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**Examination of the influence of different stress states on
the rheological behavior of starch containing food matrices**

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Abbreviations and Symbols

A	pre-exponential factor
a_T	shift factor
c	concentration
CLSM	confocal laser scanning microscopy
CO ₂	carbon dioxide
e	Euler's number
E _a	activation energy
G	shear modulus / Young's modulus
G'	storage modulus
G''	loss modulus
G*	complex shear modulus
G _e	equilibrium modulus
GMP	glutenin macropolymer
h	height
H	continuous relaxation spectrum
i	imaginary number
k	constant
k _c	characteristic constant
L	length
L ₀	initial length
ΔL_T	thermally induced increase in length
LVR	linear viscoelastic region
NaCl	sodium chloride
MSSM	microscale shear mixing
PSA	pressure sensitive adhesive
R	universal gas constant
t	time
T	temperature
T _g	glass transition temperature
T _r	reference temperature
ΔT	temperature increase
TTS	time-temperature superposition
WLF	Williams Landell Ferry equation

γ	strain
$\dot{\gamma}$	strain rate
δ	phase shift
η	viscosity
η_0	zero shear viscosity
λ	relaxation time
v	reaction rate
σ	stress / stress tensor
σ_{ij}	shear stress component
σ_0	initial stress
τ_{ij}	normal stress component
ω	frequency

1. Summary

Wheat dough is the basis for a variety of products. During its production the ingredients are exposed to different kinds of strains. For the formation but also the degradation of dough, these strains can be grouped into chemical and physical factors. During industrial dough formation, the dominating strains are temperature, ingredient composition, mixing time and mixing energy. Based on time and intensity of the strain, different stress states in dough are achieved. These determine different dough properties which affect the properties of the final product. During dough formation a gluten network is developed. Its quality determines the dough's capability to retain gas during proofing or to withstand other physical strains during further bread production. The quality of gluten and thus the quality of dough can be assessed by rheological measurements. In this work, the two strains mixing temperature and mechanical mixing energy were examined and how they influence the rheological properties of wheat dough.

The temperatures during mixing were lower than the usual 25 - 30 °C final dough temperature, as it could be beneficial to have cool dough ready for long-term fermentation. It showed that cool mixed dough exhibits a higher dough development time but also that it is more extensible. However, cool mixed dough exhibits an increased stickiness and detaching it from surfaces will induce further strains. By that the rheological properties can be altered which makes an exact dough characterization sophisticated. Then the prognosis of future bread properties will also remain vague.

In order to allow for a sensible rheological characterization without altering the properties of sticky dough, a technique was introduced that produces dough and enables to examine the dough in one apparatus. Therefore, dough was developed by the sole application of shearing as the source of mechanical energy – the second strain that was examined and which represented by a constant shear rate. This produces dough with comparable rheological and morphological properties to dough that was produced in a standard process. However, the exposure to a constant shear rate leads to a separation of gluten and starch. This led to the application of a constant deformation. Dough was developed by applying consecutive stress relaxation tests with alternating shear directions. The relaxation spectrum of each relaxation step was extracted which allowed for the computation of the rheological properties of dough at each single mixing step. The developed mixing technique and hereby the application of constant deformations produces

dough that is comparable to standard dough, delivers rheological insight in dough while mixing and allows predicting the rheological properties of standard dough.

2. Zusammenfassung

Weizenteig ist die Grundlage für eine Vielzahl an Produkten. Er entsteht dadurch, dass Belastungen unterschiedlicher Art auf ihn bzw. seine Zutaten einwirken. Im Rahmen der Teigherstellung lassen sich diese in chemische und physikalische Belastungen einteilen. In der industriellen Teigfertigung sind die Temperatur, die Zutaten, die Knetzeit und die Knetenergie ausschlaggebend. Durch Ändern der Intensität der Belastung lassen sich unterschiedliche Stresszustände im Teig definieren. Der Stresszustand des Teigs entscheidet jedoch letztendlich über die Eigenschaften des Endprodukts. Während der Weizenteigherstellung wird das Glutennetzwerk entwickelt. Seine Beschaffenheit bestimmt darüber, wie stark Gase im Teig gehalten werden können und der Teig anderen Kräften standhalten kann. Die physikalischen Eigenschaften des Glutens werden zumeist rheologisch ermittelt. In dieser Arbeit wurden die Belastungen Knettemperatur und mechanischer Knetenergieeintrag im Hinblick auf ihren Einfluss auf die rheologischen Eigenschaften von Weizenteig untersucht.

Es wurde der Einfluss niedriger Knettemperaturen wie sie bei Langzeitführung von Teig zum Einsatz kommen untersucht. Kalt gekneteter Teig bedurfte einer längeren Knetzeit, erwies sich aber als dehnbarer im Vergleich zu Teig, der bei 25 - 30 °C geknetet wurde. Aufgrund seiner erhöhten Adhäsion erfährt der Teig zusätzliche mechanische Belastung beim Versuch, ihn von Oberflächen zu lösen. Dies kann dazu führen, dass im Anschluss gemessene rheologische Eigenschaften verfälscht wiedergegeben und Vorhersagen über die zukünftigen Backeigenschaften erschwert werden.

Um die Eigenschaften adhäsiven Teigs dennoch erfassen zu können, wurde eine Methode entwickelt, bei der die Teigherstellung und -charakterisierung in einem Gerät stattfinden. Ausschließlich reines Scheren als Form der mechanischen Energie wird hierbei zur Teigherstellung aufgewendet. Es wurde die Auswirkung von kontinuierlichem Scheren als eine Form der mechanischen Beanspruchung untersucht. Der entstandene Teig wies signifikante Übereinstimmungen in seiner rheologischen Beschaffenheit mit normal geknetetem Teig auf. Zu starkes Scheren führt zur Auftrennung der Stärke-Glutenmatrix des Teigs. Schrittweises Scheren mit alternierender Deformationsrichtung zeigte diese Separation nicht. Aus den Relaxationsspektren der zum Kneten angewendeten Stress-Relaxationsschritte ließen sich in diesem Verfahren die rheologischen Eigenschaften berechnen. Diese Methode des Scher-Knetens erwies sich als geeignet, da sich der Teig noch

während der Herstellung charakterisieren lässt. Auch lassen sich weitere Teigkennzahlen aus den rheologischen Daten ableiten.

3. Introduction

With the beginning of the industrialization more technical equipment like kneaders or mixers spread in bakeries. The constant incorporation of mechanical energy by a kneader allowed producing dough with uniform properties instead of adding an unstable manual mixing action. These are prerequisite for the main focus in modern baking technology: saving time in the downstream steps and to keep the bread making process constant in order to achieve a high dough and baking quality. The quality depends directly on steady rheological dough properties. The factors that support dough with uniform properties are a stable mixing temperature, unchanging flour properties, a consistent ingredient composition, a stationary mixing time and the same level of mixing energy. Figure 1 illustrates the factors influencing the dough properties.

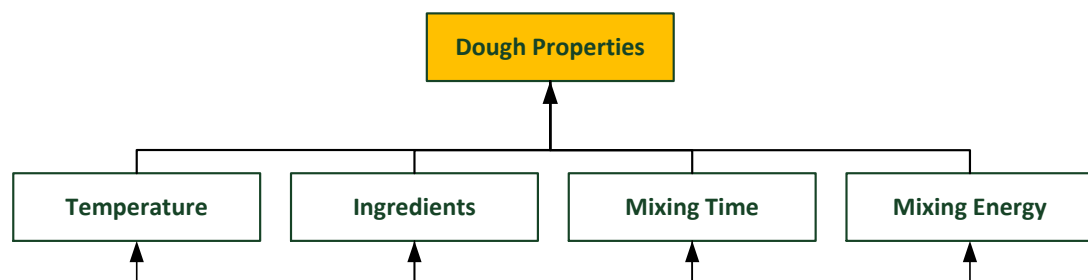


Figure 1: Stress factors that influence the properties of the forming dough.

The shown factors influence the dough properties directly but also each other. In industrial dough processing, short mixing times and a steady composition of the ingredients are favored as it is a key factor for productivity. Assuming these both factors are kept constant, the remaining variables are the mixing temperature and the mixing energy. These two physical parameters are the impact factors during dough development which need to be balanced out.

