Group Project Report:

Yummy Physics

A Coeliac's Dream: The Rise of Gluten-Free Bread.

Authors:

Alexa Hladio, Hannah Nicholson, Pablo Sandquist,

Jingyu Song, Yingxuan Li.

Advisor:

Jean-Christophe Denis

Abstract

This report provides evidence to suggest that people with coeliac disease and gluten intolerance are generally dissatisfied with the texture of current gluten free bread alternatives. It proceeds to lay out the groundwork for designing a gluten free flour that resembles the effects of wheat flour on dough and bread rheology by considering thermodynamics of concentrated polymer doughs. We found that a polymer's microscopic morphology plays a key role in dough rheology, which can be reduced to the ratio $\sqrt{N}\upsilon/l^3$ (the key ratio κ), where N is number of monomers in a polymer, υ is the monomer volume and l is the length of the monomer. The report continues to design a chemical recipe for a gluten free flour resembling strong wheat flour using proteins available in common grains. Finally, the economic, environmental, and nutritional suitability of the flour recipe is examined; with particular emphasis placed on the industrial challenges related to extracting these compounds from grains.

Table of Contents

1. Introduction

1.1 Bread: A Cornerstone of Civilisation

Since humans began domesticating crops, bread has been made in all corners of the world, becoming one of the most important sources of carbohydrates in most people's diets for over 30,000 years [1]. Made from predominantly flour and water, it is likely that the origin of bread came from experimentation with the two ingredients. Over time, the recipes for bread became more complex as the cooking abilities of humans developed and evolved; now we have over 200 different types of bread to choose from [2]! Among many cultures and traditions, bread is also considered a symbol of hospitality [3].

Although the exact timeframe of the invention of bread is disputed, sources show that the first evidence of bread was discovered around 14,000 years ago [4]. Found in present-day Jordan, this bread resembled what we now know as a flatbread, and later became the steppingstone to bread becoming a popular and common foodstuff in an area known as the Fertile Crescent [5]. Flatbread promotes the subsistence lifestyle, meaning it can support a diet on a minimal level. For example, it can be cooked a second time to dehydrate it, preventing mold growth and allowing a longer shelf-life. Flatbread also does not require an oven to be cooked, with the first evidence from Jordan being cooked from hearth ashes [6]. It is also a very simple recipe, only requiring flour and water to make it, and therefore it is very cheap.

Flour is made by grinding cereal grains, roots, or seeds; different climates and cultures worldwide have varying types of cereals which yield different types of bread (different textures, shapes and tastes). For example, cereals such as wheat, barley, rye, and oats are more commonly found in temperate climates like Europe, whereas tropical areas like South-East Asia grow rice and sorghum [7]. The type and quality of the soil also determines what kinds of cereals can be grown. Modern breeds of wheat are also commonly hybridisations, meaning they have been cross bred to achieve ideal properties [7].

Wheat is the most common grain used for making bread, covering more of the Earth's surface than any other crop [8]. The most popular kind is known as *triticum aestivum*, or 'bread wheat', which possesses a favourable high gluten content, thus yielding a springier bread texture. Although not every type of bread requires gluten as part of its recipe, the addition of it allows for bread to rise easily. Wheat-bread is the most commercially used variety, especially for making sliced bread, tortillas, cakes, and East Asian noodles [9].

About 80-85% of wheat varieties contain gluten proteins, and these play a major role in bread making [10]. When hydrated, for example when mixing flour and water to make bread, gluten adopts an elastic quality, thus yielding a stretchy and malleable dough which can then be shaped and manipulated into the desired shape. The recipe for bread has changed a lot over the years, and nowadays it normally contains yeast [10], a fungus which undergoes fermentation by using a fermentable sugar to produce carbon dioxide gas and ethanol. The gluten proteins within the dough trap the gas and their elastic quality allows the bread to rise, which yields the risen loaves we know and love today. Originally, before people discovered that yeast could be used, bread relied on accidental fermentation to achieve a risen loaf [11].

The properties of the gluten protein are unique and are not found in similar cereals such as barley or rye. It is therefore difficult to reproduce the qualities of bread without using gluten. Wheat is used for a range of foodstuffs besides bread, including pasta, cakes and several types of noodles [12]. Since gluten-containing cereals like wheat are such ubiquitous crops, humanity has become extremely reliant on foods that contain gluten.

1.2 The Significance of Gluten

Rheology is the science of matter that flows, primarily fluids [13], but we will investigate one of its more niche topics: bread categorised as soft matter. We will explore the physical features of bread, or more specifically gluten's response to stress. Gluten has the unique property of network formation needed for an optimal dough rheology. Specifically, it has a flexible and elastic network that is stretchy and allows the dough to be manipulated and rolled without breaking [14]. This structure is essential to help achieve the texture in a dough required to retain gas during proofing and baking. When yeast ferments during the proofing time, it produces carbon dioxide gas. The gluten then helps trap the carbon dioxide and air bubbles inside, causing the dough to expand and stretch, thus producing an airy and light dough.

When gluten is combined with water it becomes sticky and stretchy due to the mesh-like network made by its constituent parts, similar to the one shown in Figure 1. Gluten is made of two proteins called glutenin and gliadin which are polymers consisting of amino acid monomers. Polymers are composite molecules made of one repeating subunit, or monomer, and can be linear (like a chain) or branched (cross-linked to form networks) [15, 17].

The characteristics of bread can differ based on the proteins present within. For example, bread with no gluten but that contains starch can be sticky, but not as stretchy as bread with gluten which contains long protein strands. This is because starch is not a long-stranded polymer like glutenin in Figure 1 but is a linear chain polymer instead [16].

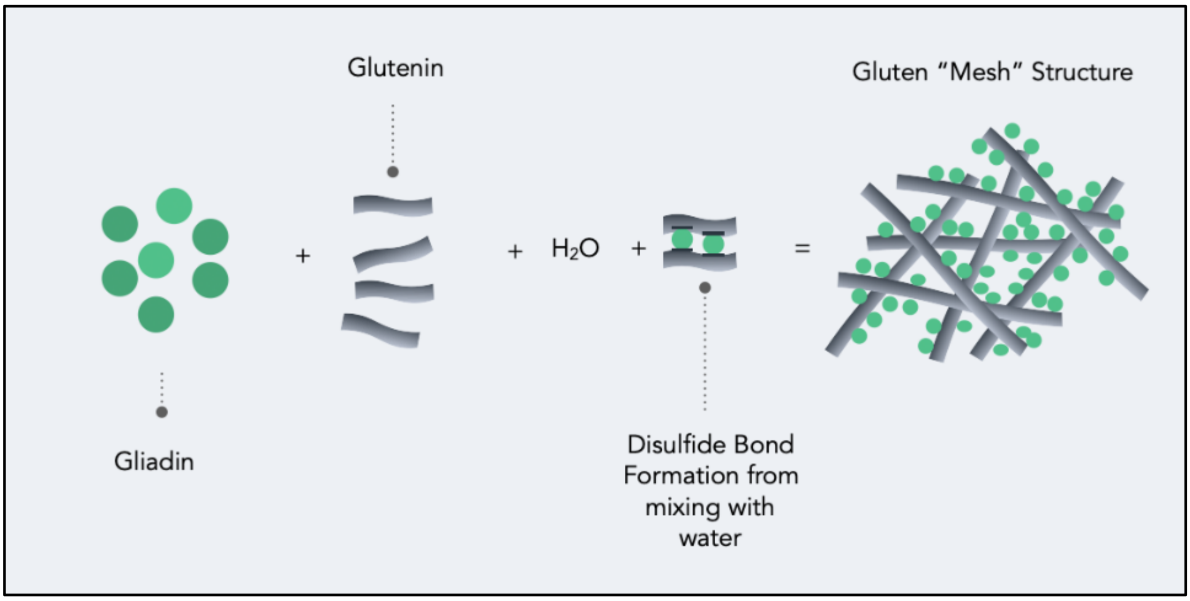

Figure 1: The shape of glutenin and disulphide bonds and how they interact once they are free to move and hydrated. Obtained from [14].

At the molecular level, gluten proteins are made up of long chains of amino acids folded in a specific way into a complex, three-dimensional structure [17]. Amino acids are organic compounds containing large numbers of functional groups, which branch off from hydrocarbon chains and are often charged [15]. These usually determine proteins' electrostatic interactions with other compounds.

Glutenin is responsible for the dough's elasticity and strength. The chains of glutenin proteins are held together by strong covalent bonds called disulphide bonds, which are formed when two amino acid side groups containing sulfur are linked together [18]. The disulphide bonds are very difficult to break and therefore the bonds between the monomers are not easily broken in the kitchen environment [18]. Glutenin forms many disulfide bonds creating a long chain of monomers that can be entangled with each other, therefore it increases the elasticity of the dough.

In comparison, gliadin is a group of proteins with shorter chains and is less structured than glutenin [17]. It is responsible for the dough's stickiness and, along with starch, helps give bread its soft, chewy texture. Together, glutenin and gliadin form a matrix of proteins that gives bread dough its characteristic rheology. This can only happen when the proteins can move relatively freely and monomers can link together, which is why dry wheat flour has no gluten, but bread dough has [16, 35]. Water acts as an enabler to make the proteins extend and unfold in a process called hydration, and gluten production can only begin when water and wheat flour are combined.

Dough preparation is also essential; including kneading, mixing, and resting to ensure the proteins can find each other and interact [17]. The gluten structures are also highly affected by dough freezing and frozen storage, mixing conditions (such as hydration level and temperature), and external substances [16].

Gluten with its two constituent parts is clearly very important to dough rheology.

If it were not present, bakers would not be able to manipulate the dough to its desired shape. Without gluten, pizza would crumble, bread would not be light and fluffy, and panettone wouldn't be as large. The interconnections between the comparatively short polymers of gliadin and the long thin strands of glutenin create a very complex interlinked network that is very difficult to replace.

1.3 The Rise of the Gluten-Free Market

You may have noticed in recent years that there is a growing popularity of gluten-free (GF) products on the shelves of supermarkets, and there is good reason for this. Coeliac Disease, also known as CD, is a condition in which the body reacts to the gluten protein and causes the immune system to attack the lining of the small intestine, leaving the person unable to take in nutrients. CD can cause a wide range of symptoms, including abdominal pain, diarrhoea, bloating, and malnutrition [19]. Other conditions exist which cause uncomfortable reactions when gluten is consumed, known as gluten sensitivity (GS), which also encapsulates CD.

The first known cases of CD date back to ancient times: a Greek physician named Aretaeus of Cappadocia described this condition as patients experiencing abdominal pain and malnutrition after consuming wheat [20]. However, it was not until the 20th century that CD was fully understood and recognised as a medical condition. In the 1950s, a paediatrician named Dr. Willem Karel Dicke discovered that a GF diet could help improve the symptoms of CD in children [21].

As per the study by the CD Foundation, in 2018, the prevalence of CD was 0.4% in South America, 0.5% in Africa & North America, 0.6% in Asia, and 0.8% in Europe & Oceania [22]. These figures go up when including people with all types of GS. It also appears that CD has been on the rise for the last several decades, but this may be due to improved methods of diagnosis rather than an increase in the number of people suffering from the disease. Moreover, the frequency of CD is likely to increase for developing countries due to the westernisation of their diet [22]. Unfortunately, CD is a genetical condition with no cure, so people with it must follow a strict diet to help control symptoms and prevent long-lasting complications [19]. With such a large proportion of the population taking on a GF diet, companies have been incentivised to develop quality GF food products. Despite recognition of CD only existing for around 100 years, humans have been baking GF bread for thousands of years, using a variety of grains such as millet, rice, and maize, providing a suitable solution for those with GS [11]. This incentive for companies has led to a wide range of GF breads, furthering the types of grains used such as rice, quinoa, and oats. These products can be found in many supermarkets and health food stores.

In addition, increasing government promotion programs related to the intake of GF products for the treatment of all GS have further contributed to industry growth [23, 24]. These promotional activities have increased consumer demand for coeliac disease diagnosis and increased product demand. The rising trend of following a healthy diet in developing countries is expected to provide ample opportunities for market growth. As a result, high demand for frozen GF baked goods is driving industry expansion, offering a diverse product range and continuous improvements. The global GF food market has grown from 5.6 billion USD in 2021 and expected to be at 7.41 billion USD by 2026 [25].

Despite the availability of GF bread, people with CD still face challenges when it comes to finding safe and convenient food options. Cross-contamination is a major concern [26], as even small amounts of gluten can cause harm to those with CD. To minimise the risk of exposure, many people with CD choose to cook and bake their own GF bread at home, using dedicated GF equipment and ingredients.

Overall, the relationship between GS and viable GF options has a long-spanning history. GF food alternatives are becoming more available as the prevalence of GS increases, and thus the size of the GF market. The main product types in the GF food market are baked goods, dairy products, meat, desserts and ice cream, pasta, and rice [24]. The distribution channels for GF food products are rarely independent bakers but large companies, due to the laborious methods involved in production [24].

1.4 Industrial Techniques for making GF bread

As said before, the market demand for GF bread is growing year by year, prompting the food industry to pursue new production techniques for a higher quantity of bread, with a quality resembling that of regular bread. To obtain GF bread that is similar in flavour and nutrition to regular bread in an inexpensive way, factories use a variety of processes in their production: special external processing, the use of additives and special storage techniques. When a factory makes dough, it does not use only one type of grain flour as in the case of ordinary bread, but a mixture of different types of grain flour, the proportion of which varies according to the manufacturer [27].

Three other additives are also often used in industry: proteins, enzymes, and salt. Protein improves the dough's fermentation properties and increases the bread's specific volume. It replicates the colour and flavour of gluten bread better while adding more nutrients. The most common protein additives are egg white, pea, soya, whey, and milk [27]. The addition of enzymes improves the dough's ability to hold water, strengthening the dough structure and increasing the bread's softness. Lastly, salt reduces the specific volume and porosity of the dough while increasing the total volume.

