large range of relaxation times, it will be helpful to non-dimensionalize the results in order to gain further insight. Strain rate can be non-dimensionalized by
the strain hardening time to form the effective Deborah number $De_{eff}$

$$De_{eff} = \tau_{sh} \times \dot{E}$$

(64)

where $\dot{E}$ is the strain rate at which the experiment was conducted at.

$De_{eff}$ is the ratio between the time scale of the material and time scale of deformation. At high deformation rates (deformation time scale small compared to material time scale), protein polymer chains deform faster than it can relax, thus uncoiling in extension. The elasticity associated with this uncoiling gives rise to strain hardening. On the other hand, at low rates, chains have plenty of time to relax, viscous behavior is dominant and the material flows like a fluid. Therefore $De_{eff}$ can also be considered as an indicator of the relative importance between elastic and viscous effects. The results for various mix time and strain rates can be re-plotted on a single graph.
Figure 35 Non-dimensional presentation of results from filament stretching of Wheat flour dough. $c, E_f$ vs $D_e$.

\[ c = C_{D_e} \log D_{e_{ff}} + D_{D_e} \]  
\[ (65) \]

where $C_{D_e} = 0.63 \pm 0.04$, $D_{D_e} = 1.06 \pm 0.06$

The strain hardening exponent increases with increasing $D_{e_{ff}}$. This will mean an increase in both failure strain and strain at maximum tensile force, as indicated on Figure 35b. The data can be approximated by the following function:

\[ \varepsilon_{\text{failure}} \approx C_{\text{failure}} \log D_{e_{ff}} + D_{\text{failure}} \]  
\[ (66) \]
The non-dimensional constants have values: \( C_{\text{failure}} = 0.26 \pm 0.02, D_{\text{failure}} = 1.72 \pm 0.04 \)

The difference in flow behavior between experiments with high and low \( D_{\text{eff}} \) could be seen by looking at images taken near the point of rupture. At low \( D_{\text{eff}} \), segments of dough could be seen sliding past each other, and the shape of deformation near rupture is extremely irregular because tearing occurs simultaneously over large portions of the sample. The ruptured sample showed little elastic recoil. On the other hand, at high \( D_{\text{eff}} \) sample deforms homogeneously. At the point of rupture, a localized tear forms causing the sample to break cohesively and rapidly. Significant elastic recoil could be seen.

![Figure 36 Rupture at low \( D_{\text{eff}} \))=0.15; the nominal strain at onset of tearing \( E_c=0.86 \).](image)
Figure 37 Rupture at high $D_{eff} \approx 400$; the nominal strain at onset of tearing $E_c = 2.15$.

Different Flour Types

Dough mixed from different flour types show significantly different mixing characteristics (Figure 32) and stress-strain behavior.
Figure 38 Stress strain curves for various flours (30g), mixed with 20g of water for 180s.

Using the non-dimensional approach, we can compare flours mixed from different flour types.
Figure 39 Non-dimensional comparison between HRS, OSRW. Red dotted line represent equation (65) in (a), and equation (66) in (b).
Figure 40 Non-dimensional comparison between HRS and DF. Red dotted line represent equation (65) in (a), and equation (66) in (b).

Experiments described in the previous sections were repeated for Ohio Soft Red Winter (OSRW) and Durum Flour (DF) to find the respective characteristic time at different mixing times so that their strain-hardening \( @c \) and extensibility \( @E_{fai} \) characteristics can be plotted non-dimensionally on Figure 40. The trends are fitted to a logarithmic law:

\[
@c, E_{fai} = C \log D_{eff} + D
\]  

(67)

The respective values are given in

Table 4
Table 4 Non-dimensional parameters fitted from equation (67).

The two wheat flour showed a similar non-dimensional behavior while the Durum flour representing a very different type displays a different trends. We hope that using this method we can illustrate and understand some fundamental parameters which distinguishes the rheology of different flour types.