The temperature, as the first factor that causes stress to dough, has influence on the mixing process and on the later fermentation. The effects during fermentation or storage are well understood but during mixing the influence of the temperature is only scarcely examined. The effect of warmer mixing temperatures than 30 °C on fundamental dough rheological properties is known. The resulting dough is softer when mixed at temperatures above 30 °C. Mixing at higher temperatures shortens the mixing time. When the dough temperature gets too high during mixing serious

handling problems occur. An increase in mixing temperature results from an input of mechanical energy of the mixing hooks. At higher temperatures chemical reactions but also deterioration occur faster. There are numerous studies that focused on dough properties at different temperatures. In turn, the influence of cool mixing temperatures is mostly excluded from scientific research. Except for Başaran and Göçmen (2003), there are no previous studies that investigated the dough development or the after mixing-treatment after mixing at cool temperatures. It is possible that the mixing time would increase when mixing at low temperatures. The energy input during mixing could be needed to be more efficient in order to prevent the mixing time from exceeding the allowed maximum. The benefit of having ready cool dough would be advantageous for pastry production. Cooling of the fat and sugar containing dough is essential for further processing as sugar increases adhesiveness of dough (Tan et al. 2016) and dough shaping is dependent on the melting point of the contained fats and oils (Devi and Khatkar 2018).

The mechanical or mixing energy represents the second factor that causes stress to dough during formation. The mechanical energy during mixing comprises the amount of energy for a continuous deformation of dough and the formation of flow fields in the mixing vessel. The amount of mechanical energy is crucial for the dough development. A low energy will not lead to dough with a fully developed gluten network. Water is not homogeneously distributed and thus water poor areas lack in elasticity (Zheng et al. 2000). As a result, the capacity to retain fermentation gases is reduced and gas nuclei are less distributed in the dough matrix. But both are the prerequisite for a soft, sponge-like crumb texture of the baked wheat bread (Romano et al. 2013; Zghal et al. 2002). A too high input of mechanical energy will result in overmixed dough in which the formerly developed gluten network is partially disrupted. This will lead to an extremely inhomogeneous distribution in the gas cell size of the final bread crumb.

Both factors, mixing temperature and mechanical energy, are related reciprocally. In order to achieve fully developed dough, mixing at higher temperatures will demand for less mechanical energy input and vice versa. The relationship between these both factors is only predictable and balanced out when the other stress factors (temperature and ingredient composition) are kept constant. Otherwise, they also need to be regarded in modelling the dough development and bread baking process. In case of long-term fermentation ready dough is cooled and low

temperatures are applied in the proofing stage. Since the process of cooling dough is time consuming it can be advantageous to produce cool dough already while mixing. But as the mixing temperature is lowered it is possible that more mechanical energy needs to be incorporated in order to still develop dough in adequate time.

The following chapters give an overview about wheat dough, its rheology and the stress that develops during dough making. It will be shown how certain stress states can be achieved by dough production with regard to mixing temperature and mixing energy.

3.1. Wheat dough – the unicum

In the western hemisphere starch containing food matrices appear in different forms. They appear as raw material like cereals, legumes or roots and they appear as processed food like pasta, bread or dumplings. In processed foods the starch is converted in a more digestible form due to a thermal treatment like baking, cooking, frying or steaming. A pre-stage of the processed starch containing food can be dough. Dough in its simplest form consists of a certain ratio of flour and water. By the application of mechanical energy flour and water are thoroughly mixed to form sponge-like dough. Special attention is paid on wheat dough since it has the unique capability to retain gas and thus to result in leavened products. Besides the effect of the dough components, the properties of the final product are established during dough mixing – a gas holding matrix is formed and gas nuclei are distributed (Baardseth et al. 2000; Contamine et al. 1995; Gan et al. 1990; Osella et al. 2008; Struyf et al. 2017). This makes the mixing stage crucial for the quality criteria of products deriving from dough. The dominating influence on dough properties comes from gluten (Anjum et al. 2007; Barak et al. 2013). Gluten is not contained in cereals like rice, corn or pseudocereals. It is contained for example in wheat, rye, barley or oat whereas wheat flour has the highest technological importance.

Gluten is made up from the glutelin and prolamin Osborne protein fraction of the cereal proteins. In case of wheat these are the polymeric glutenin and the monomeric gliadin. Both can be separated into sulfur-rich and sulfur-poor types. Glutenin can be additionally grouped into different high molecular weight proteins (Figure 2). The contribution to the gluten properties of gliadin and glutenin depends on their sulfur content which derives from the amount of cysteine amino acids.

During mixing, the incorporation of mechanical energy together with the input of oxygen promotes cysteine to form intra- and intermolecular disulfide bonds (Auvergne et al. 2007; Don et al. 2005). The intermolecular bonds and hydrogen bonds are responsible for the elastic and viscous behavior and the extensibility of wheat dough. Changing the protein content but also the ratio of gliadin and glutenin influences the dough rheological properties drastically. Increasing the protein content in dough results in an increased overall consistency and an increased resistance towards rupture (Færgestad et al. 2000; Gan et al. 1995). Increasing the glutenin content affects the consistency positively and the resistance towards rupture negatively. Adding gliadin produces softer dough. The same effect is caused by the addition of the glutathione (Chen and Schofield 1996; Mair and Grosch 1979). It is a tripeptide and like gliadin which consists of 200+ amino acids it is able to form disulphide bonds. Additionally, it is able to cleave existing disulphide bonds, e.g. those between gliadin and glutenin. It occupies them and hinders the formation of a stronger gluten network with more possible intermolecular interactions (Verheyen et al. 2016).

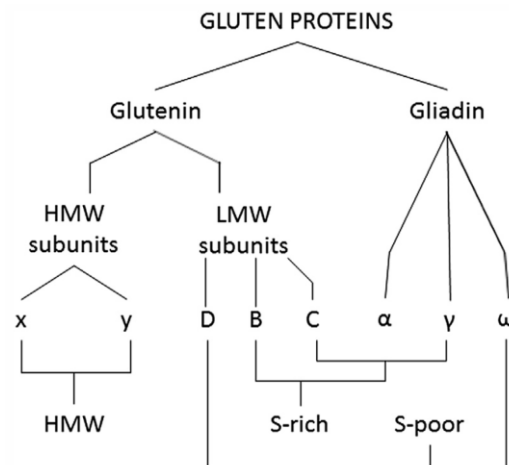


Figure 2: Schematic summary of the classification of gluten proteins (Shewry and Tatham 2016).

During mixing the protein molecules of both fractions interact by forming disulphide bonds between the cysteine amino acids. When reaching the highest degree in interaction a fully developed three-dimensional gluten network has formed. It is characterized by viscoelastic stretching properties and the ability to retain gases. Both can be modified by adding chemical agents. The most widely-used additive in dough is sodium chloride. By altering the hydrate shell and settling between the protein molecules it increases the strength of ionic and hydrogen bonds (Beck et al. 2011). The application of glutathione breaks the disulfide bonds reacting in a thiol exchange by binding to the free sulfur atoms. The former inter- and intramolecular

bonds are partially degraded and the capability of gluten to retain gas is diminished. Oxidizing agents like ascorbic acid scavenge gluten softening molecules like glutathione. They strengthen the gluten network (Grosch and Wieser 1999). Other oxidizing agents like glucose oxidase are added up to a critical amount in order to strengthen gluten (Bonet et al. 2006; Vemulapalli et al. 1998).

A high amount of retainable gases in the dough during mixing or proofing is a prerequisite for appealing baked goods as is the texture of the frame that surrounds the air – the actual bread crumb. During fermentation the loaf gains volume due to the CO₂ produced by the contained yeast or leavening agents. The temperature increase during baking leads to the denaturing of the proteins by which they solidify. The starch which makes up to 80 % of the components in flour gelatinizes and builds up films along the protein frame. The sponginess of the bread crumb as well as the freshness preservation and bread staling kinetics can be influenced by adjusting the water content or the amount of water storing hydrocolloids (Biliaderis et al. 1995; de la Hera et al. 2014; Gil et al. 1997; Kurek et al. 2017; Zeleznak and Hosney 1986).