Next, factories often carry out direct physical processing of the dough itself. The most used process is called high pressure processing, in which food is subjected to pressures of 100 to 1000 MPa to create new structures and textures by inducing starch pasting and protein polymerisation. Under high pressure, the starch in the dough expands and creates a sticky paste without destroying the integrity of the starch granules [28]. These processes can be extremely expensive because of the equipment and energy needed to pressurize the dough. This can result in high-priced GF bread when compared with wheat bread.

1.5 Problems with GF Bread

It has already been shown in previous studies that many GF alternatives for bread rate poorly in terms of price, nutritional, sensory, and textural properties. A recent study discusses how it is often difficult for consumers to find a GF alternative bread which is satisfactory as a replacement for wheat bread [10]. It is also difficult to find a good GF flour that strikes a balance between having nutritional benefits and good taste.

To support the motivation and importance of our direction of research, we made a survey[1] to assess the public's opinion on GF foods, which ultimately lead to some interesting and surprising results. It was especially important as the team has little to no experience with GF bread. The survey was posted to an online forum that was targeted at GF individuals, although not all the participants were GF.

In total, 308 people participated in this survey, with 74% being unable to eat gluten. The survey results show that 93% of all 308 participants have tried GF foods before, regardless of being physically able to eat gluten or not. Out of the individuals who have had a gluten alternative, about a third later stated that they did not think the alternative was sufficient as a replacement for the original food.

The participants were also asked to give their opinions on alternative foods in general (such as vegan or dairy alternatives). Only a tiny fraction (7 people) thought that the alternative food was nice and mimicked the original food. The majority of individuals (56.2%) said that only some alternatives are nice, and one would need to spend more money to get the nicer options, with the rest of the responses stating that either none of the alternatives are nice, or that most need improvement.

To investigate any issues that individuals may have with specifically GF bread, we asked the survey participants who have sampled it to rate GF bread on a scale of 1 to 10, from most negative to positive respectively. Figure 3 shows the results from this questionnaire with an average rating of 5/10 - if that was a movie rating you would think twice about watching it!

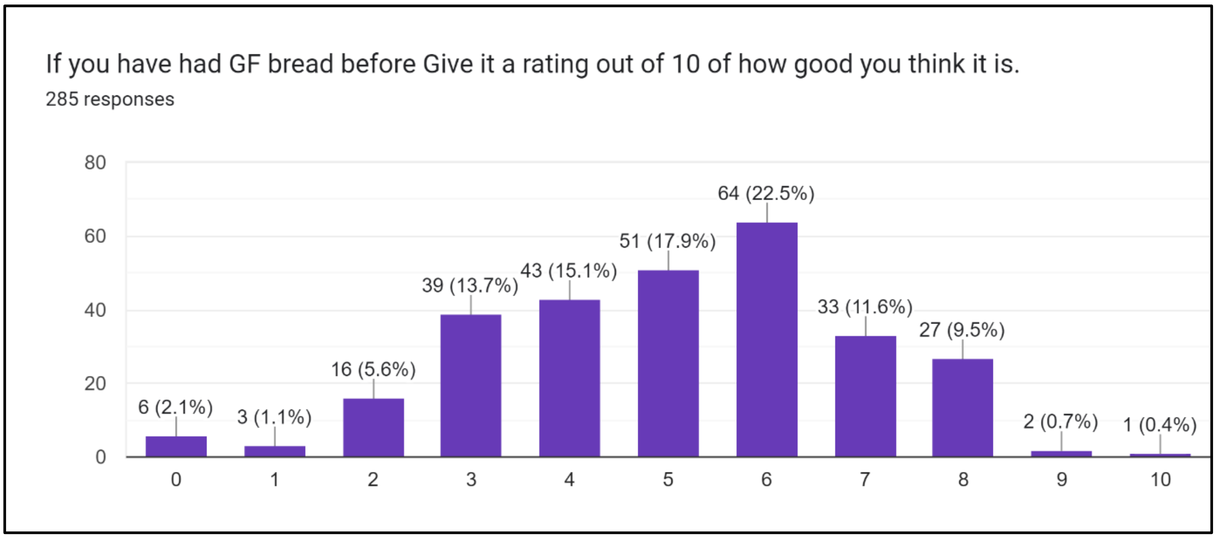

Figure 2: The percentage ratings of what the public's view is on GF bread today. This is a general rating across all factors that are important to GF food eaters. For more information about the survey see appendix 9.1 and [29].

It is clear that GF bread, and alternative foods in general, need to be improved. Figure 3 shows the results when the participants were asked to choose the property of GF bread that they think requires the most improvement. The majority vote was for texture, having two-thirds of the votes, with the next largest share going to price. Our research will therefore

[1] See appendix Section 9.1 and [29] for full details.

focus on replicating the texture of normal bread as this is the dominant aspect that requires improvement.

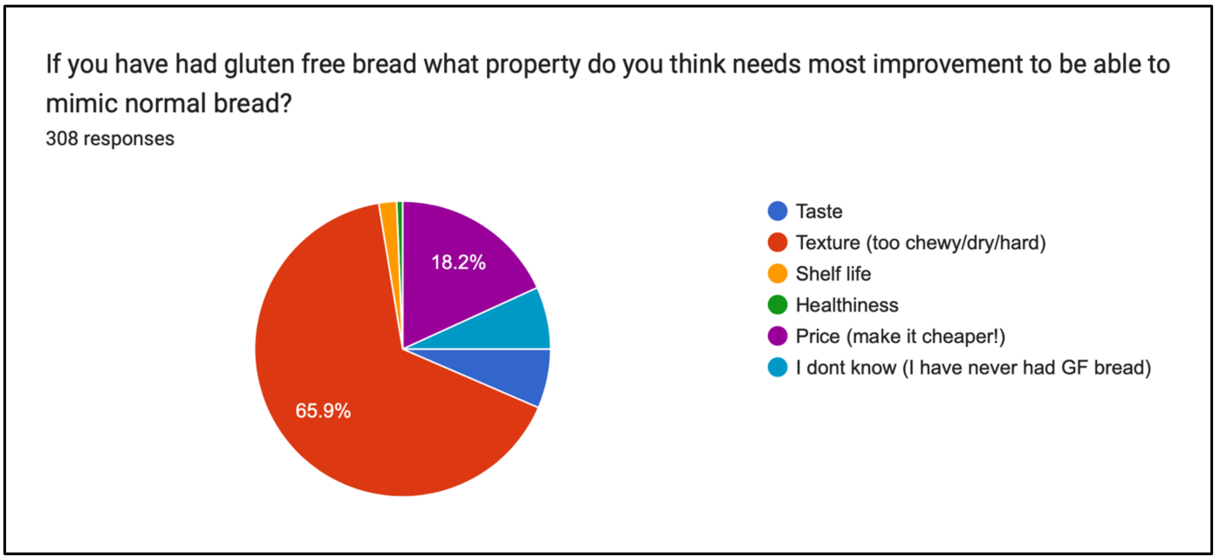

Figure 3: From the survey the results giving the aspect of GF bread that people thought needed the most improvement. With 66%, the majority vote, going to the texture and the next most voted going to the price. For more information about the survey see appendix 9.1 and [29].

Overall, our survey clearly shows that the demand for decent food alternatives is not being well met, both in food resemblance and price. In particular, the data highlights the need for improving GF bread texture and reducing its price. Other incredibly useful feedback was provided in the comments section such as one participant saying, *“I'm tired of paying [US]$6 for a half-sized loaf of bread just to get home and realize it's got a 3 inch diameter hole going all the way through it”* (see appendix 9.1). Examples of other prices in the comments go up to US$20, which is simply not affordable for the general public. Another individual said the bread *“feels like a fourth [of the size] of a regular slice of bread, not even the size of a slice of cheese these days”*. Some brands only taste good after being toasted and others use copious amounts of sugar to mask the taste of the crucial structural additives.

This feeling of being cheated is a serious issue along with price that affects customer’s opinion heavily. Some respondents mentioned they stopped buying GF bread from shops and started making their own at home because it is more affordable and flavourful. There are decent GF brands, but you usually have to pay a higher price for them and they are not sold in most stores. Mentioned brands that are considered good by respondents include Canyon Bakehouse LLC and Carbonaut LTD.

For around 1 in 100 people, having coeliac disease means eating a normal bread is not possible; with the many different types of bread being a part of so many different diets and meals, GF bread should be more accessible and much more enjoyable than it currently is.

1.6 Aims

The results of our survey in the previous section have clarified that people with GS are dissatisfied with the texture and the prices of GF bread substitutes. We aim to make the lives of people with GS better by laying down the physical groundwork to design GF flour producing the same texture bread as wheat flour. We will also propose a chemical recipe for a GF flour based on our findings and discuss how it compares to existing GF recipes, as well as its environmental sustainability and economic viability based on how hard it is to obtain the compounds in our recipe.

2. Solving the mystery of texture

2.1 What's the dream?

When the word texture is mentioned, your first question may well be "*what exactly is meant by the same texture as wheat bread*"? To the layman, texture is an umbrella term relating to the human sense of touch. However, when it comes to the study of bread, texture is a combination of trapped air, the size of air bubbles, how crumbly or stretchy it is and its moisture content. Therefore, human sensory perception experiences texture and defines what is pleasant. This means that any metric used to measure texture must be tailored to the consumer. When using different flours to make western-style bread, different structures are formed, resulting in different textures.

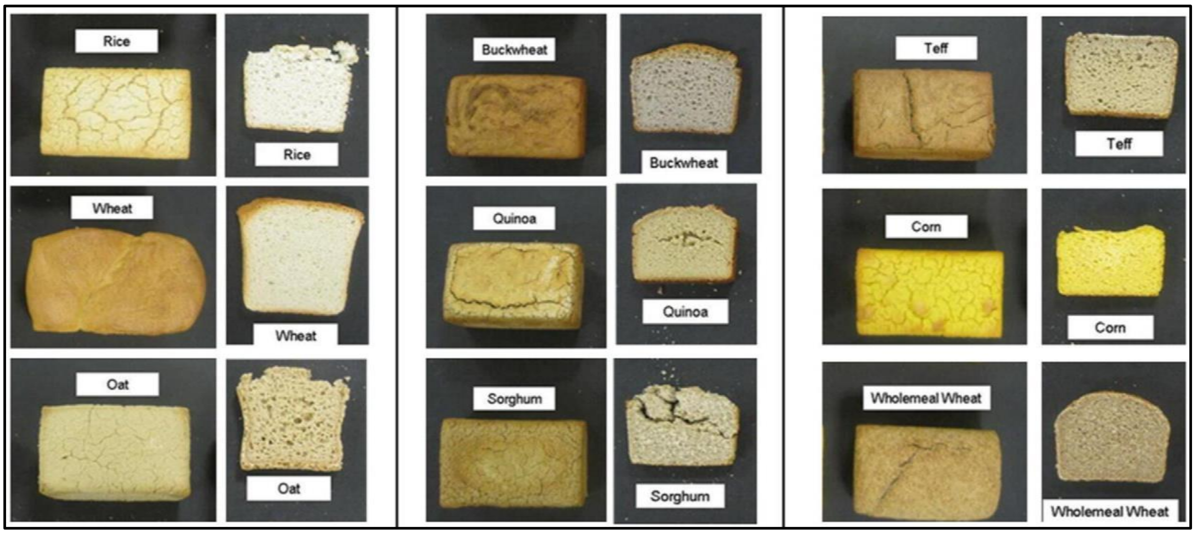

Figure 4: Comparison of doughs and bread with different flours. Extracted from [30].

Let's follow the story of a loaf of bread in someone's kitchen. An average person will slice it with a serrated knife, maybe toast the resulting slice or spread some topping like butter, grab it with their hands and bite into it. This means that how the bread stretches when compressed by someone's hands or by their teeth, plus whether it crumbles or deforms when a localized stress is applied by a knife, is paramount to defining the consumer experience.

We will therefore focus on a bread's response to stress in one direction: uniaxial stresses. The term *elasticity* is colloquially used to talk about these responses. This is a misnomer since this term is also associated with the behavior of springs and Hookean solids [31]. Viscoelasticity may be a better term since it encompasses all behavior between a Hookean solid and a Newtonian viscous liquid [31]. A more general term would simply be *stress-strain* relation, or *rheology* since there’s no guarantee that a material’s behavior under stress will be viscoelastic. As we will see later, polymer structures don’t have a linear response to stress, neither do they flow like a liquid [31, 32].

Dough clearly behaves more intricately than how it will be modelled in the following section, but to understand it, the concepts are simplified. There are also only a few papers detailing the complexities of dough’s behaviour, and hopefully with the increasing need for GF products this will drive further scientific research.

So, what is a coeliac’s dream? It is bread containing no gluten that has the same rheology as one containing gluten. Our focus is on rheology, but you cannot forget that it must also taste good. This is a simple concept but because gluten polymers are complex and often poorly described in the literature, it is a task that has yet to be successfully completed. In this section, we will lay down the framework to achieve this by modelling the effect of polymer characteristics on the uniaxial stress-strain relationship of bread.

2.2 Modelling bread elasticity

Since bread is an incredibly complex system, we chose to create a simplified model for the impact of flour on dough elasticity based on proteins that are free to move once hydrated, in a way like Brownian motion. We will then obtain the dough stress-strain characteristics starting from first thermodynamic principles, namely free energy, and add increasing levels of complexity to the model. Variables crucial to the final product include the level of hydration, starch content, yeast, temperature, and pressure. By assuming a flour has the same dough elasticity and history as its wheat counterpart, beginning at the time of hydration, both breads will have the same texture after baking. This is an oversimplification but is extremely useful for modelling and designing flours.

2.2.1 From Free Energy to Stress-Strain Relationships

The free energy of a system measures the work that can be extracted from a system. For a system with a fixed volume, this reduces to the Helmholtz free energy (*F*):

$$F = E - TS,$$

which represents a balance or competition between the internal energy (*E*) and the entropy (*S*) of a system at a given temperature (*T*). Maximising the entropy of the universe is equivalent to minimising the free energy of a system in thermal contact with its surroundings. Free energy works effectively as a conservative potential since systems reach equilibrium when free energy is minimised. By analogy to the familiar result from classical physics, $\vec{f} = -\nabla V$, where the force on a particle is related to the potential by a spatial derivative, the force on a system at a given non-equilibrium state will be $\vec{f} = -\nabla F$ evaluated at the state [32]. We will use this to find a stress-strain relationship for doughs when subjected to uniaxial stress, as shown in Figure 5 below.