<table>
<thead>
<tr>
<th></th>
<th>HRS</th>
<th>OSRW</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.48±0.03</td>
<td>0.46±0.05</td>
<td>0.61±0.06</td>
</tr>
<tr>
<td>D</td>
<td>1.16±0.07</td>
<td>1.04±0.07</td>
<td>1.05±0.06</td>
</tr>
<tr>
<td>$E_{\text{fail}}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.26±0.02</td>
<td>0.25±0.05</td>
<td>0.39±0.04</td>
</tr>
<tr>
<td>D</td>
<td>1.58±0.04</td>
<td>1.65±0.06</td>
<td>1.71±0.05</td>
</tr>
</tbody>
</table>
Mixing

In the previous chapter, we first characterized the dough through careful measurements on a filament stretching extensional rheometer. Next we consider some of the ideas suggested by Gras et al [72]. Further assumptions were made on the deformation within the mixograph and its relationship to dough properties. Finally we assess the validity of these assumptions by comparing with filament stretching results.

Introduction

Mixing is the first step in the bread-making process. The respective constituents are blended evenly and the application of mechanical energy “forms” the dough by changing its molecular structure. The process was described in the previous chapters.

Mechanical mixers come in various forms, industrial mixers are designed to handle a large quantity of dough, some examples are agitator arm, spindle and planetary mixers etc... In the laboratory, the dough are produced in much smaller quantities, the mixers are used to produce samples of consistent properties for testing. Some mixers also monitor the properties of the dough during mixing and are therefore can be considered to be a crude form of rheometer or indexer.

Deformation of dough in the Mixograph

We begin by considering the motion of mixing. The mixer used in our laboratory
is a National Mfg 30g Mixograph. The moving pins describe an epicrohoidal motion in the mixing pin. An epicrohoid is the path traced by a point on a circle rolling around the outside of another fixed circle Figure 41. An example of epicrohoids is the pattern traced out by the educational toy called the spirograph which was popular in the 1970s. In the mixograph, the position (x,y) with respect to rotation θ of the moving pins are described by equation (68) [73]:

\[
\begin{align*}
    x &= r_1 \cos(\theta + \theta_j) + r_2 \cos \left( \left( 1 + \frac{n}{m} \right) \theta + \phi_j \right) \\
    y &= r_1 \sin(\theta + \theta_j) + r_2 \sin \left( \left( 1 + \frac{n}{m} \right) \theta + \phi_j \right)
\end{align*}
\]

where \( r_1 = 1.78\text{cm}, \ r_2 = 0.89\text{cm}, \ (\theta_j, \phi_j) = (0,0), \ (0,\pi), \ (\pi, \ 1/4\pi), \ (\pi, \ 5/4\pi) \) for the four moving pins respectively.
Figure 41 Schematic of Mixograph, epitrochoidal set-up, and motion of pins within mixing bowl

Figure 42 Spirograph

Figure 41 also shows the motion of a moving pin around the stationary pins. The gear ratio of the mixograph is 3:4, in other words, a pin returns to its original position after four cycles of rotation.

To form the dough, the constituents of dough (Table 5) are poured into the mixing bowl. At the beginning, the moving pins simply stir the flour and water dispersing the constituents evenly around the bowl; the torque required initially is relatively low. As mixing progresses, the motion of moving pins drag the dough along, stretching and folding it around the stationary pins. The force to perform the stretching motion increases during the early stages of mixing. This increase (reflected in the increase in torque) is commonly associated with dough
development, in which the gluten from the flour is hydrated and forms an elastic network.