In wheat flour starch makes up to 80 % of the dry matter. It consists of the two polysaccharides amylose and amylopectin. The ratio between both depends on the botanical origin of the starch but ranges between 2:10 and 3:10. Both polymers consist of glucose molecules. In the unbranched amylose the glucose molecules are connected by $\alpha(1\rightarrow4)$ glycosidic bonds. In contrast to amylose, amylopectin has branches that derive from additional $\alpha(1\rightarrow6)$ glycosidic bonds. These branches allow for an easier access to the starch by other chemicals. In this native state starch is present as granules of different size – the larger A and the smaller B granules. Their volume ratio depends on the cultivar and harvesting time but ranges around 9:1 (Zhang et al. 2016). Due to their higher surface-to-volume ratio the B granules can take up more water which result in a higher farinograph water absorption but also a lower baking volume (Soh et al. 2006; Stoddard 2000). The same effect of decreased bread volume can be observed when increasing the content of damaged starch granules in the flour. It retains more water than undamaged starch granules (Barrera et al. 2007).

During dough making the starch granules undergo little to no physical or chemical changes. The granules can be regarded as inert fillers in the gluten network. During the baking process, the temperature rises above the gelatinization temperature of starch. From this point on, the starch granules do not remain inert but begin to gelatinize and to change their shape irreversibly.

3.2. Stresses developed in dough – the chemical side

In the same manner as starch is exposed to strains that change its physical or morphological state, strains also act in different forms on the whole dough. They can be of physical or chemical nature. Depending on the food they can be harmful or harmless or they can be hindering or helpful in achieving a wanted food behavior. It is also possible that only one stress factor acts separately or that multiple stress factors act at the same time. In the end, stress factors can have direct effect on dough or they can have an effect on another stress factor for dough and therefore act indirectly (see Figure 3). During mixing, flour and water form dough. Stress due to chemical arises when oxygen promotes the formation of disulphide bonds between certain amino acids. This contributes to form a stable protein network in the dough which is essential for leavened bread. The sole presence of oxygen does not promote flour and water to form dough. Mechanical strain develops during stretching, compressing and shearing of dough while mixing. It causes changes in the constitution of the formed protein network whereas thermal strain also causes changes in other flour constituents next to the proteins. Thermal strain may cause changes in color, surface structure or stickiness.

Depending on their origin or their acting target, the stress factors that act during dough formation can be assigned to three categories: chemical and/or physical, and influencing the dough properties directly or indirectly (see Figure 3). The stress induced by chemicals during dough formation derives from the dough ingredient composition and flour constitution. The ratio of proteins and carbohydrates and the content of other components are crucial. Further stress can derive from the ratio of flour in the dough but also from the ratio of gliadin and glutenin in the protein fraction.

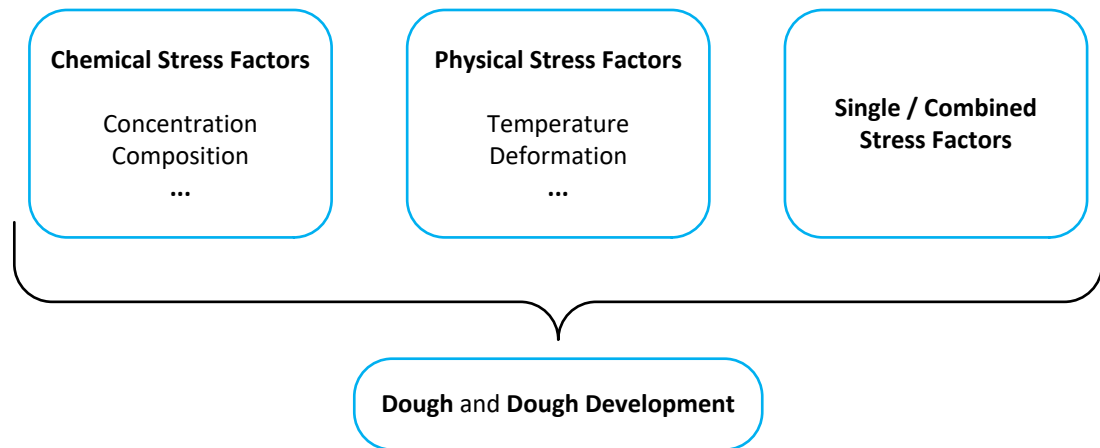


Figure 3: Alternative composition of stress factors acting on dough during or after dough formation.

Chemical strain arises as soon as the ingredients are brought in contact. The water dissolves the proteins, soluble carbohydrates and minor components. Unlike undamaged starch granules the damaged ones begin to take up some water and begin to swell.

Changing the amount of single ingredients can have drastic effects on the dough rheological properties. Water is the plasticizer for several dough constituents. Decreasing the amount of water reduces the mobility of both harmful and helpful enzymes that act during dough formation. Water is also the plasticizer for the gluten network forming protein fractions. Experiments with different water contents in dough showed that the consistency of dough is changed whereas the ratio of elastic to viscous properties (G' and G'') remains constant (Berland and Launay 1995). The general effect of water during mixing is it supports the transportation of molecules, sets the molecules in a reactive state and thus promotes the dough formation positively (Farahnaky and Hill 2007). Gliadin and glutenin are more hydrated and as a result are more mobile. Thus an increased amount of water decreases the necessary mixing energy and mixing time. Starch is another main component in flour. During dough formation the starch is in an inert state and only water accessible parts like semi-crystalline layers or the B granules will be dissolved (Tang et al. 2000). The main part of the starch granules is water insoluble at room temperature. Changes in the rheological behavior of starch and thus in the dough will only occur when exceeding the denaturation temperature of the proteins and the gelatinization temperature of the starch (Dreese et al. 1988; Eliasson 1986; Xue et al. 2008). The starch loses its native crystalline state and will be transformed into a network-like structure. The granules start to soak up water and begin to

swell. Simultaneously, amylose is leached out of the granules which is a prerequisite for the starch network (Lii et al. 1995; Palav and Seetharaman 2006). Decreasing the temperature afterwards will lead to a viscoelastic gel. Petrofsky (1995) but also Miller and Hosney (1999) showed that the botanical origin of starch in dough has a significant influence on the dynamic moduli and consistency of dough which can be attributed to the starch granule size distribution. Delcour et al. (2000) concluded that the interaction phenomena do not base on starch granule surface properties but on physical inclusion of starch granules. This was also confirmed by studies from Jekle et al. (Jekle et al. 2016). Starch and protein are major constituents in flour. Changing their ratio has an immediate result on the dough properties. The effects of increasing the protein content are known and widely examined especially for the protein fractions that contribute to gluten development. Yang et al. (2011) analyzed the mechanical spectra of dough samples with different starch-gluten ratios. They demonstrated that starch contributes positively to the plateau modulus and zero shear viscosity which indicates a higher dough consistency. But they also observed that starch decreases the linear viscoelastic region as stated earlier by Khatkar and Schofield (2002) which will make it more sophisticated to build dough rheological models. Proteins in dough have direct impact on the rheological behavior whereas prolamins (gliadin) and glutelins (glutenin) dominate the dough rheological properties of wheat dough. Increasing the content of gliadin increases the consistency of developed dough, decreases the dough development time but also decreases the final bread volume and the dough stability (Barak et al. 2013; Khatkar et al. 2013). Glutenin affects the rheological properties in quite the opposite way. An increased level of glutenin increases the dough shear viscosity or consistency but reduces the stretchability (Uthayakumaran et al. 2000). Overall, glutenin contributes to dough elastic properties whereas gliadin contributes to the flow properties of dough (Shewry et al. 2000). Improving the properties of the proteins is often needed but also wanted. It is achieved by the addition of salt or other additives. This way, it is possible to partially design gluten proteins and doughs with desired attributes. Salt or NaCl stabilizes the fermentation rate of added yeast and fortifies the gluten proteins. These will exhibit higher extensibility but also will increase the dough durability which is recognized as a prolonged dough mixing time (Miller and Hosney 2008). Beck et al. (2012) showed that NaCl is responsible for an increase in dough stickiness as it affects the protein charges – the proteins contract and displace water. Significant rheological changes of gluten