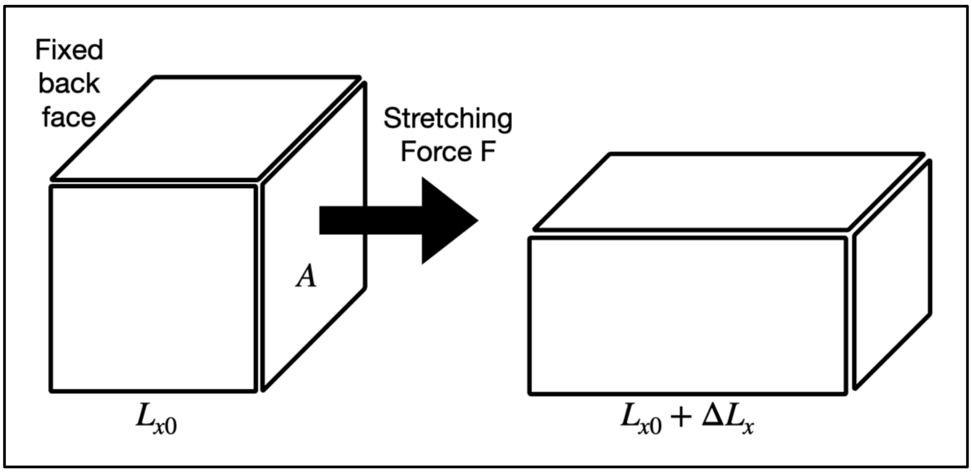

Figure 5: A schematic of uniaxial stretching. Made using Keynote™ by the authors of this report.

The tensile stress σ is the force per unit cross-sectional area that the dough resists a stretching force called strain [31]. The strain, $e = \Delta L_x / L_{x0}$, is a dimensionless measure of how far the dough stretches when a force is applied. From our free energy analogy, we know that the force on the material when stretched to a length L_x is the negative derivative of F with respect to L_x. Then, if our dough is static, the force applied on it must be equal and opposite to its resistance to being stretched. Therefore, the resistive force is the derivative of free energy with respect to sample length in the direction of stretching, which thus yields the stress-length relationship of the sample when divided by its cross-sectional area (*A*):

$$\sigma = \frac{1}{A}\frac{\partial \Delta F}{\partial L_x},$$

where ΔF is the total change in free energy of the sample compared to the unstressed case, and L_x is the sample length. Bread dough tends to be incompressible at room pressure [33], which further constrains our model such that stress and strain can be related analytically.

2.2.2 The Ideal Chain Model for Polymers

Biopolymers like glutenin and gliadin are complex molecules with poorly understood morphologies[2]. However, building a model of the rheology of polymer solutions from first principles can give us very useful insights. To start with a toy model, consider a chain of *N* links of length *l*, where the links can undergo Brownian motion.

[2] Shapes and sizes.

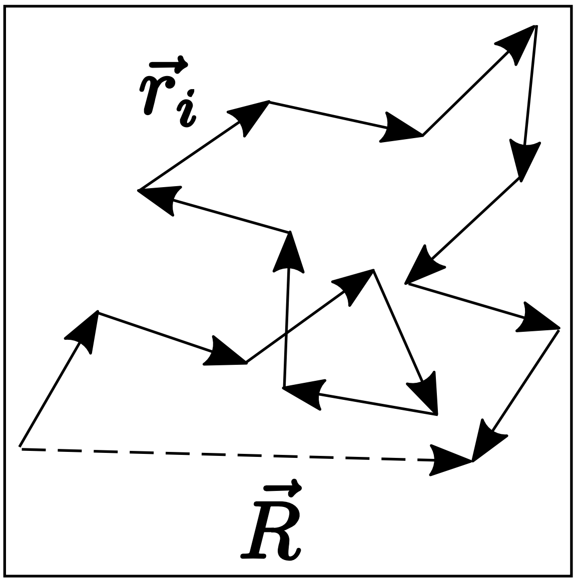

Figure 6: A diagram of the ideal polymer chain. Obtained from [34].

As with any three-dimensional Brownian motion problem, the average end-to-end displacement of the chain $\langle\vec{R}\rangle = 0$ and the variance is $\langle R^2\rangle = Nl^2$, since the average position of random motion is the origin, but the total distance covered increases with the number of links N in the chain. For very long chains, the probability distribution of an end-to-end vector R will approach a gaussian with these parameters, $P(\vec{R}) \propto exp(-3R^2/2Nl^2)$ [32], leading to an entropy of,

$$S = k_B \ln(\Omega) = k_B \ln(P) \Rightarrow S_{\text{ideal}} = -\frac{3\text{k}_\text{B}R^2}{2Nl^2} + const.$$

There is no internal energy change associated with changing R in this system and thus free energy reduces to

$$F_{\text{ideal}} = 3\text{K}_\text{B}TR^2/2Nl^2 ,$$

which is entirely entropic [31]. The rheology of an ideal chain dough is therefore entropic in nature. The resulting equation for the stress-strain relationship is,

$$\sigma_{\text{ideal}} = \rho k_B T\left((1+e)^2 - \frac{1}{1+e}\right),$$

where ρ is the number of monomers per unit volume [31]. Despite how simplified the ideal chain model is, this equation captures some of the main characteristics of a dough. As seen in Figure 7 this model dough can be stretched out with more ease than it can be compressed, and it resists uniaxial compression asymptotically as the dough gets extremely thin. We have included the red mask to highlight at what extension we expect the dough to break and our model to fail.

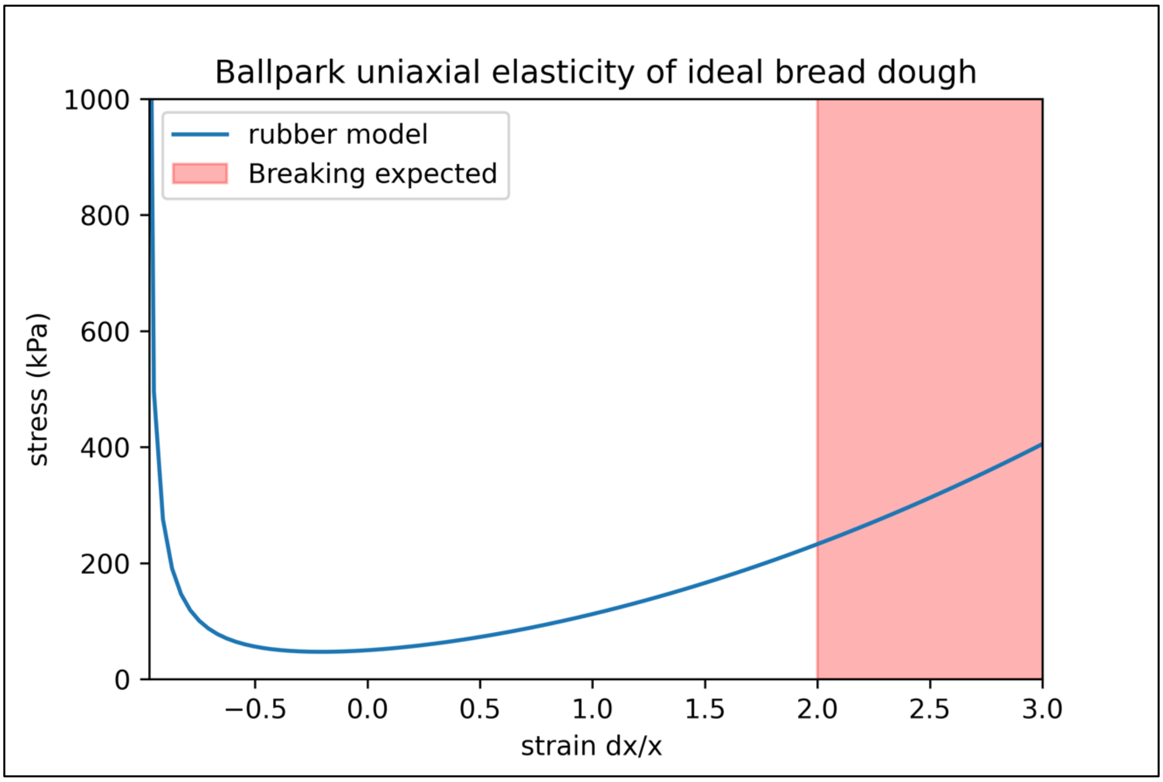

Figure 7: A graph of an approximate ideal chain model elasticity of bread based on gluten content in strong wheat flour. Made using Jupyter notebooks by inserting the stress-strain relationship for the ideal chain model for a polymer as described in the previous page.

However, this model is incomplete since this relationship has no dependence on monomer morphology or the polymer chain length. For this, depletion interactions and excluded volume between monomers must be accounted for. We will introduce these effects in the next subsection.

Furthermore, we have not accounted for the fact that dough breaks when extended several times its own length. However, because we care about the properties of baked bread, the strain range relevant to us lies around –0.5 to 1. Breaking at this stage is unlikely for wheat-bread that does not crumble easily, such as sourdough. Evaluating the crumbliness of bread experimentally would be much easier than doing it theoretically, since the bonds holding gluten proteins together are incredibly strong covalent (disulphide) bonds *(bond energy* $\gg k_b T$) [35]. Breaking of the bread or dough does not imply the breaking of polymer chains, which are short enough to end up in one or another side of the broken dough. First-principles analyses of breaking dough and crumbliness may require a comprehensive understanding of its protein networks and the statistical mechanics related to directional weak hydrogen bonds between water molecules in the bread. Figure 7 shows a shaded area indicating where we expect breaking based on our day-to-day experiences. However, we do not have a theoretical framework to model dough breaking with enough accuracy to provide any results useful for designing GF bread alternatives.

2.2.3 How Polymer Morphology Affects Dough Elasticity

Imagine a polymer of N monomers, uniformly distributed within the volume $\approx R^3$ of the rubber/dough. The average number of 'second' monomers in the excluded volume v of a given monomer is the product of their number density in the chain, N/R^3, and the excluded volume. The energetic cost of being excluded from v is vNk_BT/R^3 per monomer, which over the entire chain gives a free energy of,

$$F_{excl} \approx k_B T \, \frac{vN^2}{R^3}.$$

The total free energy is therefore the sum of this energetic interaction and the entropic contribution [3] discussed previously for the ideal chain. This approximation is generally referred to as the Flory approximation or Flory model and yields a stress-strain relationship similar to a large polynomial, which is included in Appendix 9.1 for completeness (in case you like line-long equations). Despite its apparent complexity, the resulting stress-strain relationship is extremely useful since it captures a key bit of physics relevant to substituting gluten: the elasticity depends on polymer chain length and monomer morphology! It takes the form:

$$\sigma = \sigma_{ideal}\left(1 - \frac{\sqrt{N}v}{l^3}\, g(e)\right)$$

where σ_{ideal} is the stress-strain relationship shown in the previous subsection and $g(e)$ is some function of strain. In the limit of infinitely long monomers (where $l \gg \sqrt{N}v$), the ideal chain model is recovered from our Flory model as seen in Figure 8.

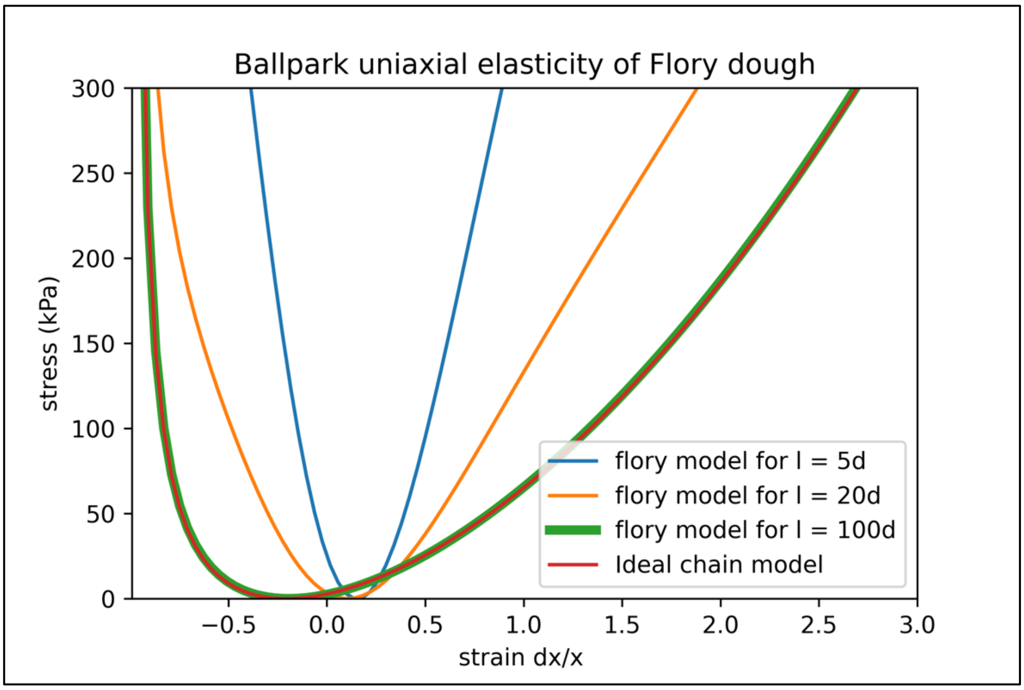

Figure 8: Recovering ideal chain behaviour for a Flory model of a cylindrical polymer of increasing monomer length while retaining the same molecular weight. l represents monomer length, and d represents monomer diameter. The ideal chain model is the case when $l >> d$. Note that the stress-strain profile for a chain with monomers of length 100 times their diameter is completely covered by the ideal chain elasticity curve. This plot shows the more involved Flory model converges to the ideal chain for chains with long monomers Figure made using Python3 by authors.

Additionally, the relationship depends on the ratio between the monomer excluded volume and the volume spanned by a cube of the monomer length, as well as the number of monomers per polymer chain. This gives us a parameter to tune if we want to produce the same rubber/dough elasticity with different polymers. At this point, we can compare the elasticity produced by different polymers based on their morphology.