<table>
<thead>
<tr>
<th>Flour type</th>
<th>Hard Red Spring (HRS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hard red winter (HRW)</td>
</tr>
<tr>
<td></td>
<td>Ohio Soft Red Winter (OSRW)</td>
</tr>
<tr>
<td>Flour weight</td>
<td>30g</td>
</tr>
<tr>
<td>Water Content</td>
<td>20g (66% weight ratio)</td>
</tr>
<tr>
<td>Mixing time</td>
<td>0 to 600s</td>
</tr>
</tbody>
</table>

**Table 5 Specifications of the dough**

At longer mixing time, the torque decreases. Dough mixed to this stage is referred to as over-mixed. A possible explanation for this feature can be that rather than building up an elastic network, mechanical energy supplied at this stage breaks down the micro-structure within the dough.

The point at which the torque peaks (transition from network formation to over-mixed) is known as the peak-mixed condition. Dough mixed to this stage is often considered to give optimum baking properties. However, some studies have shown that this peak-mixed condition might not be a universal guide to dough quality [72]. The stretching motion can be considered as a series of extension tests, we can estimate the strain rate from equation (69).

\[
\dot{e}(t) = \frac{1}{l(t)} \frac{dl}{dt}
\]  

(69)

where \(l(t)\) is the distance between moving and stationary pins.

An average strain rate can then be estimated by considering the root mean
square value of $\dot{e}(t)$. In the case of the mixograph rotating at 90rpm ($3\pi \text{ s}^{-1}$), the RMS strain rate was found to be $\sim 7 \text{ s}^{-1}$.

Figure 43 a. Distance of moving pin from stationary pins, b. mixograph torque, c. Estimate of strain rates within mixing bowl.
This deformation stretches the dough between the pins. We have concluded from filament stretching experiments that dough extended at such high rates undergo strain-hardening, therefore we expect a fluctuation in mixograph torque (at frequency $\sim 2/3$ Hz Figure 43c) which is associated with the pin motion. Detailed studies using high resolution mixograph confirm that the torque increases at instances which coincides with periods where extensional strain-rates are large [72].

The analysis presented concerns the position of one moving pin relative to the three stationary pins, while the actual mixograph output reflects the contribution of stretching motion from all four moving pins. In practice, it is extremely difficult to separate the contribution from individual moving pins.

Nevertheless, we obtained a good estimate for the relevant deformation rates and frequencies. In view of this analysis, we divide the mixograph torque output into two components.

The first is a slowly varying component ($\ll 2/3$ Hz). This component has long been used as an indicator for dough development. As mentioned previously, during mixing, the initial period where the magnitude of this component increases is commonly associated with gluten net-work formation/development. At longer mixing times, this component decreases. The decrease is linked to over-development/network break-down.

The second is a rapidly varying component ($\sim 2/3$ Hz). This is analogous to what Gras et al [72] referred to as the “bandwidth”, they suggested this component to be associated with dough extensibility.

In this article we reconsider the significance of these two components, in
relationship to strain-hardening quality. From the analysis of mixograph pin motion, we concluded that the high frequency component arose from the stretching motion generated by the change in relative distance between moving and stationary pins. At each instance of this stretching, the stress/torque increases because of strain-hardening. Since strain-hardening is intrinsically linked to resistance to necking failure [70, 74], Gras and co-workers have correctly concluded that this “band-width” is a qualitative indicator for extensibility.

However, when characterizing strain-hardening, one is in fact only interested in the relative increase in stress as strain is increased, while the bandwidth alone, can only be a measure of absolute increase in stress. This means that dough with different stiffness cannot be meaningfully compared by just the bandwidth.

As for the low-frequency component, even though it cannot be directly related to strain-hardening/extensibility, it can be considered as a characteristic stress/torque (Figure 7c), and will be useful in normalizing the high frequency component to give relative stress increase.

Under these assumptions, it is reasonable to suggest that the strain hardening exponent $c$ will be related to the ratio in magnitude of these two components. This pseudo-dimensionless parameter will be referred to in this document as the Mixing Number ($Mn$):

$$Mn(c) = \frac{\text{Rapidly varying component}}{\text{Slowly varying component}}$$  \hspace{1cm} (70)

**Separating the two components**
The analysis above was realized through a data processing set-up shown schematically in Figure 44.