due to salt addition were also reported by Farahnaky and Hill (2007), McCann and Day (2013) and by Tuhumury et al. (2014). Others showed that the fortifying effect of NaCl is reduced when the total protein content in flour is increased. Thus, there appears to be a natural limit for salt induced changes. Another widely used additive for dough is ascorbic acid. It lowers the pH which leads to changes in the distribution of charges of the protein amino acids. Adding too much ascorbic acid will lower the pH too drastically. Proteins lose their tertiary structure and enzymes lose their functionality – they denature. The loss of functionality of enzymes has no sudden effect on dough. It is rather a continuous process since enzymes are involved in the dough development and dough proofing. Added yeast releases α -amylases which liquefy starch into more accessible disaccharides. Depending on the microbial origin of the amylase, the pH stability varies between 2 and 12 (Gupta et al. 2003). Infused with foreign genes from *Bacillus subtilis*, the bakery relevant yeast *Saccharomyces cerevisiae* is able to produce an α -amylase that has its optimum at pH 5 (de Moraes et al. 1999). Leaving the optimum conditions of the enzyme inhibits its functionality. The starch granules would stay untouched and no digestible carbohydrates would be released. The metabolism of the yeast is suppressed and the softening effect of the produced CO₂ on the developing or proofing dough is missing (Akdoğan and Özilgen 1992; Turbin-Orger et al. 2015). From the rheological perspective, a too low CO₂ production during proofing prevents or limits the rising of dough and the rheological properties of dough containing gas nuclei remain unchanged during proofing. After proofing, dough would still exhibit the rheological properties of ready dough. Yet, leaving dough to rest still affects the gluten. As described by Weegels et al. (1996) gluten and GMP (glutenin macropolymer), respectively, are partially disrupted after mixing. When left to rest they begin to re-aggregate. This will lead to changes in the rheological properties of dough that experiences no gas formation during proofing. The lack of CO₂ during proofing and baking has influences on the amylases but also on the gluten proteins and other enzymes like glutathione dehydrogenase which strengthen the gluten network. During mixing glutathione is the antagonist to gluten interlinking reactions. Glutathione cleaves the inter- and intramolecular disulphide bonds in gluten and occupies the free thiol groups so that a reformation of disulphide bonds in gluten is hindered (Belton 2012; Grosch and Wieser 1999). These sulphhydryl/disulphide interchange reactions with gluten proteins weaken the dough and the gluten network. Adding ascorbic acid promotes the formation of disulphide bonds during dough formation (Elkassabany and Hosenehy 1980) but the

degrading effect of glutathione is not prevented. But adding glutathione dehydrogenase scavenges glutathione and drives it to form glutathione disulphide which leaves the disulphide bonds of the gluten proteins unharmed. Operating at low pH below 2 reduces the effect of dehydroascorbic acid (Wechtersbach and Cigić 2007) and the scavenging potential is gone. It is complicated to evade the effects of glutathione as it is present in flour by nature. Another source for glutathione can be also yeast, especially the dead cells (Verheyen et al. 2015). The effect becomes more dominant when aiming for long-term proofed doughs as they can soften unwantedly.

Another dough softener released from yeast cells is CO₂. In contrast to glutathione it does not alter the gluten network. The rheological properties of dough are changed significantly under the influence of CO₂ or other artificially injected gases. During mixing inclusions of gas in the dough matrix form nuclei which are the precursors for the pores in the later bread crumb. During proofing the yeast produces CO₂. It migrates through the dough matrix and accumulates in the nuclei which will then expand. As the dough gains volume, the gluten filaments are extended and even disrupted. At a high fermentation rate of the yeast, the stress increases faster than the strain due to volume increases. The gluten filaments are extended rapidly and thus strain hardening of dough proteins can occur. Thinned dough filaments increase in resistance towards strain compared to thicker dough parts (Van Vliet et al. 1992). Based on strain hardening effects, Dobraszczyk and Roberts (1994) developed a criterion to estimate the stability of gas cell walls during proofing. They also showed that the extension of dough during proofing exhibits both, softening and hardening effects. The hardening effects contribute positively to the gas cell wall stability and gas retention capacity. The increase in gas volume fraction contributes to the softening of dough. But it is not only the gas fraction in dough that determines the rheological properties. The rheological properties of the gluten network itself determine how much gas can be incorporated during mixing. With an initial gas free density of app. 1.25 g/cm³ leavened dough will have densities of around 0.7 g/cm³ (Bellido et al. 2009; Chin and Campbell 2005b). Bellido et al. (2006) showed that it is possible to entrain more air into softer dough. At the same time, there would be a higher risk in producing dough that is less resistant towards mechanical influences like extension. Chin et al. (2005) revealed that mixing with additional aeration produces dough that is even more susceptible to extension since the strain hardening index and the failure stress to gas wall rupture decrease. On the other hand, enriching the additional atmosphere with

oxygen will produce more resistant dough. Other experiments with different gas fractions in dough demonstrated that the elastic modulus derived from ultrasound measurements is inversely proportional to the gas fraction in dough (Elmehdi et al. 2004). The more gas is entrained in dough the less elastic it appears. Gluten dominates the rheological properties of the whole dough more dominantly when the gas fraction of dough is low. The ratio of the major constituents in dough affects the final dough rheological properties directly. The amount of minor constituents can exhibit side effects on other constituents – they can act indirectly on the dough rheological properties. The same applies for physical stress factors.

3.3. Stresses developed in dough – the physical side

Rheology is the science of deformation of matter. It describes the flow of materials when being exposed to a physical strain. During dough formation the strain is applied as mechanical force. Thermal strain can be applied separately or additionally or thermal strain can derive by the dissipation of mechanical energy. For a better understanding of the mechanical dough formation, rheological test methods are applied. These methods can be separated into empirical and fundamental rheological methods. Empirical rheological methods comprise measurements of the dough mixing characteristics with a recording mixer like the Farinograph (or comparable) or comprise the examination of the starch gelatinization characteristics with a heated stirrer like the Amylograph. Other measurements use a texture analyzer or an Extensograph in order to determine properties for rupture, sponginess or stretchability of dough. The empirical methods have a strong relationship to the everyday dough and flour evaluation tests in bakeries. They are helpful in the estimation of the future baking performance. But they work with arbitrary units which makes comparisons to other methods and measurements difficult or even impossible. The fundamental rheological methods work with SI units which makes the results comparable.

In fundamental rheological methods the stress in a material is caused by a deformation deriving from tension, compression, torsion, bending or shearing. The relative deformation is expressed as the strain γ . For small strains in the direction of deformation, γ is defined as:

$$\gamma = \frac{L - L_0}{L_0} \quad 3.1$$

in which L_0 is the initial length of the material and L the length of the material after being deformed. For a shear flow as it would be typical in a rheometer layers of the material are shifted (see Figure 4).

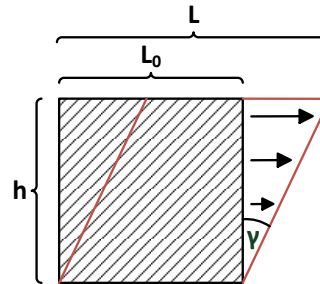


Figure 4: Schematic shift of layers in a body when exposed to a deformation.

Then for sufficiently small strains γ is defined as:

$$\gamma = \frac{L - L_0}{h} \quad 3.2$$

where h is the height of the sheared material.

The nine components of the second order stress tensor σ describe whether a material is stretched, compressed or sheared (see Figure 5).

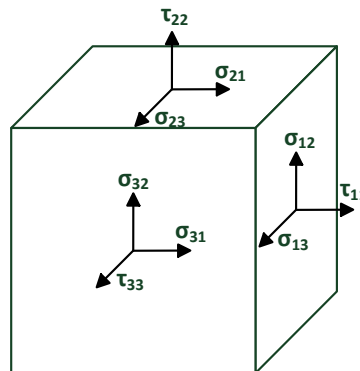


Figure 5: Geometric illustration and mathematic representation of stresses in a three dimensional body.

$$\sigma = \begin{bmatrix} \tau_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \tau_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \tau_{33} \end{bmatrix} \quad 3.3$$

If only three normal stress components τ_{ii} are unequal to zero then the material is stretched or compressed. The stress tensor is reduced to:

$$\sigma = \begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \quad 3.4$$

Being stretched or compressed depends on whether the τ_{ii} are acting outward or inward the plane to which they are perpendicular to.