A caveat to this is that Flory theory overestimates the repulsion energy from the excluded volume because it assumes that there is no correlation between monomers along the chain. This is not the case for a real chain because successive monomers are linked. This type of mean-field estimate for the depletion energy may be crude but provides useful intuition about what factors influence bread elasticity. For example, this lets us determine that a polymer with the same ratio $\sqrt{N}v/l^3$ as gluten should provide the same bread elasticity if intermolecular forces are negligible and that the polymer concentrations in the dough are the same. These two assumptions can be made since doughs are hydrated enough for these polymers to move around, allowing water molecules to screen electrically charged groups in the monomers. More complicated models might be impractical to use unless we understand what the monomers look like at the molecular level. It is also important to note that when the bread is stretched past its elastic limit and it tears, it is not the covalent bonds breaking within the polymers, but rather the long chains being pulled apart and unraveled. To break the covalent bonds, it would take a much greater force than it takes to pull the chains apart, which is why the chains are unraveled rather than broken.

Based on this, we will refer to the ratio $\sqrt{N}v/l^3$ as the key ratio (κ) since it is the key quantity relating a polymer's shape and size to the dough rheology. The key ratio essentially tells us whether the ideal chain entropy or the excluded volume free energy dominates the polymer dough's behaviour. $\kappa = 0$ corresponds to an ideal chain with the viscoelasticity discussed in the previous subsection, which is determined only by the entropy of the system, and $\kappa \gg 1$ refers to a chain with very little freedom of movement because the monomers occupy so much space that their movement is restricted as seen in Figure 9.

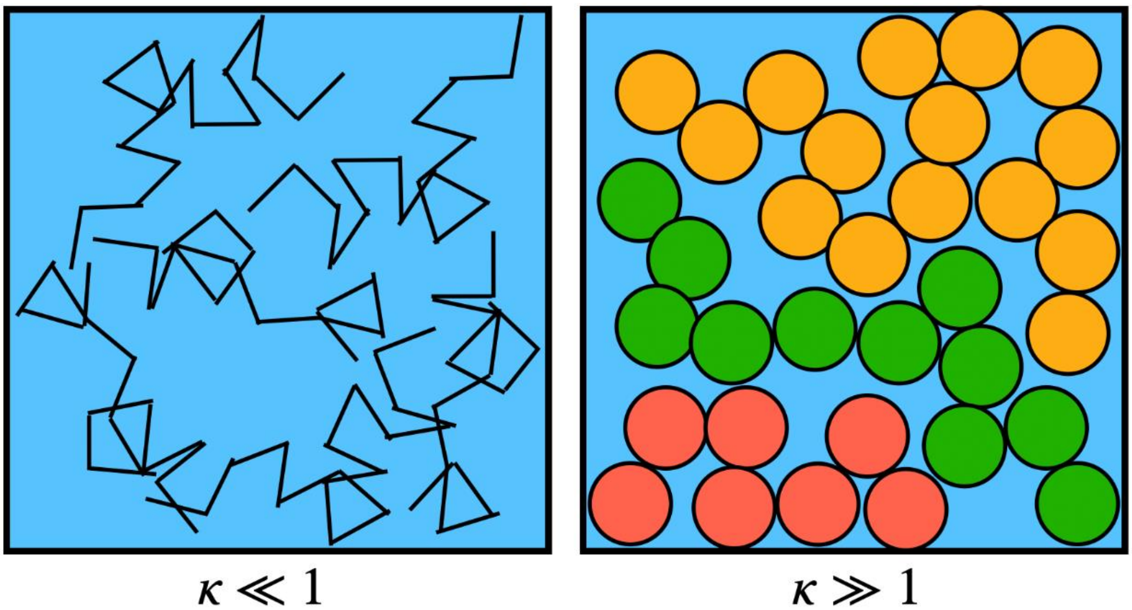

Figure 9: Diagrams of the microscopic arrangements of polymer doughs with (left) low Key Ratio and (right) high Key Ratio. Made by the authors of this report using Keynote™.

Note that in the high κ ratio diagram on the right of Figure 9 that since the circular monomers occupy most of the space inside the dough and they can't overlap, the green, red and yellow polymer chains will have much less room for movement if stretched with a 'microscopic tweezer' than the black ideal chains on the left. Because of this, the stress required to stretch the high κ dough will be much higher than the stress required to stretch the low κ dough by the same amount. A polymer chain's length also plays an important role in the key ratio. As the number of monomers in a chain increases, the number of possible arrangements of the entire chain also increases, but the space occupied by the monomers increases as well. These effects compete with one another since they have an opposite impact on the dough's viscoelasticity, but the excluded volume dominates as the chain gets longer. It also allows us to say that, even if two monomers have slightly different shapes, the dough will have the same rheology if the number of monomers in a polymer chain is very large. This might be instrumental in our search to engineer a GF alternative to wheat flour in the case that one of the main polymers in wheat flour is poorly characterised.

Now that we have an idea of what a polymer's morphology on the microscopic level does to the resulting dough viscoelasticity, we will consider the rheology of something closer to a real system. Wheat flour is a composite system of many different polymers. Hence, we need to determine how mixing different polymers will affect dough viscoelasticity. This will be explored in the following subsection.

2.2.4 Effect of Mixing Different Polymers in the Same Dough

For practical matters, comparing gluten substitutes using the ratio above requires characterising the relevant monomers and the chain length including their dispersity, and then computing the excluded volume for their monomer geometry. Doing this with sufficient accuracy allows us to compare the properties of dough/bread made with any flour if we understand its components. We will proceed to use the composition of wheat flour to determine what a substitute flour must have.

Flour contains a range of polymers. The free energy of the flour contains contributions from all ingredients but also from the entropy of mixing [31]:

$$F_{total} = \sum_{polymers\ i} F_i + TS_{mixing}$$

However, since the entropy of mixing is only dependent on the volume of the sample and the volume fractions of ingredients [32], it will be unchanged by dough length for an incompressible dough. Thus, it does not contribute to the derivative of free energy with respect to length and the stress of the dough is the sum of the contributions from each flour component. This means that the texture of our final dough will be related to the sum of the viscoelastic behaviors of all its ingredients.

Our next task is therefore to find substances in common grains with similar geometries to glutenin and gliadin. Mixing these with the right amount of starch should produce a flour resulting in reasonably similar dough/bread texture as produced with wheat flour! This leaves us much closer to creating a GF flour recipe that mimics wheat for breadmaking.

2.3 Model Conclusions

Over this section, we have learnt that the morphology of polymers contained in a dough plays an instrumental role in dough and bread viscoelasticity. More specifically, we have discovered that this effect can be described by a characteristic ratio κ related to the monomer shape and the number of monomers contained in a polymer chain. We will be mostly using κ for the rest of this report as a metric for comparing the effects of different polymers on bread texture. In the following sections, we will compare the key ratio, κ, of the constituents of gluten with the value for potential substitutes suitable for people with CD. Hence, we can choose the substitutes that produce the closest bread texture to wheat.

To do this, we will need to delve deeper into the structures of both polymers that make up gluten; glutenin and gliadin. We will then do the same for potential substitute proteins and select which is ideal by combining κ, and certain factors such as overall charge content, digestibility, nutritional value and availability of sources for each protein.

3. Finding Substitute Proteins to Gluten

3.1 What is in wheat flour and how do we replace it?

3.1.1 What is in wheat flour?

Now that we understand the effect of polymer shape and size in a putty-like solution on rheological behavior, we need to know the shapes of the polymers in wheat flour to design an alternative which produces the same texture. Wheat flour is composed of starch (70-75%), proteins (10-12%), water (14%), non-starch polysaccharides (2-3%) and lipids (2%) [30]. Polysaccharides are chain polymers of glucose, of which starch is the largest. In addition, proteins are polymers where the monomer type is an arrangement of complex molecules called amino acids. Out of all the proteins in wheat flour, glutenin and gliadin make up 30% and 50% respectively [36]. The other 20% is made of globulins and other commonplace proteins. Now we will use the key ratio derived in the previous section to find viable substitutes with similar geometries to gluten's components.

3.1.2 Replacing Glutenin

Glutenin is part of a family of proteins used by grains for energy storage, called glutelins. To avoid confusion, we will refer to the glutelin family as the GLUFam. GLUFam proteins all form large polymeric structures through covalent bonds between monomers and are rich in hydrophobic functional groups [37].

Despite its instrumental role in breadmaking and other food-related contexts, glutenin is an incredibly poorly characterised molecule. Estimates for its monomer molecular weight and for the polymer's mass vary from 30-90ku to 2-3Mu, respectively[3] [38]. It is clear from this

[3] u being the atomic mass unit along with k and M being the unit prefixes.

that the number of monomers per chain varies by a large margin. Taking a monomer with molecular weight of $\sim$ 50ku and a polymer of mass $\sim$ 2.5Mu gives us a polymer length of 50 monomers. As for the monomer shape, accurate quantitative measurements of glutenin are rare and usually difficult to interpret from light scattering and other experimental data since glutenin is usually found mixed with other compounds [39].

Figure 10 shows an atomic force microscopy image of glutenin polymer formation made by [40] and a diagram of a chain polymer with $\kappa \ll 1$, approximating the ideal chain model. The roughly uniform monomer length and extremely thin monomers means that there’s no further need to characterise its structure for our purposes. Our model suggests that glutenin behaves like an ideal chain polymer. Any other nearly-ideal-chain biopolymer with similar functional groups will produce the same outcome.

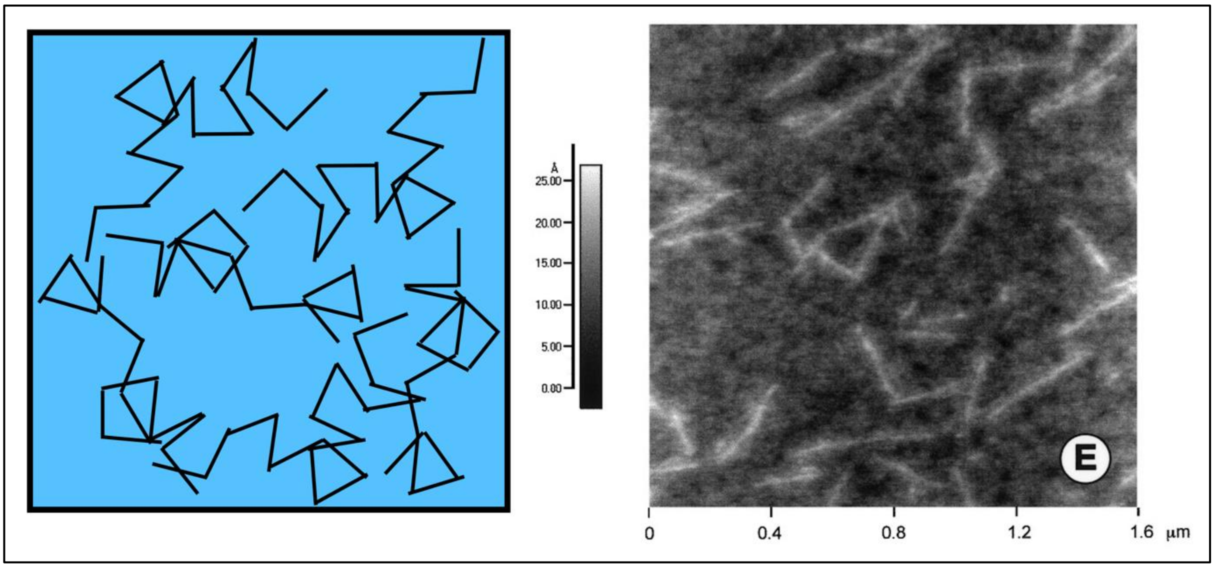

Figure 10: Comparison between an ideal chain polymer with the Key Ratio tending to zero (left) and an atomic force microscopy image of glutenin polymers (right). Figure adapted from [40].

Because of their ubiquity in grains, other GLUFam proteins are likely to be good candidates for replacing glutenin in a GF baking flour if they also resemble ideal chain polymers. Chickpea glutelins and oryzenin (from rice) are some of the more common GLUFam proteins not associated with CD or gluten intolerance [37].

Oryzenin comprises 60-80% of the protein content in rice grains and has a variety of food related applications including meat substitute production [41]. However, commercial rice proteins used as supplements are known to have a bitter taste that limit their usability if not masked by other flavourings. However, whether this is due to oryzenin or some other protein is currently unknown. Oryzenin can also form bonds with starch just like glutenin does [42, 43], suggesting that it will form a cohesive dough in a similar way to glutenin. Under certain conditions, oryzenin chain-like networks were shown to have straight fibrils that are a few nm thick and 200-500nm in length [40]. This aspect ratio corresponds to a low κ polymer. Even if oryzenin chains had 100 monomers per average polymer strand, this would result in $\kappa \sim O(10^{-3})$. It is therefore likely to behave like a near-ideal chain polymer just like glutenin, meaning oryzenin can have the same impact on dough texture as glutenin.

Given that chickpeas are also a GLUFam protein, they are also likely to be appropriate substitutes for glutenin. However, we could not find experimental measurements of the shape of chickpea glutelin; instead we found studies of the functional groups in the protein. This means that we cannot use our model to predict the rheology of a dough where glutenin is replaced for chickpea glutelin. Furthermore, glutelin comprises around 18% of the total protein content in chickpeas [44], meaning that the yield from extracting this protein from chickpeas would be low and therefore make a chickpea GF bread expensive. This leads us to choose rice oryzenin as a glutenin substitute for GF flour making.

3.1.3 Replacing Gliadin

Gliadin, one of the main proteins causing an allergic response in coeliac patients, is part of a family of proteins called prolamins. These can all be obtained from grains and share a low solubility in pure water and high solubility in aqueous alcohol, suggesting they have similar functional groups and thus interact with hydrogen bonds in similar ways [45].