**Figure 44 Schematic of data processing for mixograph output**

The mixograph deflection/torque was digitized through a string pot and data acquisition system. The rapidly and slowly varying components were separated by a high and low-pass filter respectively. The cut-off was set at 0.375Hz. This frequency corresponds to the four mixograph cycles or the period in which a moving pin returns to its original configuration and is chosen so that all components associated with the short-term motion of the pins will be included in the high-passed signal, while the low-passed component predominantly contains
information associated to average stress state and dough development.

After the high-pass filter, the magnitude of the rapidly varying signal was averaged by performing a root mean square over a period of 4 mixograph rotation cycles.

In Figure 45 we present results that show the relationship between Mixing number ($Mn$) and strain-hardening exponent ($c$ fitted from filament stretching experiments). To further demonstrate the appropriateness of using the low-frequency component in normalizing the data, results from two other flour (HRW, OSRW) were included.

![Figure 45 Relationship between strain hardening and mixing number ($Mn$)](image)

**Figure 45 Relationship between strain hardening and mixing number ($Mn$)**

Within reasonable errors, results exhibit trends that can be described as follow:

- **Region a.** $c$ increases with $Mn$ give equation linear fit
Region b. $c > 2.5$, decreases with increasing $Mn$

Results in Region a confirm the validity of our assumptions. We expect a dough which exhibit a greater degree of strain-hardening to give a larger fluctuation in torque. As strain-hardening decreases ($c \to 0$), mixing number tends to zero as expected of a fluid like behaviour. One must bear in mind that the stress associated with the extensional deformation of different flour types can be very different, but the use of the slowly varying component to normalize the data appears to reduce the data to a single master-curve. Data in this region can be used to perform a quantitative comparison between dough of different flour content, high $Mn$ translates to good strain-hardening quality (high $c$). Instead of the low-frequency component of Mixograph torque commonly used to assess the development/over-development of dough, $Mn$ provides better evaluation of the quality in terms of strain-hardening and extensibility.

The reversal of trend in Region b was unexpected. This points to weaknesses in the assumptions. These assumptions are indeed very bold, the deformation of dough within the mixograph bowl is extremely complex and to consider it as a series of extension tests is a gross simplification. The relation between torque and stress is not straightforward either. The torque not only depends on the value of stress/tensile force in the stretched dough, it also depend on the direction and distance of stretch relative to the centre of the bowl. The analysis also does not address situations where the dough in the mixograph ruptures before reaching maximum extension nor in instances where sudden increase in torque arising from dough lumping asymmetrically to one side of the bowl. Mixing numbers in this regime are extremely sensitive to filter settings; it remains to be seen whether
an appropriate choice of averaging parameters can collapse the data onto a single curve. Another possibility is that the strain-hardening index $c$ may not be the most appropriate parameter for studying the significance of the mixing number. After all it is derived from a "pseudo" constitutive equation that is not frame invariant. The constitutive equation it was derived from was meant to be a starting point for studying the behavior of dough in extension because it allows us to simply characterize the various features of the stress strain curve. The fact that it is not frame invariant means that there is no consistent way to translate the results to a form appropriate for studying other forms of deformation, which we are trying to do in this case.

**Conclusion**

Results for un-axial extension in a filament stretching rheometer demonstrated a significant change in strain-hardening capability as mixing progress. One of the interesting conclusions is that what we refer to as peak-mixed condition which is in fact equivalent to a maximum in the slowly varying component, is not indicative of good dough quality if the desired property is strain-hardening and extensibility. The "bandwidth" can give qualitative assessment of this particular property, but when dough of different stiffness is to compared, the mixing number ($Mn$) is more appropriate.
Conclusion

After a series of initial studies, we arrived at a consistent method of measuring the rheological behavior in extension for bread dough on the filament stretching rheometer. Various difficulties such as sample preparation and mounting were dealt with by using a special end-plate fixture. We also developed an appropriate protocol to investigate the effects of strain rate, mixing time and flour type on the stress strain behavior.