Under equilibrium conditions where $\sigma_{ij} = \sigma_{ji}$ the original stress tensor reduces to:

$$\boldsymbol{\sigma} = \begin{bmatrix} \tau_{11} & 0 & 0 \\ \sigma_{21} & \tau_{22} & 0 \\ \sigma_{31} & \sigma_{32} & \tau_{33} \end{bmatrix} \quad 3.5$$

with six remaining independent components.

The relations between strain and stress are illustrated by constitutive equations. Specific equations can be derived for any type of material and how it responds to strain. The response of wheat dough towards mechanical strain is governed by elastic and viscous flow behavior. In case of shear the elastic flow is described by the Hooke's law:

$$\sigma = G \cdot \gamma \quad 3.6$$

The stress depends on its elastic modulus G and the strain γ . When releasing the strain the material recovers completely by which elastic flow is reversible. In a mechanical model, elasticity is illustrated by a spring:



Figure 6: Spring as the representation of a Hookean body.

Viscous flow is described by Newton's law:

$$\sigma = \eta \cdot \dot{\gamma} \quad 3.7$$

The development of stress in viscous flow is time-dependent and depends on the viscosity η and the strain rate $\dot{\gamma}$. Opposed to elastic flow, this process is not reversible. In a mechanical model, viscous flow is displayed as a damper:

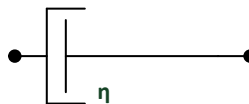


Figure 7: Damper as the representation of a Newtonian body.

Rubber can be regarded as purely elastic whereas water is purely viscous. Wheat dough instead is neither purely elastic nor purely viscous. It exhibits both properties and is therefore viscoelastic. Two different basic models exist for viscoelasticity, the Kelvin-Voigt model, and the Maxwell model. The difference between both lies in the reversibility of the modelled material when being strained.

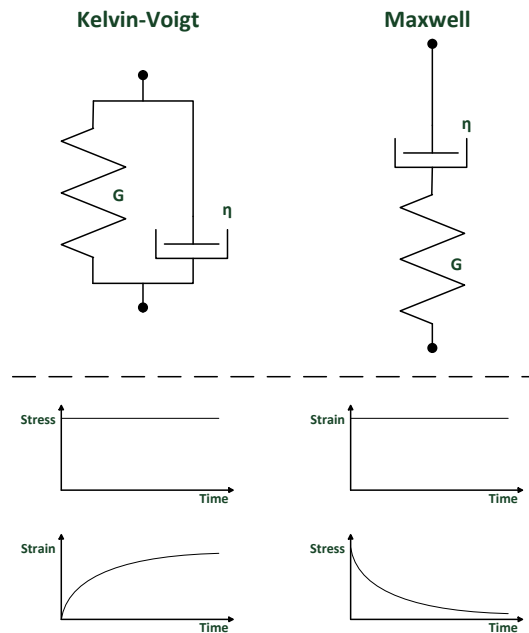


Figure 8: Viscoelastic solids and fluids represented by the Kelvin-Voigt and the Maxwell model (top). Development of strain and stress when material is exposed to a sudden stress and strain, respectively (bottom).

Depending on its overall consistency, dough can be subjectively regarded as a solid or a liquid. The solid can be represented by the Kelvin-Voigt model. Here, a spring and a damper are arranged in parallel (see Figure 8). Due to the nature of the elastic spring the deformation of the damper becomes also reversible but the forward and backward motion becomes delayed. When the specimen is exposed to a strain, the stress will develop as follows:

$$\sigma = G\gamma + \eta\dot{\gamma} \quad 3.8$$

Due to the nature of the damper element, the material cannot be exposed to a sudden strain. In suitable test setups a respective specimen is exposed to a strain rate that will guarantee that the resulting stress is constant. The material is then driven to creep which gives the test its name – Creep(-Recovery) Test. Solving the above differential equation will result in:

$$\gamma(t) = \frac{\sigma}{G} \cdot \left(1 - e^{-\frac{G}{\eta}t}\right) \quad 3.9$$

Introducing the relaxation time

$$\lambda = \frac{\eta}{G} \quad 3.10$$

which results in

$$\gamma(t) = \frac{\sigma}{G} \cdot \left(1 - e^{-\frac{t}{\lambda}}\right) \quad 3.11$$

allows a more direct comparison between different materials and their rheological properties. Opposed to dough regarded as a solid, the Maxwell model describes the flow of dough when it is regarded as a liquid. Here, spring and damper are

arranged in serial. In the consequence, the deformation of the material is only partially reversible which is due to the irreversible damper. The Maxwell model is applied when the material is exposed to a sudden and constant strain during a Stress(-Relaxation) test. The resulting stress follows the equation:

$$\sigma(t) = \sigma_0 \cdot e^{-\frac{t}{\lambda}} \tag{3.12}$$

Both tests will reveal that dough exhibits both solid and liquid like behavior. In order to allow for that and for a better fit of the equations the models can be extended by integrating additional dampers and springs. An often used model for wheat dough is the Burgers model which comprises a Maxwell and a Kelvin-Voigt model in serial.

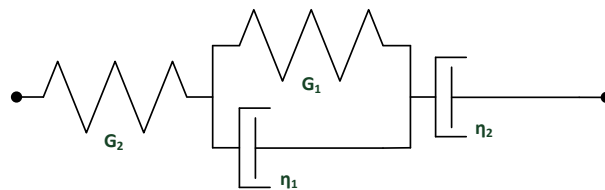


Figure 9: Maxwell and Kelvin-Voigt model in series as the representation of the Burgers model.

The Burgers model is used when the rheological behavior is more complex and cannot be described accurately by a single or double element model. This composed model is favored for dough as it includes both, the sudden deformation response of dough towards an initial stress at the beginning, the exponential response in the middle section and the linear deformation in a long term measurement. Another approach in achieving the different response states is the arrangement of multiple Maxwell or Kelvin-Voigt models in parallel or serial. In the consequence, the modelling of the respective material becomes more accurate but also more complex. The resulting models are referred to as generalized models.

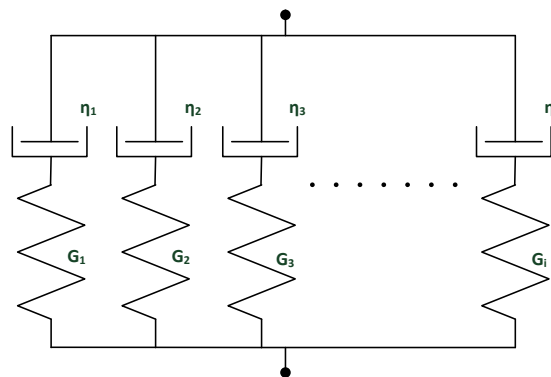


Figure 10: Mechanical representation of the Generalized Maxwell model.

Expanding equation 3.12 and using equation 3.6 leads to the equation for the Generalized Maxwell model as it is shown in Figure 10:

$$\frac{\sigma(t)}{\gamma} = G(t) = \int_{-\infty}^{+\infty} H(\lambda) e^{-\frac{t}{\lambda}} d\lambda \quad 3.13$$

The Generalized Maxwell model is crucial for the examination of the influence of mechanical strain on dough. It enables to visualize the relaxation spectrum (Figure 11).