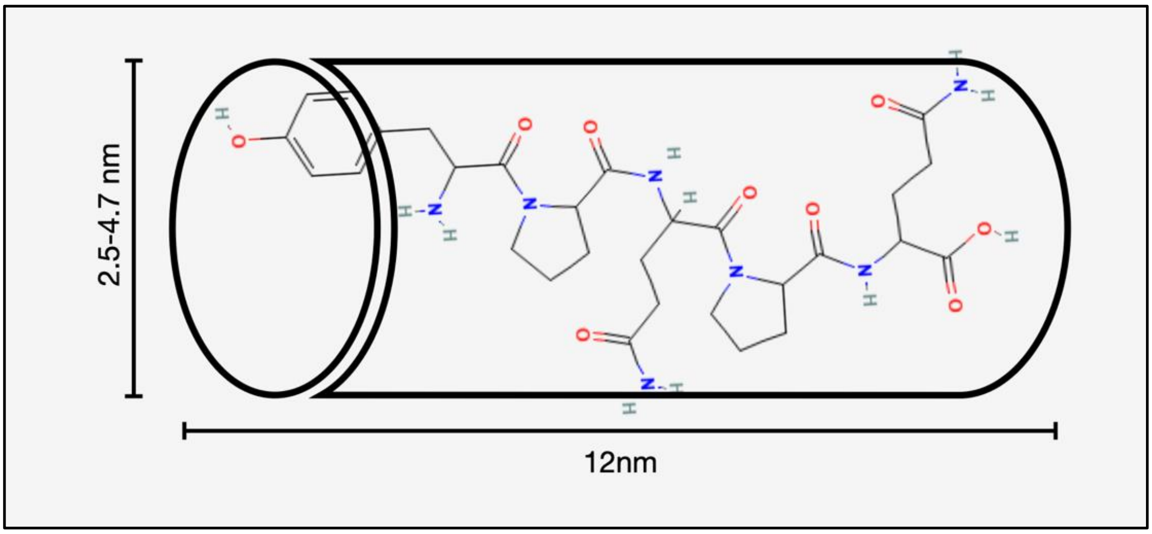

Figure 11: Diagram of gliadin molecular structure and cylindrical monomer shape approximation. Adapted from [46]

A simplified model for gliadin, which we will use to look for alternative proteins, is to treat it as a chain of cylindrical monomers corresponding to the approximate size of a gliadin monomer as seen in Figure 11. This is a crude estimate, but it helps us predict how the viscoelasticity of a dough with gliadin will compare to a dough made with a substitute protein. Based on the molecular mass of the monomer and the polymer chains measured by [47] and [48], we estimate that there are about 90 monomers in the average gliadin chain. This yields a key ratio of $\kappa \simeq 0.67$. Now we can begin our quest for a polymer with a comparable key ratio to replace gliadin and thus make the ideal GF bread.

The easiest place to look for substitute proteins is gliadin’s cousins: other prolamins. They are readily available, as mentioned previously, and by definition have similar characteristics to gliadin [45]. Avenin, a protein obtained from oats, may be a suitable candidate. Research in low-gliadin-content bread serves as a proof of concept for this idea [49]. However, there is a possibility that some non-gluten-prolamins like those in rice, oats and maize may cause a gluten-like immune response in a minority of coeliac patients due to their similarity at the molecular level [50]. Since our project aims to appeal to the broadest section of the market and these responses have only been found in a minority of coeliac people in tests, we will continue to consider grain-related prolamins as substitutes for gliadin.

Hordein (from barley), secalin (from rye), zein (from maize) and kafirin (from sorghum) may still be suitable replacement proteins for gliadin. Kafirin's low nutritional value and poor digestibility limits the amount that can be used for breadmaking [51], explaining why current GF recipes using sorghum employ it in small amounts; this results in bread that does not fully mimic wheat bread. Barley hordein and rye secalin can cause an allergic response in people with CD. We will thus consider only the prolamins in rice and maize.

Let's look at maize prolamins: zeins. Zein is a biopolymer found in the centre of maize kernels and has been used historically as animal feed because of its low price. It comprises 35-65% of the protein content in maize and has a variety of uses in food and medicine, including films and membranes for pill making [52].

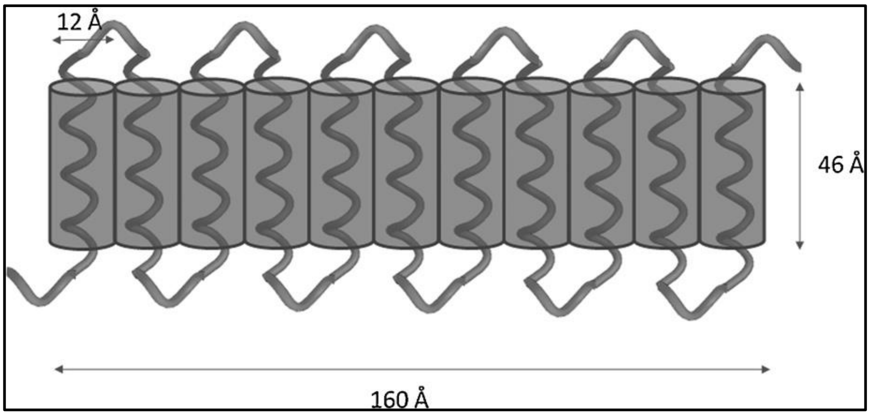

Figure 12: Diagram of the molecular structure of the zein monomer contained in maize. Obtained from [53].

Regarding its morphology, the zein monomer has a structure comprised of helical sections that self-assemble into a cuboid-like structure as shown in Figure 12 to produce the same κ as the gliadin. This would mean that the mean chain length should be around 31 monomers. However, zein naturally exists in its monomeric form or in coils [54]. A relevant challenge in using zein chains in flours for industrial GF breadmaking will be to design a cheap and scalable method for making sure that its polymer chains will have the right number of monomers.

Another option may be preventing the zein protein from developing the plate structure in Figure 12. This would result in a key ratio $of\ \kappa \simeq 0.69$, which is incredibly close to the value for gliadin. The textures of structures made with either of these proteins should therefore be nearly indistinguishable according to our model! Thanks to being part of the same family of proteins, zein and gliadin even have extremely similar charges [46], which would mean they should have similar interactions with water and other molecules. This suggests that the two proteins have similar behavior, even in relation to characteristics which were not accounted for in our model for bread viscoelasticity. However, further research is needed to figure out how to prevent the formation of this plate structure cheaply and in a way that ensures all byproducts are suitable for human consumption.

Rice prolamins are another reasonable candidate but are largely indigestible and have poor nutritional value [55]. Furthermore, the shape and size of rice prolamins have not been studied at a scale useful for obtaining the physical properties related to the key ratio, κ, even if some subunits of these proteins have been characterised. We can't use our model to predict rice prolamins' effect on dough elasticity. Because of this, the best readily available grain protein to replace gliadin within the scope of our investigation is maize zein.

3.1.4 Adding Starch to the Mix

Starch is the longest type of polysaccharide, and therefore the most complex [56]. The starch you are familiar with is in corn (maize) flour or potatoes, and it helps in cooking to create stickier and thicker consistency in foods, making it a great ingredient in GF bread. In the ideal GF bread, starch is easy to add to the mix, and very crucial. It is the main component in wheat flour [30], and it also plays a key role in determining bread elasticity. Starch also has a high nutritional value [56, 63] and does not contain gluten. Therefore, we must choose a source to extract starch from with a high starch yield and that is and relatively cheap.

3.2 A recipe for the Coeliac's Dream

We have found two proteins that mimic the effect of glutenin and gliadin on dough rheology: oryzenin (from rice) and zein (from maize). We can therefore swap glutenin and gliadin proteins for these components in our flour recipe while maintaining the same proportions of other components as in wheat flour. Our recipe for a flour that replicates the texture of bread made with strong wheat flour is to mix the following:

INGREDIENT	**Starch**	**Water**	**Zein (maize)**	**Oryzenin (Rice)**	**Globulins (Grains)**	**Fat (oil)**
AMOUNT (%VOL)	73	14	5	3	2	3

Table 1: Our molecular recipe for an ideal gluten free flour that mimics the viscoelastic behaviour of strong wheat flour. The values were found using the Key Ratio in our model, applying it to gluten's proteins then comparing those values to non-gluten proteins. The most similar values to gluten's were chosen.

Because our model for bread viscoelasticity ignored the effect of hydrogen bonding, inter-polymer interactions and assumed that polymers exist only in chain instead of crosslink form, there is limited confidence that our recipe will produce the same texture as bread without confirming this experimentally, refining the model and better characterising glutenin and gliadin as well as other similar proteins.

Our recipe for a GF flour, which we will call *the coeliac's dream*, has one caveat: where do you get the ingredients from? If we want to sell *the coeliac's dream* to the masses, we need to source all these components cheaply enough to be manufactured. Bringing together starch [57], zein (obtained from MilliporeSigma) [58], rice protein [59] and sunflower oil [60] (from retailers) in the right ratios would result in a flour costing around 9.21 GBP per kg, compared to 1.60 GBP for strong bread flour at Sainsburys' ltd [61]. The difference between the two prices becomes astronomical if you replace rice protein with pure oryzenin, which retails at 207 GBP per 5mg [62] and would make the flour completely unviable.

This is a rough estimate and is based on retail rather than wholesale prices, but it highlights our issue; *the coeliac’s dream* must be able to make bread cheaper than other GF bread alternatives. Reducing production costs means finding ways to isolate the compounds in our recipe that are energy and labour efficient, environmentally sustainable, and scalable to an industrial scale. We will therefore review some of the most common methods for extracting the compounds needed to produce *the coeliac’s dream* over the next section.

4. How do we make our GF flour?

Now we have a recipe for *the coeliac’s dream* we need to evaluate it. Even though it may produce texture like that of wheat bread we still need to consider the cost, effort, safety, sustainability, and effectiveness of extracting the proteins. Most importantly the process cannot leave byproducts that could be harmful to humans. If these requirements are not met to a high enough standard, the flour recipe must be tuned to compensate for these shortcomings before it can be produced for use in any commercial settings. For example, if the cost of extracting a protein is too high, then a lower purity version or a similar, more accessible one would be acquired instead. The following sections will briefly discuss the methods of extracting the ingredients you need for the recipe while evaluating their advantages and how to counteract their downsides.

4.1 Extracting the necessary components

This section will go through an overview of existing industrial processes for extracting starch, corn zein and rice oryzenin for use in foodstuff. This overview will elucidate some of the issues associated with producing the ingredients *the coeliac’s dream* flour and why some processes might be inefficient, expensive, or not suitable for foodstuff.

4.1.1 Starch

Starch can be obtained from a wide variety of sources including cereals, roots, tubers, and legumes, among others [63]. Potato and rice are two common sources of starch, with the cheapest being potato.

Potato starch can be obtained by a process of crushing or grating the potatoes and stirring the resulting potato ‘paste’ in hot water for several hours. The resulting product is then centrifuged. The starch is heavier than other components of the potatoes, so it is separated, and the resulting wet starch is allowed to dry into a powder [64, 65]. This is a common industrial process which produces high purity starch without the protein content of the potatoes. This process has the advantage of excluding any proteins and therefore would allow future GF flour manufacturers to fine-tune their GF bread elasticity by varying the amount of starch without inadvertently also varying the number of different proteins in the flour. However, keeping large volumes of water hot for extended periods of time requires expensive heating, and centrifuging large amounts of material constantly requires lots of electricity and specialised equipment. Thankfully, this process is common, and potato starch is sold wholesale at around 1.69 GBP per kg [57].

4.1.2 Zein

Zein is a by-product of maize purified by the food industry from starch production. Its protein is rich in nutrients, so it can be used directly as a raw protein material at moderate purity without further processing. There are various methods of extracting zein from maize but we will focus on extracting zein using organic solvents.

The common organic solvents used to extract zein from maize are ethanol and isopropanol. When using isopropanol as a solvent to extract zein, the yield is higher compared to ethanol. Unfortunately, the final product has an offensive smell and is therefore not suitable for use in food processing [66]. Ethanol based extraction is carried out by crushing the maize protein powder, adding 80% ethanol, and extracting it at a temperature of around 60 °C for 24 hours. The result is centrifuged, and the liquid layer left on top (ethanol and zein) is separated. The ethanol-zein mixture is then diluted with cold water and centrifuged again. Finally, the zein precipitate is washed and dried, resulting in a powder. This method is efficient and low cost if done at an industrial scale [67].

Zein extracted by alkaline extraction and acid precipitation (also referred to as acid/alkaline extraction) and salting methods contain large amounts of inorganic ions absorbed onto the protein. If the product is not repeatedly rinsed, the ions remain on the product, which reduces the water resistance of the product [66]. This may result in water waste and extra costs related to maintaining the water at pH 7.

Some studies show that among the above processes, ethanol extraction has the highest extraction rate and the lowest protein deformation rate [67]. Therefore, ethanol should be the most suitable zein extraction process for use in GF flour making.

4.1.3 Oryzenin

Oryzenin, more commonly known as thiamin or vitamin B1, is widely used as a food additive with a known process to extract it from rice. The market for it is also increasing as it is commonly used in many food products including plant-based substitutes. The largest problem with oryzenin is its price, going at 207 GBP per 5mg [62]. This would massively increase the cost of our designed flour loaf so other solutions must be found [58-61]. Luckily this is a very concentrated form so a less pure version can be acquired for much cheaper. Less pure versions are marketed as supplements readily available for around 9 GBP for 50 grams [68], making a big difference to the price of our loaf.

There are a few oryzenin extraction methods, but we will focus on Alkaline Extraction and Acid Precipitation as these are the most traditional and common technical routes.

Firstly, the rice is washed and then soaked in an alkali for 2-3 hours. After grinding the solution and the rice into a pulp, it is centrifuged for 15 minutes. The upper layer is collected and then an acid is added, stirring simultaneously. By centrifuging again, collecting the precipitate, adding more alkali solution, and repeating this process several times, then drying it, oryzenin is obtained [69].

It is worth noting that although this method is widely used, the high concentration of alkali solution may cause chemical changes to the oryzenin, affecting the yield of and even producing toxic substances [70]. The need for a better method of high purity oryzenin extraction is therefore evident, but as said before oryzenin can be found in less pure forms in the health industry as a supplement. This level of purity may be sufficient for breadmaking, but further testing is needed.