The material response at low strain rates ($10^{-3}$ s$^{-1}$) can be dramatically different from that observed at relatively high rates ($10^{0}$s$^{-1}$). It is therefore necessary to perform tests over a relatively large range of strain rates in order to extract the viscoelastic material parameters relevant to the bread making process.

A surprising result during the mixing time study was that the peak-mixed condition does not give the most desirable dough condition if extensibility is the property which we want to optimize. Maximum extensibility and strain-hardening occurs at much shorter mixing time than the point of maximum torque. This can be seen as evidence contrary to the commonly held belief that maximum gluten network development occurs at the peak mixed condition. Baking and proofing tests will be required to show that conditions corresponding to maximum extensibility on filament stretching do indeed translate to greater loaf volume while novel methods through AFM or cryo-SEM might be able to demonstrate conclusively the level of gluten structure development through various stages of mixing.

We also demonstrate that by deriving a characteristic time, how doughs mixed
from different flour types can be differentiated through a non-dimensional stability plot.

In terms of constitutive modeling, we used a simple power-law model to characterize relevant features of the stress-strain curves under extension without invoking complex equations or large numbers of fitted parameters while being pragmatically useful. Other than giving reasonable description of the rheological behavior for the specified deformations, the equation was also able to predict the point where necking instability begins through a linearized energy analysis. We believe the subsequent development of the neck to rupture can be described by a non-linear differential equation based on this result. However, accurate knowledge of non-uniformity is required as the initial conditions for the integration. This will be the subject of further work.

Finally we prototyped a potentially useful enhancement to existing mixographs so that the torque signal previously recorded on a strip chart can be electronically recorded for more detail analysis. This digitized signal can be filtered to extract (i) a rapidly varying torque signal corresponding to stretching motions generated by the mixograph pins and (ii) a slowly varying torque signal representing a characteristic stiffness of the dough. We show how a ratio of these signals, referred to as the mixing number \((mn)\) can be representative of the strain-hardening capability of the dough and is appropriate for comparing doughs of different stiffness. However, above a critical \(mn\), corresponding to very elastic dough, the value of \(mn\) can be very sensitive to filter settings and can become double valued. Currently, a large strain extensional test method such as filament stretching or SER technique is still required to assess the large strain extensional
properties in this regime until an appropriate filter setting can be determined which collapses the data onto a single master curve.

The extensional rheology of dough provides many interesting challenges both technically and conceptually. The potential parameter space is enormous, future work will include extensive studies involving variable water content, additives etc... While the current interest in health foods might mean studies on whole-wheat flour can be of industrial significance. Filament stretching though powerful for its ability to probe a large dynamic range of deformation conditions, is time and labour intensive making it experimentally difficult. A continued search and refinement of experimental techniques will be important. At the moment, the SER universal testing platform appears to be a suitable alternative. Finally, a true constitutive equation able to describe the rheological behavior of dough in a wide variety of deformation conditions remains elusive. Such an equation will at last lead us to the fundamental material functions and parameters that will allow us to understand results from the myriad of methods available to the dough rheologists in relationship to each other.
References


9. Martinez-Anaya, M.A. and T. Jiménez, Functionality of enzymes that


43. Blackwell, R.J., T.C.B. McLeish, and O.G. Harlen, Molecular drag-strain


52. Bloksma, A.H., A calculation of the shape of the Alveograms of some


60. Rock, K., Rheological modelling of bi-axial inflation of bread dough, in Department of Mechanical Engineering. 2002, Massachusetts Institute of Technology: Cambridge.

61. Larson, R.G., T. Sridhar, L.G. Leal, G.H. McKinley, A.E. Likhtman, and


70. McKinley, G.H. and O. Hassager, The Considere condition and rapid