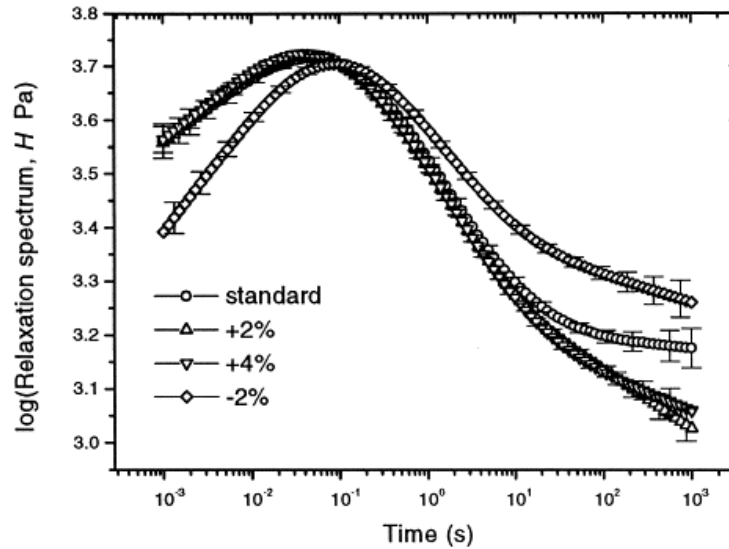


Figure 11: Relaxation spectra for flour-water dough at four different water concentrations (Phan-Thien and Safari-Ardi 1998).

The relaxation spectrum is unique for every material and therefore unique for each dough. For approximation and easier mathematical access, equation 3.13 has been simplified to:

$$\frac{\sigma(t)}{\gamma} = G(t) = \sum_{i=1}^n G_i \cdot e^{-\frac{t}{\lambda_i}} \quad 3.14$$

The integral of the continuous relaxation spectrum $H(\lambda)d\lambda$ has been replaced by the sum of the relaxation moduli G_i . For the visualization of the resulting discrete relaxation spectrum, the G_i instead of $H(\lambda)$ are plotted over the respective relaxation times λ_i . The prerequisite for the computation of the relaxation spectrum are the static stress-relaxation tests. From creep tests, it is possible to compute the related retardation spectrum which is interconvertible with the relaxation spectrum.

But the relaxation spectra can also be obtained from dynamical tests instead of static tests. In dynamic tests the strain is not constant. It oscillates and is applied sinusoidally by which the strain becomes a function of time:

$$\gamma = \gamma_0 \cdot \sin(\omega t) \quad 3.15$$

Since the sample is viscoelastic and is deformed sinusoidally the resulting oscillating stress will exhibit a phase shift of the angle δ :

$$\sigma = \sigma_0 \cdot \sin(\omega t + \delta) \quad 3.16$$

The total stress can be decomposed into a stress component that is absolutely in phase with the strain and another stress component that is out of phase:

$$\sigma = \sigma'_0 \cdot \sin(\omega t) + \sigma''_0 \cdot \cos(\omega t) \quad 3.17$$

The quotient of both components will then lead to the loss factor $\tan\delta$:

$$\tan \delta = \frac{\sigma''_0}{\sigma'_0} \quad 3.18$$

With the replacement of σ by equation 3.6 the loss factor can be rewritten to:

$$\tan \delta = \frac{G''\gamma_0}{G'\gamma_0} = \frac{G''}{G'} \quad 3.19$$

G' represents the storage modulus and G'' the loss modulus whereby G' represents the elastic part that is in-phase with the oscillating strain. G'' represents the viscous part that is out-of-phase with the strain and which is dissipated during oscillation. For fully developed wheat dough the loss factor $\tan\delta$ is between 0.3 and 0.5 (Weipert 1990). Combining equation 3.6 and 3.17 leads to:

$$\sigma = G'\gamma_0 \cdot \sin(\omega t) + G''\gamma_0 \cdot \cos(\omega t) \quad 3.20$$

With the definition of a complex number by

$$e^{i\omega t} = \cos \omega t + i \cdot \sin \omega t \quad 3.21$$

and following Euler's formula will ultimately lead to the complex modulus G^* defined by:

$$G^* = \sqrt{(G')^2 + (G'')^2} \quad 3.22$$

G^* can be defined as the consistency of dough whereby fully developed wheat dough shows G^* values of the order 10^3 to 10^4 Pa (Meerts et al. 2017; Petrofsky 1995).

From dynamic tests, the relaxation spectrum $H(\lambda)$ can be extracted when solving the following two equations:

$$G'(\omega) = G_e + \int_0^{\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad 3.23$$

$$G''(\omega) = \int_0^{\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d\tau \quad 3.24$$

with the equilibrium modulus G_e at zero frequency. The equations show frequency dependent G' and G'' which can be obtained from frequency sweep tests. The dough specimen is exposed to a frequency sweep test with a sinusoidal excitation with a varying frequency ω and a constant amplitude γ_0 . For this test γ_0 needs to be in the linear viscoelastic region of the material (LVR). This region is determined with an amplitude sweep test before the actual frequency sweep tests is conducted. In that region, G' and G'' are independent on the applied strain (see Figure 12).

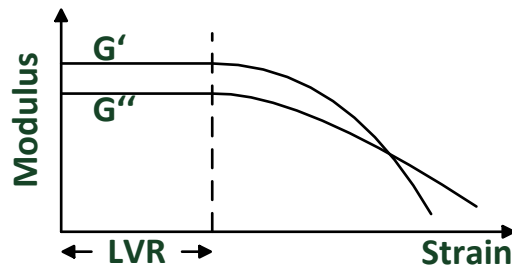


Figure 12: Illustration of the development of storage and loss modulus (G' and G'') during an amplitude sweep test. LVR indicates the linear viscoelastic region of the material.

Tests with a constant stress can cause irreversible changes to the sample during the measurement. Setting γ_0 to an order that is in the linear viscoelastic region prevents from unwanted changes or even destruction during simple and sinusoidal deformation tests. It was shown that for wheat dough γ_0 should not exceed 10^{-3} (Phan-Thien and Safari-Ardi 1998; Uthayakumaran et al. 2002). The limitation for a strain is due to strain hardening effects that occur when exceeding a material dependent strain too fast (Van Vliet et al. 1992). This results in a higher dough consistency. Like the protein composition it is a prerequisite for the gas retaining capability of dough. It is consensus that gliadin increases the viscous ratio and glutenin increases the elastic ratio of gluten. The ratio in the elastic part is related positively to the overall dough consistency. But it is also related negatively to the possible loaf volume which can be attributed to the recoiling forces that reverse the stretching process of the expanding gas in the dough. In order to avoid strain hardening during sinusoidal rheological testing, high frequencies should be avoided.

Different kinds of strains act during dough formation. The kneading hooks or mixing blades extend, compress and shear the dough. There is no single kind of strain – they all occur simultaneously during dough production and they all provoke stress in the dough matrix. The equations 3.9 to 3.24 are valid when shearing is the kind of deformation that is applied to dough. Using extension or compression, the equations can be generally applied but need to be modified. The conclusion remains similar but the order of values will be different.

When dough is exposed to a strain, a part of the applied energy can be restored. This is related to dough elasticity but another part is dissipated due to viscosity. The amount of dissipated energy can be derived from $\tan\delta$. Besides an active heating, it is responsible for the increase of the dough temperature during mixing. The rise in dough temperature can be regarded as a separate kind of strain for the forming dough (compare Figure 1).

3.4. Empirical rheology

The dough rheological properties are assessed by empirical fundamental methods but similar conclusions can also be drawn from fundamental rheological measurements. These are related to dough processing and try to imitate the respective processes or handling steps. All methods follow international standards. They assess data about stickiness, resistance to rupture, gas holding capacity, gelatinization behavior and many more.

In order to determine mixing related flour properties laboratory scale mixers are widely used as there are the Farinograph™, the DoughLAB™ or the Mixolab™. The mixing elements of these tempered mixers are connected to torque recorders. The course of torque during dough mixing allows to estimate the baking performance of the examined flour but also the water absorption capacity (Greer and Stewart 1959; Hlynka 1962). These recording mixers are suitable for the characterization of wheat (Hadnađev et al. 2011; Munteanu et al. 2015; Shurpalekar and Venkatesh 1975). Figure 13 shows a Farinograph™ mixing curve for wheat dough and the assessable characteristic numbers: Stability, Development Time, Quality Number and Softening.