4.1.4 Other plant-based proteins

The change from animal to plant-based proteins is the focus of many food industries;
Some of the proteins added to *the coeliac’s dream* are globulins since they constitute most of the non-gluten protein in wheat flour and have high nutritional value [70]. These are found in oats at a higher concentration than in other grains, such as barley or wheat [71].
Globulins are the focus of current research into methods of extracting plant proteins [70]. There are a variety of globulins for various purposes used in industry.

A common method of extracting globulins from rice is as follows: Rice is first ground into rice flour, then is repeatedly degreased 3-5 times to produce degreased rice flour. A solution is then made from this flour. Salt is then added to the rice solution and the protein is precipitated using an acid solution. Finally, the precipitate is added to a vacuum freeze-dryer to produce a rice globulin mixture. This technique is appropriate for industrial production and may be used to extract rice globulin complexes easily, quickly, and efficiently [72].

4.1.5 Fats and Additives

The coeliac’s dream flour requires some source of high purity fat. Common GF bread recipes use butter in their dough, but vegetable oil and olive oil can also be used and are vegan [58]. The source of fat in our flour should be a low-flavour oil that does not spoil easily, is low-cost and is environmentally friendly. Palm oils and olive oil are therefore not a suitable fat source for *the coeliac’s dream* [73, 74]. Rapeseed or sunflower oil might be ideal to use in our recipe.

In addition to oil, there are other special ingredients that need to be added to the flour to give the GF bread a texture closer to that of traditional bread. Hydroxypropyl methylcellulose (HPMC) is used in some recipes and could be used in our recipe in case the dough produced is not sufficiently soft. HPMC is a hydrophilic and biodegradable polymer which has a wide range of food-related applications. It is also soluble in polar organic solvents, making it possible to use both aqueous and nonaqueous solvents [75].

HPMC can mimic the viscoelastic properties of bran, reducing spoilage and improving water binding and the overall structure of the bread. In addition, some studies have shown that soluble fibre or carboxymethylcellulose (CMC) used together with HPMC can enhance the effect of HPMC, encapsulating starch granules and flour particles and making the structure more stable [75].

5. Discussion

We have used our model of polymer rheology to design a flour that suits the main need highlighted in our survey (see Appendix 9.1): GF bread with comparable texture to wheat bread. However, due to time constraints, no actual bread has been produced from the recipe for tasting and testing. As a result, the content of the recipe has also not been quantified and compared in this paper. The ingredients listed in the recipe are essentially derived from the model results and the nutritional composition of the wheat, which has not been analysed in depth in this paper. For example, the source of starch can be potato or rice flour, and the difference between the two is not explained in detail. On the other hand, it is more common for bread to be made directly from a mixture of flours, rather than extracting the main nutrient powder for mixing. At this point the distinction between potato and rice flour, whose main role is to provide starch, becomes more obvious and hence requires an analysis of their differences. Furthermore, target price for producing our GF flour recipe and the possible viability of selling it has only been discussed superficially. This section will deepen our overview of our recipe's viability and how it compares to existing GF bread recipes.

5.1 The Recipe's Impact

5.1.1 Economic Viability

The second biggest complaint raised in our survey (figure 3) is the price of GF bread, which some responders quoted as being up to £16 for a loaf half the size of wheat bread[4]. GF customers have the choice between buying GF bread, making their own or not having GF bread at all. Our survey suggests that a deciding factor for this decision is price. GF bread must be a similar price to wheat-bread or replicate wheat-bread incredibly well to make up for an increased cost.

As explored in the previous section, producing *the coeliac's dream* is a much more involved process than milling wheat grains into a powder and therefore production costs will always be higher than those of wheat flour. However, making GF flour prices as close to their wheat counterparts is instrumental to effectively reaching the budget-conscious market revealed by our survey. We will evaluate the economic viability of producing *the coeliac's dream* for sale at a benchmark price 3 GBP per kilo of flour, as opposed to the wholesale price of 1.39 per kilo of strong wheat flour from British wholesaler Brakes [76].

Given that the processes for isolating potato starch, maize zein and rice oryzenin require large specialist equipment[5], local bakeries and private individuals wanting to make *the coeliac's dream* would need to buy these ingredients from chemical retailers or wholesalers[6] gives a price of 9.21 GBP per kg, making any reasonably priced bread from it at this scale is unlikely. Using 300g of flour per loaf means each loaf would cost 2.76 GBP just in flour, which our survey suggests is not attractive to consumers. Thus, only large-scale industrial manufacturing of *the coeliac's dream* is plausibly profitable.

[4] See Appendix 9.1 for more information about people's responses in the survey.
[5] For more information see Section 4 of this paper
[6] See section 3.2 for more information.

Economies of scale, proportional saving of costs gained by increasing the level of production of a product [77], might be the only hope to commercialise *the coeliac's dream* GF flour. To be competitive in the market and attractive to businesses, *the coeliac's dream* should be able to be sold at our target price while resulting in similar profit margins to wheat-flour.

Flour mills are generally low to medium profit-margin businesses, with Reuters[7] reporting a gross profit margin of 14.76% for flour producer TC Flour Mill PCL as of February 2023 [78]. We will use this metric instead of the net profit margin since we want to account only for production costs and not administrative overheads. Taking this into account and setting a target wholesale price of 3 GBP per kilo for *the coeliac's dream* means that production costs should be GBP 2.61 per kg. Given that most of the cost associated with producing *the coeliac's dream* relates to isolating zein and oryzenin to reasonable purity[8], more research into industrial methods of extracting these is required.

5.1.2 Sustainability

To create good, commercial substitutes for GF bread, the sustainability of using any alternative ingredients must be considered, as well as packaging and preparation procedures. Although there is a lot more research that must be conducted in this field, there are previous studies which have already explored the effects of using the GF substitutes we discuss in this paper as a commercial alternative for GF products.

Sliced GF bread is not only currently more expensive, but also has a shorter shelf-life compared to wheat bread [79]. In order to be a good substitute, GF bread should be able to last as long as wheat bread under the same conditions, if not longer. A previous study compares[9] different types of packaging methods when used for GF bread [80]. It compares MAP (modified atmosphere packaging) and active packaging. Normally, bread is packaged using the MAP method, which uses a mixture of carbon dioxide and nitrogen gas to prevent staling/mould growth. This is favourable because it inhibits bacterial growth very well but it does make for poor sensory properties, such as hard and crumbly texture. Active packaging is a method which controls the conditions within packaging by adding anti-microbial materials or chemicals, thus extending shelf-life while maintaining the food quality of GF bread. The study concludes that a cinnamon oil infused active packaging method could be a good substitute for traditional MAP packaging as it maintains a good shelf-life while retaining an ideal texture and sensory experience of the bread. It is not expensive as it does not require any special machinery, but further research is needed to test how this method would work on an industrial scale, and investigate potential environmental impacts. The shelf-life of bread has big implications environmentally – a short shelf-life would increase the amount of food waste produced as people would be less likely to consume it before its expiration date.

A study into the effects of zein on GF bread showed that zein-based bread appears to have a similar shelf life to wheat-based bread under the same conditions [81]. Hence, a new type of packaging would not be necessary to keep the zein-based bread as fresh as normal bread.

The energy ratio of a crop can also be used as a guide of how sustainable it is. A higher energy ratio means the crop provides more energy through consumption in food compared to

[7] Reuters Thomson Corp, a major source of business analytics.
[8] For more details see sections 3 and 4.
[9] Although longer would be nice this is obviously not a priority.

the energy required to grow it. Maize has a higher energy ratio than wheat, meaning it is more energy efficient. It also has a higher yield than wheat [82]: more of it can be harvested per unit area. However, a recent study by NASA which studied how global climate changes will affect crop yield has found that the production of maize (a type of corn) is expected to drop by 24% within the next decade, whereas the yield of wheat will increase by around 17% [83]. The consequences of this imply that in the future, maize may become more sought-after, rendering it more expensive and making GF bread even more expensive in comparison to wheat than it already is. On the other hand, despite more of the world being covered with wheat than any other crop, more rice and maize is harvested in weight which means the latter two are more efficient crops to use [84].

Another point to consider is how the price of GF substitutes will vary around the world, which mostly depends on the availability of the crops in a specific location. A study in Brazil found that GF alternative breads are 33% more expensive on average, suggesting this would be a big issue both economically and sustainably [85]. For example, most of the world's rice is produced in Asia [86], hence oryzenin would likely be cheaper to obtain in these areas. To be able to use oryzenin in other parts of the world, it would have to be transported which is more expensive and uses more fossil fuels, which we would ideally like to minimise when creating a GF bread substitute. Wheat is a lot more spread out across the globe which tends to keep the price of transporting low when making wheat bread commercially [87].

The processes for extracting potato starch, maize zein, and rice oryzenin covered in Section 4 require large amounts of heated water, centrifugation, and use of organic solvents. This is energy inefficient, costly and could potentially result in water contamination if not conducted properly. It is important that these extraction methods be perfected to reduce the amount of water used and to avoid any potential adverse environmental effects. This includes the location of growing the crops and how the crops are grown (if pesticides or fertilisers are used). This can also affect the health of people if not washed properly after harvest, but currently there are standards for controlling chemicals used in crop growth meaning it will not have any significant effect unlike other aspects in the next section.

5.1.3 Customer Health

From our research, we deduced that hordein, secalin, zein and kafirin are all proteins which mimic the texture of gliadin in normal bread (extracted from barley rye, maize, and sorghum respectively). However, there are health properties of their usage that must be considered to qualify these as appropriate substitutes for gluten. Sorghum requires a lot of it to be added to bread to achieve the desired texture. However, unless it is added in small portions, sorghum can cause indigestion in humans which renders it a poor gluten alternative. Hordein can cause an allergic response in people who have CD. This can be caused by certain non-gluten proteins such as alpha-amylase inhibitors, which are found in barley, amongst other crops.

Since 2021, folic acid (vitamin B9) has been required by law to be added to white flour in the UK, which is used to make white bread [88]. This is part of a process known known as flour fortification and is a way of adding additional vitamins and minerals to the bread. This is a great way of ensuring people get a larger health benefit from bread, a food which makes up a large part of many people's diets. For example, fortified flour has been shown to both reduce risk of spine abnormalities if consumed by pregnant women, and also aids in the formation of healthy red blood cells [89]. However, GF bread is exempt from this law [89], which may mean that people on a GF diet inadvertently miss out on important vitamins and minerals. It is therefore important to consider whether a GF flour substitute could be fortified in a similar way, and if the body would react to it differently. Combinations would need to be tested to ensure the added vitamins do not interfere with the rheology of the bread. A previous study has shown that zein improves folic acid uptake by preventing the degradation of folic acid, in comparison to folic acid by itself [90]. This implies that the fortification of flour containing zein may work, but further research is needed to investigate how the compounds within folic acid and non-gluten proteins may interact, and how that will influence digestion in humans.

Although zein shows positive results as a gluten alternative, the extraction process holds potential health issues. As previously mentioned zein comes from maize kernels, however the kernels contain traces of gluten in the form of gliadin. Therefore, the two proteins must be completely separated before being used in a GF bread to ensure no contamination which would risk the health of people with CD. This highly precise separation would require more complicated procedures as mentioned previously.

A previous study also showed that current GF substitutes tend to be too sweet to be healthy, containing overall more calories, sugar, and carbohydrates than regular bread [91]. Upon nutritional assessment, most GF alternatives were classified as confectionary or baked goods, further highlighting their high sugar content. Unfortunately, there is an assumption among many consumers that GF, or other food alternatives, are healthier for you than the original food. This is known as the 'health halo' and is promoted by many GF manufacturers to encourage business and make their products seem healthier than they are.

5.2 The Final Product

5.2.1 Comparison with existing recipes

There are many different recipes for GF bread in the available research. Of these, rice, maize, and buckwheat are the three most common base flours. The ingredients in *the coeliac's dream* have been used to varying degrees in other studies, supporting our choice of ingredients. Table 2 shows a review of several recipes from the sources mentioned, of which all have common ingredients with our proposed recipe.

Recipe	**Ingredients**
Perez-Quirce et al. (2014)	Rice flour, HPMC, barley β-glucan
Sciarini et al. (2010)	Rice flour, corn (maize) flour, micronised and defatted soy
Sivaramakrishnan et al. (2004)	Rice flour, HPMC
Torbica et al. (2010)	Rice flour, unhusked buckwheat flour husked buckwheat flour, amaranth flour, soybean flour
Sabanis et al. (2009)	Maize starch, rice flour, HPMC, wheat, maize, oat and barley

Table 2: Ingredients from a selection of gluten-free bread recipes. These were all compiled in [27]. Condensed from [27].

Some other recipes add ingredients like egg white or milk for more protein or nutrients. This may result in bread with better nutritional value and taste. However, studies have shown that additives such as egg whites can reduce the effectiveness of HPMC and reduce the stability of the dough [27,75], resulting in lower customer acceptance. Furthermore, we made the choice not to consider animal-based additives since we want our recipe to appeal to a wider audience. Therefore, the question of how to enhance the nutritional diversity and flavour of our recipe without compromising bread texture remains open. Future investigation could focus on the flours' nutritional value while retaining the same texture and taste as wheat bread. This would be instrumental in achieving *the coeliac's dream,* giving the recipe a unique texture and nutritionally optimised selling point.

Since there already exists a wide variety of wheat and other flours for use in breadmaking, useful GF flours must also be adapted for different baking purposes. *The coeliac's dream* was designed to replicate strong wheat flour, but can be easily adapted for a variety of uses. The procedure for doing so follows the lines of analysing the composition of the target wheat flour to replicate and adjust the amount of Zein and Oryzenin to match the amount of gluten. Other additives can also be used for replicating altered flours such as self-raising wheat flour. Since the amount of starch in our recipe is the same as that of wheat flour, the same amount of yeast would be needed to replicate a bread recipe that uses wheat flour.

To conclude, there are more factors we are aware of, but have not considered, that would improve other features besides texture. More research and especially lab testing of the ingredients must be done to optimise every aspect of the recipe for use in breadmaking.

6. Conclusion

To cope with the widespread emergence of global GS, there is an urgent need to develop a variety of high-quality GF alternative foods. However, due to the lack of rheology creating proteins in GF flour, it is difficult to form the dough characteristics needed to make GF bread with similar texture to wheat bread.

This paper introduced various alternative proteins to substitute gluten based on a model of polymer elasticity we developed by refining the ideal chain model for polymers. These proteins are zein, oryzenin, starch, fat, and other non-specific globulins. We then designed a GF flour recipe based on our findings and assessed its viability as a commercial product. We also produced an overview of the techniques needed to extract the compounds necessary to make this recipe.

Even if someone decides not to follow our recipe, our model of the effect of polymers on dough rheology may serve as a base to test different recipes and to build more complex models of the viscoelasticity of polymer networks. This field of research has a vast variety of applications related to flexible materials and coatings, polymer films, biophysics, and food science. Since many of the mentioned fields are related to complex soft materials, modifications to our base model may need to be made to tailor it to different contexts.

Throughout our research, we have found a significant gap in research related to the morphology of monomers in biopolymers. Understanding the overall shape of these monomers is key to describing the rheological behaviour of dough-like materials and other physical systems.

In terms of our recipe, it has not been tested experimentally for texture or taste. Next steps in producing GF bread based on this recipe should follow a path similar to: testing our model experimentally for a variety of well characterised polymer solutions; characterising the glutenin monomer experimentally; and then comparing our recipe to doughs made from strong wheat flour. Finally, cheaper techniques to extract zein and oryzenin from maize and rice respectively can be explored to make *the coeliac’s dream* a product to be sold wholesale to bakeries and other producers of bread.

On a broader note, we hope that our work will play a useful role in the development of GF food including bread, pastry, and pasta. This project’s success is dependent on its level of outreach; exposing our results to the right people will help to influence the way GF products are actually made. We remain committed to, the rise of, gluten free bread.

7. Acknowledgements

Thank you most of all to Dr. Jean-Christophe Denis for guiding us all the way through writing this paper and giving us advice throughout the planning stage. Your help in bringing together all our different approaches to this project was as important as gluten is to bread. Thanks to Dr. Daniel Hodgson for redirecting our project from experimental to theoretical research by going through the intricacies of experimenting with dough rheology. You saved us a lot of time that we otherwise may not have had. Thank you also to Dr. Aidan T. Brown and Prof. Alexander Morozov for guiding us through the relevant theoretical literature. Thanks finally to the School of Physics and Astronomy and Prof. Philip Woods, FRSE for the opportunity to work on such a relevant piece of physics, with the potential to impact the daily lives of people worldwide.

8. References

1. Origins of Bread and Bakery. History of Bread Making. http://www.historyofbread.com/bread-history/history-of-bakery/. Date retrieved: 3 January 2023.
2. How many kinds of bread are there? What are the different types of breads? Which type of bread is best?. future of Journalism. https://futureofjournalism.com.au/. Date retrieved: 3 January 2023.
3. Katharina Graf; The Price of Homemade Bread. Gastronomica 1 February 2019; 19 (1): 107–108.
4. Prehistoric bake-off: Scientists discover oldest evidence of bread. BBC News. https://www.bbc.co.uk/news/science-environment-44846874. Date retrieved: 3 January 2023.
5. Pasqualone, A. (2018). Traditional flat breads spread from the Fertile Crescent: Production process and history of baking systems. Journal of Ethnic Foods, 5(1), 10-19.
6. Grains of History. Wessex Archaeology. https://www.bbc.co.uk/news/science-environment-44846874. Date retrieved: 5 January 2023.
7. Belderok, B. (2000). Developments in bread-making processes. Plant Foods for Human Nutrition, 55(1), 1-14.
8. Staple Food Crops of the World. National Geographic. https://education.nationalgeographic.org/resource/wbt-staple-food-crops-world. Date retrieved: 5 January 2023.
9. Types of Wheat: What to Grow and How to Use It . Mother Earth News. https://www.motherearthnews.com/real-food/types-of-wheat-zm0z14fmzmat/. Date retrieved: 7 January 2023.
10. Yeşil, S., & Levent, H. (2022). The influence of fermented buckwheat, quinoa and amaranth flour on gluten-free bread quality. LWT, 160, 113301.
11. bread. Britannica. https://www.britannica.com/topic/bread. Date retrieved: 9 January 2023.
12. Sissons, M. (2008). Role of durum wheat composition on the quality of pasta and bread. Food, 2(2), 75-90.
13. Rheology. Britannica. https://www.britannica.com/topic/bread. Date retrieved: 14 January 2023.
14. What is Gluten?. Paleo Foundation. https://paleofoundation.com/gluten/. Date retrieved: 15 January 2023.
15. Numata, K. How to define and study structural proteins as biopolymer materials. Polym J 52, 1043–1056 (2020).
16. Goesaert, H., Brijs, K., Veraverbeke, W. S., Courtin, C. M., Gebruers, K., & Delcour, J. A. (2005). Wheat flour constituents: how they impact bread quality, and how to impact their functionality. Trends in food science & technology, 16(1-3), 12-30.
17. Kłosok, K., Welc, R., Fornal, E., & Nawrocka, A. (2021). Effects of physical and chemical factors on the structure of gluten, gliadins and glutenins as studied with spectroscopic methods. Molecules, 26(2), 508.

18. Rajpal, G., & Arvan, P. (2013). Disulfide Bond Formation. *Handbook of Biologically Active Peptides*, 1721–1729. https://doi.org/10.1016/b978-0-12-385095-9.00236-0
19. Ludvigsson, J. F., Leffler, D. A., Bai, J. C., Biagi, F., Fasano, A., Green, P. H., ... & Ciacci, C. (2013). The Oslo definitions for coeliac disease and related terms. Gut, 62(1), 43-52.
20. Hoyt AM. Gluten free-dom: my journey to becoming an unintentional expert. Proc (Bayl Univ Med Cent). 2014 Jul;27(3):276-82.
21. van Berge-Henegouwen, G. P., & Mulder, C. J. (1993). Pioneer in the gluten free diet: Willem-Karel Dicke 1905-1962, over 50 years of gluten free diet. Gut, 34(11), 1473.
22. Sapone, A., Bai, J. C., Ciacci, C., Dolinsek, J., Green, P. H., Hadjivassiliou, M., ... & Fasano, A. (2012). Spectrum of gluten-related disorders: consensus on new nomenclature and classification. BMC medicine, 10(1), 1-12.
23. Policies Around the World. Celiac Disease Foundation. https://celiac.org/gluten-free-living/global-associations-and-policies/policies-around-the-world/. Date retrieved: 28 January 2023.
24. Gluten-free Bakery Market Size, Share & Trends Analysis Report By Product (Biscuits & Cookies, Bread, Cakes), By Distribution Channel (Online, Supermarkets & Hypermarkets), By Region, And Segment Forecasts, 2022 - 2030. Grand View Research. https://www.grandviewresearch.com/industry-analysis/gluten-free-bakery-market-report. Date retrieved: 20 January 2023.
25. Gluten-Free Bread Market. Fact.Mr. https://www.factmr.com/report/647/gluten-free-bread-market. Date retrieved: 30 January 2023.
26. Wieser, H., Segura, V., Ruiz-Carnicer, Á., Sousa, C., & Comino, I. (2021). Food Safety and cross-contamination of gluten-free products: A narrative review. *Nutrients*, *13*(7), 2244. https://doi.org/10.3390/nu13072244
27. Monteiro, J. S., Farage, P., Zandonadi, R. P., Botelho, R. B., de Oliveira, L. de, Raposo, A., Shakeel, F., Alshehri, S., Mahdi, W. A., & Araújo, W. M. (2021). A systematic review on gluten-free bread formulations using specific volume as a quality indicator. *Foods*, *10*(3), 614. https://doi.org/10.3390/foods10030614
28. YUSTE, J. O. S. E. P., CAPELLAS, M. A. R. T. A., PLA, R. E. Y. E. S., FUNG, D. A. N. I. E. L. Y. C., & MOR-MUR, M. O. N. T. S. E. R. R. A. T. (2001). High pressure processing for food safety and preservation: A Review. *Journal of Rapid Methods and Automation in Microbiology*, *9*(1), 1–10. https://doi.org/10.1111/j.1745-4581.2001.tb00223.x
29. A Coeliac's dream. Google Forms. https://docs.google.com/forms/d/1qm4umq0_zZihd1waJDOU9_wnsOgYgCTPc3ZuOMloCdI/edit#responses. Date retrieved: 4 February 2023.
30. Shewry, Tatham, A. S., & Shewry, P. R. (Peter R. . (2000). Wheat gluten edited by Peter R. Shewry, Arthur S. Tatham.
31. Richard A.L. Jones. Soft Condensed Matter. (Oxford University Press, 2002).
32. Michael Rubinstein. Polymer Physics. (Oxford University Press, 2003).
33. Wang, C., Dai, S., & Tanner, R. I. (2006). On the compressibility of bread dough. Korea-Australia Rheology Journal, 18(3), 127-131.
34. *File:ideal chain random walk.svg*. Wikimedia Commons. (n.d.). Retrieved February 4, 2023, from

https://commons.wikimedia.org/wiki/File:Ideal_chain_random_walk.svg#/media/File:Ideal_chain_random_walk.svg
35. Rajpal, G., & Arvan, P. (2013). Disulfide Bond Formation. *Handbook of Biologically Active Peptides*, 1721–1729. https://doi.org/10.1016/b978-0-12-385095-9.00236-0
36. Urade, R., Sato, N., & Sugiyama, M. (2018). Gliadins from wheat grain: an overview, from primary structure to nanostructures of aggregates. Biophysical reviews, 10, 435-443.
37. Dhara, A. K., & Nayak, A. K. (2022). Biological macromolecules: Sources, properties, and functions. *Biological Macromolecules*, 3–22. https://doi.org/10.1016/b978-0-323-85759-8.00005-1
38. Jones, R. W., Babcock, G. E., Taylor, N. W., & Senti, F. R. (1961). Molecular weights of wheat gluten fractions. Archives of Biochemistry and Biophysics, 94(3), 483-488.
39. Wahlund, K. G., Gustavsson, M., MacRitchie, F., Nylander, T., & Wannerberger, L. (1996). Size characterisation of wheat proteins, particularly glutenin, by asymmetrical flow field-flow fractionation. Journal of Cereal Science, 23(2), 113-119.
40. Li, S., Jiang, Z., Wang, F., Wu, J., Liu, Y., & Li, X. (2020). Characterization of rice glutelin fibrils and their effect on in vitro rice starch digestibility. *Food Hydrocolloids*, *106*, 105918. https://doi.org/10.1016/j.foodhyd.2020.105918
41. Taiji Kawakatsu, Masayuki P. Yamamoto, Sakiko Hirose, Masahiro Yano, Fumio Takaiwa, Characterization of a new rice glutelin gene GluD-1 expressed in the starchy endosperm, Journal of Experimental Botany, Volume 59, Issue 15, November 2008, Pages 4233–4245
42. Influence of Storage on Peptide Subunit Composition of Rice Oryzenin,J. Agrie. Food Chem., Vol. 40, No. 6, 1992
43. Jekle, M., Mühlberger, K., & Becker, T. (2016). Starch–gluten interactions during gelatinization and its functionality in dough like model systems. Food Hydrocolloids, 54, 196-201.
44. Grasso, Nadia, Lynch, Nicola L, Arendt, Elke K, & O'Mahony, James A. (2022). Chickpea protein ingredients: a review of composition, functionality and applications. Compr Rev Food Sci Food Saf, 21, 435– 452.
45. Holding, D. R. (2014). Recent advances in the study of prolamin storage protein organization and function. Frontiers in plant science, 5, 276.
46. National Center for Biotechnology Information (2023). PubChem Compound Summary for CID 17787981, Gliadins. Retrieved 5 February 2023 from https://pubchem.ncbi.nlm.nih.gov/compound/Gliadins.
47. Vensel, W. H., Tanaka, C. K., & Altenbach, S. B. (2014). Protein composition of wheat gluten polymer fractions determined by quantitative two-dimensional gel electrophoresis and tandem mass spectrometry. Proteome science, 12(1), 1-14.
48. Dahesh, M., Banc, A., Duri, A., Morel, M. H., & Ramos, L. (2014). Polymeric assembly of gluten proteins in an aqueous ethanol solvent. The Journal of Physical Chemistry B, 118(38), 11065-11076.
49. Gil-Humanes, J., Pistón, F., Altamirano-Fortoul, R., Real, A., Comino, I., Sousa, C., ... & Barro, F. (2014). Reduced-gliadin wheat bread: an alternative to the gluten-free diet for consumers suffering gluten-related pathologies. PloS one, 9(3), e90898.