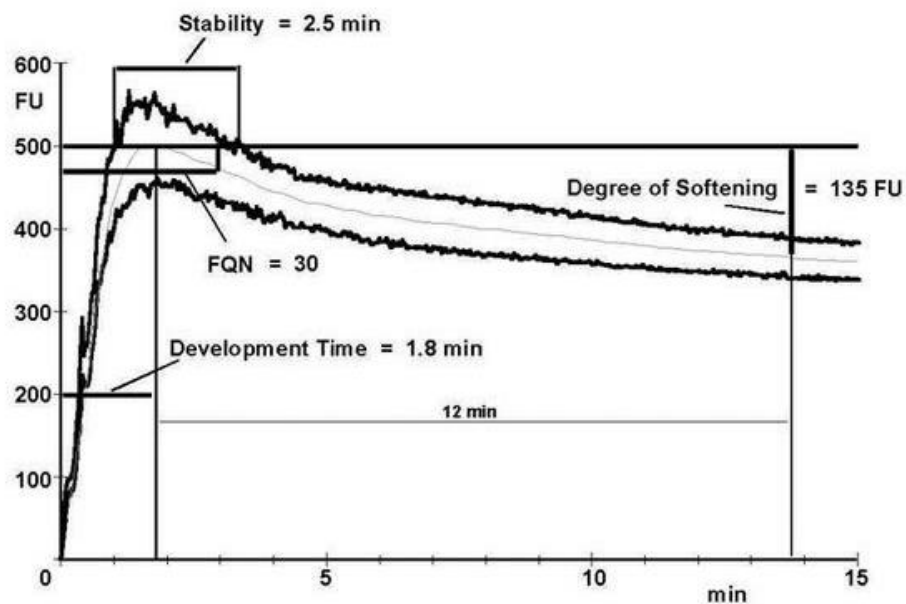


Figure 13: Typical mixing curve for wheat flour and water and the characteristic numbers that can be read from the curve (Source: www.brabender.com).

For other cereals and their doughs, the proportion of the characteristic numbers needs to be adjusted to fit the respective material (wheat, rye, corn etc. and blends) (Haridas Rao et al. 1986; Oh et al. 1986). Also the conclusion needs to be corrected when the examined material is intended for the different purposes (bread, cake, pasta) (Bahnassey and Khan 1986; Sai Manohar and Haridas Rao 1999). Another

way of assessing different characteristics is the use of specialized empirical measuring devices. In addition to the dough mixing behavior there is interest in dough extensibility, stickiness and expansion, starch gelatinization, gluten content any many more. They all support in evaluating the dough and bread quality and they can be used to relate to future properties but despite of the chemical components the other properties are more or less derivatives of the fundamental rheological properties. Orth et al. (1972) showed how to predict the future baking quality by correlating it with the protein content, the Zeleny sedimentation value and the dough development time. Preston et al. (1982) found that a correlation to baking volume is only possible when the protein content of flour was lower than 14 %. Wikström and Bohlin (1996) as well as Banu et al. (2011) extracted sensible relations between several Mixolab™ characteristic numbers and the baking quality. Multivariate modelling enabled Kurtanjek et al. (2008) to successfully relate to baking quality and to different mixing characteristics. This shows that for the right choice of assessed dough examination variables it is possible to derive aspects that contribute to the final baking quality. However, any of these empirical methods deliver information about the actual strains that are applied during measurement. The empirical rheological methods record the torque or the force in order to indicate resulting stresses. The stress as a physical number is not directly accessible and the discrimination between different simultaneously acting kinds of strains is impossible.

3.5. Thermal stress

In the course of dough production the deformation of the forming dough affects an incorporation of mechanical energy in the dough matrix. In dependence on the dough development stage, different rheological states are passed. In the final stage, the stress response of dough follows the equations above. During dough mixing, one part of the energy of the motion of the mixing hooks is spent for the development of the gluten network, another part is spent for simple geometrical deformation of the dough (shearing, stretching, distorting) and a last part of the energy is dissipated. The dissipation results in a warming of dough. The influence of this warming has different facets. Chemistry wise, the speed of the gluten development is related positively with an increase in temperature. This concerns both, wanted and unwanted reactions towards the temperature change – development and degradation of gluten.

A convenient way to modify the rheological properties of a material at a given time is to change the temperature. With an increase in temperature the dough becomes softer and its elastic modulus decreases. Williams, Landel and Ferry established a widely used equation to describe the temperature dependent changes in the rheological properties of polymers (Williams et al. 1955). The viscosity-temperature relationship is described by their Williams-Landel-Ferry equation (WLF):

$$\eta(T) = \eta_0 e^{\left(\frac{-k_1(T-T_r)}{k_2+T-T_r}\right)} \quad 3.25$$

in which the k_i are empirical constants and T_r is a reference temperature. It was established for amorphous polymers and is appropriate for any glass forming polymers like in dough and yet, it is an empirical equation. For diluted systems, it was shown that the temperature effects on the viscosity can be well described by the Arrhenius equation:

$$\ln(\eta_0) = \frac{E_a}{R \cdot T} + \ln(k_c) \quad 3.26$$

In this equation η_0 is the zero shear viscosity, E_a is the activation energy, R the universal gas constant, T the temperature and k_c is a characteristic constant of the polymer (Lu et al. 2015). Applied to dough, an increased temperature will soften and reduce its consistency. Others demonstrated that with a xanthan solution the relaxation time λ of the polymer solution was decreased (Choppe et al. 2010). This arises from a shift from elastic towards a more viscous behavior (compare equation 3.10). The same conclusion can be drawn from experiments with psyllium (Farahnaky et al. 2010). Due to the increasing temperature the phase angle increased. This shows that the viscous component of polymers will then be intensified.

Furthermore, the WLF and Arrhenius equation are used to compute the shift factor for time-temperature superposition (TTS). Therefore, rheological measurements are performed at different temperatures including the glass transition temperature T_g which is often used as reference temperature T_r . The shift factor a_T is introduced in order to relate from one temperature curve to another:

$$\log a_T = \frac{-k_1(T - T_r)}{k_2 + T - T_r} \quad 3.27$$

At T_r the decadic logarithm of a_T is zero. The shift factor indicates to what extent the measured data needs to be shifted to the left or right at other temperatures in order to fit best to the master curve within the reference time t_r :

$$G(t, T) = G\left(\frac{t}{a_T}, T_r\right) \quad 3.28$$

The graphic below illustrates the construction of the master curve for one material from fictitious relaxation measurements at different temperatures. Thus, if the master curve and a_T are known, it is possible to relate to data from the master curve at inaccessible measurement times by shifting the dataset of another measured temperature by a_T (see Figure 14).

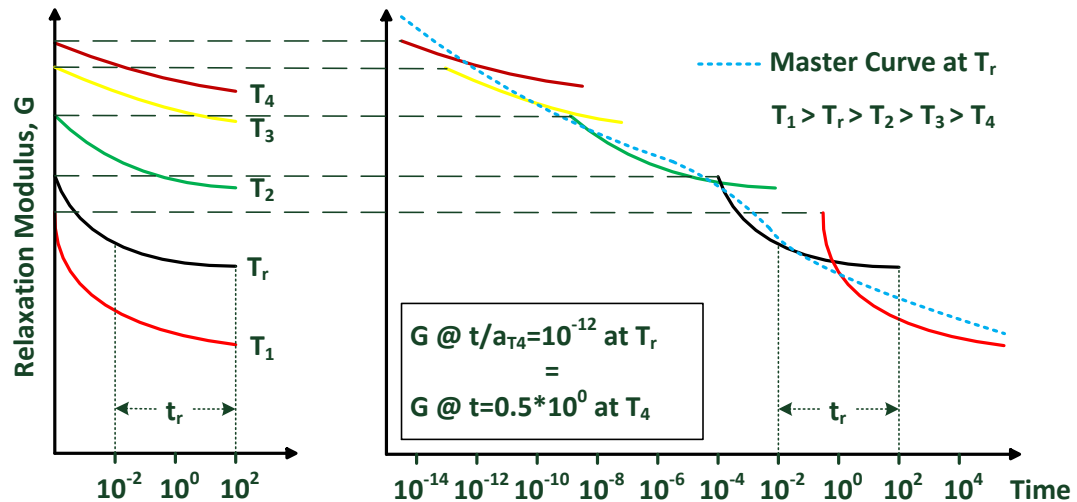


Figure 14: Schematic illustration of the construction of the master curve for time-temperature superposition and determination of the shift factor a_T at the reference temperature T_r .