50. Ortiz-Sánchez, J., Cabrera-Chávez, F., & de la Barca, A. (2013). Maize Prolamins Could Induce a Gluten-Like Cellular Immune Response in Some Celiac Disease Patients. Nutrients, 5(10), 4174–4183.
51. Xiao, J., Chen, Y., & Huang, Q. (2017). Physicochemical properties of kafirin protein and its applications as building blocks of functional delivery systems. Food & function, 8(4), 1402-1413.
52. Meng, Y., & Cloutier, S. (2014). Gelatin and other proteins for microencapsulation. In Microencapsulation in the food industry (pp. 227-239). Academic Press.
53. Sousa, F. F. O., Luzardo-Álvarez, A., Blanco-Méndez, J., & Martín-Pastor, M. (2012). NMR techniques in drug delivery: Application to zein protein complexes. International journal of pharmaceutics, 439(1-2), 41-48.
54. Wang, Y., & Padua, G. W. (2012). Nanoscale characterization of zein self-assembly. Langmuir, 28(5), 2429–2435. https://doi.org/10.1021/la204204j
55. Kubota, M., Saito, Y., Masumura, T., Watanabe, R., Fujimura, S., & KADOWAkI, M. (2014). In vivo digestibility of rice prolamin/protein body-I particle is decreased by cooking. Journal of nutritional science and vitaminology, 60(4), 300-304.
56. Lovegrove, A., Edwards, C. H., De Noni, I., Patel, H., El, S. N., Grassby, T., Zielke, C., Ulmius, M., Nilsson, L., Butterworth, P. J., Ellis, P. R., & Shewry, P. R. (2015). Role of polysaccharides in food, digestion, and health. Critical Reviews in Food Science and Nutrition, 57(2), 237–253. https://doi.org/10.1080/10408398.2014.939263
57. www.netbizgroup.co.uk, N. G.-. (n.d.). Potato Starch - Farina (edible). Bacarel Express. Retrieved 5 February 2023, from https://www.bacarelexpress.co.uk/products/native-potato-starch.php
58. Thermo Fisher. (n.d.). *Zein 9010-66-6*. 9010-66-6. Retrieved February 4, 2023, from https://www.sigmaaldrich.com/GB/en/product/sigma/z3625?gclid=EAIaIQobChMItvvbw6r5_AIVy7HtCh2SBAOyEAMYASAAEgI4O_D_BwE&gclsrc=aw.ds
59. *Buy wholefoods online: Whole foods UK: Organic Foods: Health Foods*. Buy Wholefoods Online | Whole foods UK | Organic Foods | Health Foods. (n.d.). Retrieved 6 February 2023, from https://www.buywholefoodsonline.co.uk/organic-rice-protein-powder.html
60. ASDA stored LTD. (n.d.). *KTC pure sunflower oil, 5L*. Groceries.asda.com. Retrieved 6 February 2023, from https://groceries.asda.com/product/oil-ghee/ktc-pure-sunflower-oil/910000318048
61. J Sainsbury PLC. (n.d.). *Sainsbury's Very Strong Canadian Bread Flour, Taste the Difference 1kg*. Retrieved 4 February 2023, from https://www.sainsburys.co.uk/gol-ui/product/sainsburys-very-strong-canadian-bread-flour--taste-the-difference-1kg
62. Rice glutelin (Oryzenin). Zedira. https://patents.google.com/patent/CN105085605A/en. Date retrieved: 1 February 2023.
63. Silva, G.M.d., Veloso, C.M., Santos, L.S. et al. Extraction and characterization of native starch obtained from the inhambu tuber. J Food Sci Technol 57, 1830–1839 (2020).
64. Doing holdings. What is potato starch extraction process?_FAQ. (n.d.). Retrieved 4 February 2023, from http://www.starchprojectsolution.com/faq/potato_starch_extraction_944.html

65. Silva, G. M. D. S., Veloso, C. M., Santos, L. S., Melo Neto, B. A. D., Fontan, R. D. C. I., & Bonomo, R. C. F. (2020). Extraction and characterization of native starch obtained from the inhambu tuber. Journal of food science and technology, 57, 1830-1839.
66. Aio, Hensu, Chen, Q., & Jing, S. Q. (2011). (2011). Selection and optimization of the extraction process of maize alcoholic protein. Journal of Zhengzhou Institute of Light Industry: Natural Science Edition, 26(1), 34-38.
67. Sun QJ, Tian JQ. (2003). Study on the process conditions of alkali extraction of concentrated rice protein. Food Industry Science and Technology, 24(9), 3.
68. Vitamin B1 Powder Thiamine Hcl REDWELLS No Additives GMO Free Vegan - 50g Pack. Amazon UK. https://www.amazon.co.uk/REDWELLS-Thiamine-Vitamin-Powder-Additives/dp/B07Z5YQFMJ?th=1. Date retrieved: 1 February 2023.
69. Wang, M., Hettiarachchy, N. S., Qi, M., Burks, W., & Siebenmorgen, T. (1999). Preparation and functional properties of rice bran protein isolate. Journal of agricultural and food chemistry, 47(2), 411–416.
70. Yang, J., & Sagis, L. M. C. (2021). Interfacial behavior of plant proteins — novel sources and extraction methods. *Current Opinion in Colloid & Interface Science, 56*, 101499. https://doi.org/10.1016/j.cocis.2021.101499
71. Lockhart HB, Hurt HD. 1986. Nutrition of oats. In: Webster FH, ed.
72. Yang, Lin, Liang, Mingcai, Wang, Zhengxuan, Li, Hui, & Liu, Ye. (2018, September 7). Method for extracting rice albumin and globulin mixed protein. Patent nr. CN105085605A
73. Foschia, M., Horstmann, S., Arendt, E. K., & Zannini, E. (2016). Nutritional therapy–Facing the gap between coeliac disease and gluten-free food. International journal of food microbiology, 239, 113-124.
74. The environmental impact of olive oil production in the European Union: Practical options for improving the environmental impact. commission.europa.eu. https://ec.europa.eu/environment/agriculture/pdf/oliveoil.pdf. Date retrieved: 5 February 2023.
75. Hydroxypropyl Methylcellulose. ScienceDirect. https://www.sciencedirect.com/topics/chemistry/hydroxypropyl-methylcellulose. Date retrieved: 5 February 2023.
76. Brakes Strong Flour. brake. https://www.brake.co.uk/dry-store/baking-mixes-ingredients/flour/speciality-flour/brakes-strong-flour/p/33892. Date retrieved: 1th February 2023.
77. economies of scale. Oxford Reference. https://www.oxfordreference.com/display/10.1093/oi/authority.20110803095741513;jsessionid=2D219DCF2A3C5FB670D784BE79ECB162#:~:text=Reductions%20in%20the%20average%20cost,costs%2C%20when%20output%20is%20increased. Date retrieved: 31 January 2023.
78. TMILLm.BK. Reuters. https://www.reuters.com/markets/companies/TMILLm.BK/key-metrics/margins. Date retrieved: 28 January 2023.
79. Horstmann, S. W., Lynch, K. M., & Arendt, E. K. (2017). Starch Characteristics Linked to Gluten-Free Products. Foods, 28383504. Retrieved from https://pubmed.ncbi.nlm.nih.gov/28383504

80. Gutiérrez, L., Batlle, R., Andújar, S., Sánchez, C., & Nerín, C. (2011). Evaluation of antimicrobial active packaging to increase shelf life of gluten-free sliced bread. Packaging Technology and Science, 24(8), 485-494.
81. Berta, M., Koelewijn, I., Öhgren, C., & Stading, M. (2019). Effect of zein protein and hydroxypropyl methylcellulose on the texture of model gluten-free bread. Journal of texture studies, 50(4), 341-349.
82. Canakci, M., Topakci, M., Akinci, I., & Ozmerzi, A. (2005). Energy use pattern of some field crops and vegetable production: Case study for Antalya Region, Turkey. Energy Convers. Manage., 46(4), 655–666. doi: 10.1016/j.enconman.2004.04.008
83. Gray, B. E. (2021). Global Climate Change Impact on Crops Expected Within 10 Years, NASA Study Finds. Climate Change: Vital Signs of the Planet. Retrieved from https://climate.nasa.gov/news/3124/global-climate-change-impact-on-crops-expected-within-10-years-nasa-study-finds
84. Staple Food Crops of the World. National Geographic. https://education.nationalgeographic.org/resource/wbt-staple-food-crops-world. Date retrieved: 28 January 2023.
85. Bagolin do Nascimento, A., Medeiros Rataichesck Fiates, G., dos Anjos, A., & Teixeira, E. (2014). Availability, cost and nutritional composition of gluten-free products. British Food Journal, 116(12), 1842-1852.
86. Rice Production by Country 2023. https://worldpopulationreview.com/country-rankings/rice-production-by-country. Date retrieved: 5 February 2023
87. Wheat Production by Country 2023. Retrieved from https://worldpopulationreview.com/country-rankings/wheat-production-by-country. Date retrieved: 5 February 2023
88. Grains in Relation to Celiac (Coeliac) Disease. GrainGenes.https://wheat.pw.usda.gov/ggpages/topics/celiac.html. Date retrieved: 27 January 2023.
89. O'Connor, B. M. (2021). Folic acid to be added to UK flour to help prevent birth defects. BBC News. Retrieved from https://www.bbc.co.uk/news/health-58615838 Date retrieved: 4 February 2023
90. Kasaai, M. R. (2018). Zein and zein-based nano-materials for food and nutrition applications: A review. Trends in Food Science & Technology, 79, 184-197.
91. Rothburn, N., Fairchild, R. & Morgan, M. Gluten-free foods: a 'health halo' too far for oral health?. Br Dent J (2022).

9. Appendix

9.1 The Survey

We conducted a public survey released to the physics students at The University of Edinburgh and a group on reddit named Gluten-Free. [77] There was a total of 308 participants in this survey that helped us to gather data on the public's opinions on the quality of GF bread and how it can be improved.

The questions in the survey and full results are shown below:

Question 1: Have you had any gluten alternative foods?
Question 2: If you answered yes, do you think the alternative was sufficient as a replacement?
Question 3: If you have had GF bread before Give it a rating out of 10 of how good you think it is.
Question 4: How often do you eat GF (gluten free) bread?
Question 5: If you have had GF bread what property do you think needs most improvement to be able to mimic normal bread?
Question 6: Overall, if you have had any type of alternatives (E.g. Vegan, Dairy free) we would like to know what you think about them in general?

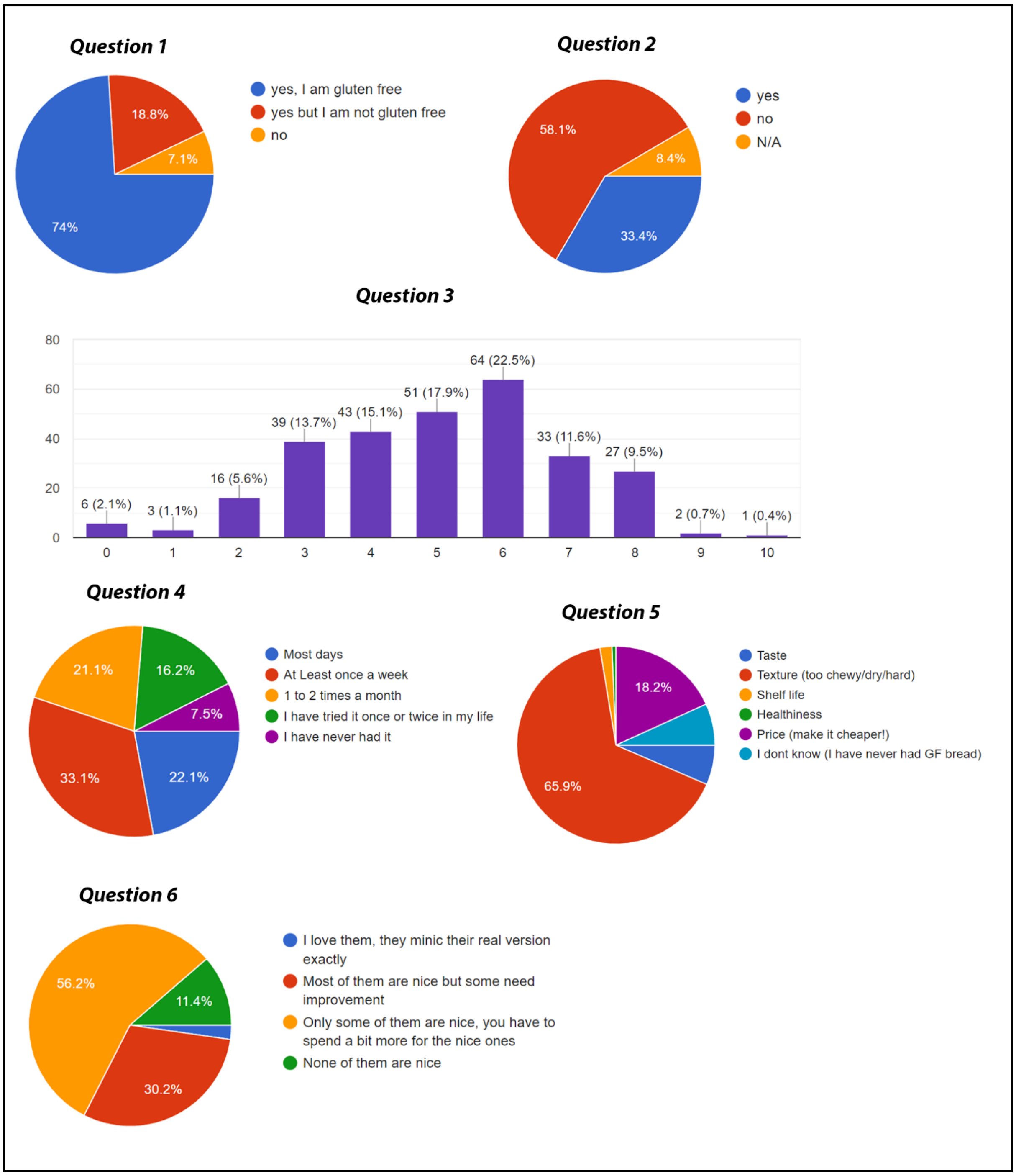

Figure 13: The results from the survey for all questions including all questions asked. The questions for the data are displayed just above this figure. Images copied from [29]

9.2 Stress-strain relationship including excluded volume term

So, you like detailed equations and you've found your way to this secluded corner of the appendix. Kudos! We have followed a similar approach to Rubenstein [32] to the free energy of a real chain polymer by using the ideal entropy of a real chain and a mean field approximation of the internal energy related to excluded volume. This yields

$$F = F_{ent} + F_{excl} \approx k_B T \left(\frac{3R^2}{2Nl^2} + \frac{vN^2}{R^3} \right)$$

where the names of all variables are the same used in section 2. By taking the derivative of this free energy with respect to sample length and applying incompressibility, we end up with our final stress-strain relationship for a dough made of a real polymer:

$$\sigma = \rho \mathrm{k_B} T \left((1+e)^2 - \frac{1}{1+e} \right) \left\{ 1 - 3^{\frac{5}{2}} \frac{\sqrt{N} v}{l^3} \left[(1+e)^2 + \frac{2}{1+e} \right]^{-\frac{5}{2}} \right\}$$

We have produced this expression. If in doubt about this model or if you want to discuss this further, please contact Pablo Sandquist[10].

[10] P.Sandquist@sms.ed.ac.uk