Abraham et al. (2008) applied the TTS principle which enable them to examine and describe the thermal and dynamic mechanical dependent behavior of polypropylene foams at non-accessible relaxation times. In analogy to TTS, Masi et al. (1998) applied a double superposition. They shifted the data along the x- and y-axis and showed that the amount of water in dough is bifunctional. Water influences the rheological properties of the dough matrix itself and also acts as lubricant between the dough compounds. The results of similar experiments were published earlier by Lefebvre and Mahmoudi (2007) who also used the principle of TTS to examine the influence of water on wheat dough. Instead, Yang et al. (2011) involuntarily showed that the application of TTS to dough has an upper temperature limit. They recommended that the increase in temperature during the production and examination of wheat dough should be limited to around 55 °C. Dreese et al. (1988) demonstrated that starch is the limiting factor for heating dough. Starch will begin to swell and to gelatinize and to reverse the changes in the rheological properties of dough which were developed during mixing. After further heating and reaching the denaturation temperature, the proteins in dough first lose their native quaternary, later the tertiary and secondary structure and finally they

can even lose their primary structure. These losses involve the loss of the protein's functionality. It comprises the activity of enzymes and concerns enzymes like dough relevant amylases. The gluten proteins gliadin and glutenin are susceptible towards modest heat as well (León et al. 2003). In a fully developed gluten network their susceptibility towards heat is lower compared to a un-crosslinked state in native flour. Falcão-Rodrigues et al. (2005) found that the endurance of crosslinked gluten networks towards heat is mainly dependent on the additional energy that is exerted on changing the conformation of the respective proteins and on breaking the disulphide bonds. This becomes more important since heat develops during dough making. Schofield et al. (1983) showed that temperatures above 55 °C will initiate the denaturation of the gluten denaturation and that the complete unfolding process of the gluten protein is finished above 75 °C. In some cases, active cooling of dough during mixing can become necessary. For developed dough this temperature region is harmless. For water as the standard plasticizer for dough, the lower temperature limit for mixing is the point of ice formation of water. Thus, there is only a narrow temperature window for the preparation of dough and moreover a narrow window where to assess reasonable measurements. Nevertheless, the development of the rheological properties of dough during mixing is primarily examined for temperatures above 25 °C. The properties of dough at low temperatures are known. But it is unknown, how the rheological properties will develop when dough is initially mixed at low temperatures.

3.6. Combined Stress Factors

Stressors that act on dough are either of chemical or of mechanical nature and both contribute to dough development and the final dough properties. Like waves, it is possible that the stressors interfere constructively or destructively or that they have no interference. The effects of single stressors are well described but interferences of two or more stressors are hardly documented. It is difficult to describe the separate effects in a combined system. Besides water, Berland and Launay (1995) used several different dough additives and examined their effect on dough rheology. They observed the effect of the addition of ascorbic acid alone or with other emulsifiers on the dough rheological properties. They were able to show that in the presence of ascorbic acid emulsifiers like lecithin had no additional effect on dough rheology or dough. The full potential in strengthening gluten has been tapped by ascorbic acid. Similar conclusions were drawn from experiments

with varying salt levels in dough made from flours that result in different dough strengths (Casutt 1984). They revealed that the dough strengthening effect of salt decreases as the initial gluten strength increases. In a series of publications, Chin and co-workers examined the influence of several factors affecting dough rheology (Chin and Campbell 2005a; b; Chin et al. 2005). They performed experiments while varying the mixing speed, the total mixing energy, the gas pressure and the flour type. From their results can be concluded that a higher mixing time at a lower mixing speed cannot compensate for a higher mixing speed at a shorter mixing time in order to achieve similar dough rheological properties like the strain hardening index. They demonstrated that the time history in dough processing cannot be neglected. Dayang et al. (2009) examined the influence of water level, salt level and mixing time on gluten development during dough mixing. In their tests, the salt level had an overall influence but water level and mixing time were negatively interrelated in their influence on the gluten extensibility.

Although the actual effect of each single stressor on the later dough properties is known, it is difficult to quantify the combined contribution. The influences of chemical strains can be easily estimated. A constant mixing procedure would make the influence of chemical stressors more exactly predictable. Vice versa, a constant recipe with raw materials with constant properties would make the influence of physical stressors directly predictable. However, flour is a nature grown material and it will always have variations in its composition. This results in a higher deviation in the accuracy of the prediction of the ready dough properties.

Stressors that act on dough are either of chemical or mechanical nature. It is difficult to differentiate between the exact influences of a single stressor as it can affect another one. Examining the influence of temperature on dough, the temperature induces a thermal strain to the specimen (see equation 3.29 and Figure 15).

$$\alpha L_0 = \frac{\Delta L_T}{\Delta T} \quad 3.29$$

The coefficient α describes the relative increase in length ΔL_T of the body compared to its initial length L_0 in dependence on the change in temperature ΔT .

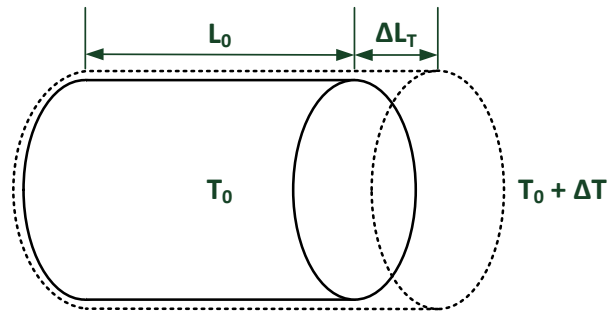


Figure 15: Illustration of a thermally induced uniaxial elongation.

The rheological measurements have to account for that otherwise the data from rheological measurements is biased. Generally, rheometers are equipped with tempering units to supply a constant temperature during the measurements. However, several empirical rheological measurements lack of tempering for instance the measurement of extensibility or stickiness. Although it is tempered before the actual measurement, the sample develops a temperature dependent history that can affect the results of the following measurement.

The same occurs when mechanical energy is incorporated into dough. The input provokes a temperature rise which will result in additional thermal expansion. In science, the dough mixing process is performed at a constant temperature but local warming of dough will still occur. It is difficult to even impossible to quantify the exact contribution of thermal and mechanical energy to dough development separately. The influence of dough warming due to mechanical energy input can be overcome if the dough specimen is very small.

4. Methodology

The general aim of this thesis is to investigate the stress response of wheat dough being exposed to different kinds of strains. Stress in materials is assessed with rheometric methods. In the field of cereal science, these methods comprise empirical and fundamental methods often acknowledged by the American Association of Cereal Chemists (AACC) and widely spread in cereal science and industry.

The test object throughout the thesis was wheat dough – depending on the test, it could have contained additional yeast or salt.

Within the design of experiment (DoE), there was only one factor that was changed in each publication. In the first one, the mixing temperature was the parameter that was changed. The second publication was a review article for which no tests were performed. In the third publication, it was the mixing time that was changed for each kind of mixing geometry. In the fourth publication, two kinds of dough processing scale were compared by which the influence of one parameter was observed.

Since one parameter was changed in each study, the DoE resulted in simple test designs following:

$$n = \sum_{i=1}^k (n_i - 1) \quad 4.1$$

with n the number of experiments, k the number of different parameters that were changed and n_i the number of levels per parameter. In order to describe the rheological properties of the dough samples different research methods were used within each study. Unless otherwise stated each test was done at least in triplicate.

Table 1 lists the procedures for dough production and dough or bread evaluation. All tests were conducted by preventing the dough sample from drying. Therefore, dough surfaces exposed to air were covered with silicone oil. It includes the preparation of dough strings for the Chen-Hoseney rig test or the edges of dough between the bottom and the top geometry in the plate-plate-rheometer.

For fundamental rheological tests, frequency or time sweeps were performed in the linear viscoelastic region of dough. The relaxation spectra were extracted from stress-relaxation data by applying the Matlab routine `contspec` which is part of the open source `ReSpect` package (Shanbhag 2013).

Statistical relations were computed using the software GraphPad Prism 5.

Table 1: Procedures for dough production and evaluation

Purpose	Procedure
Determination of bread volume	AACC Method 10-16.01
Production of dough on lab scale	AACC Method 54-70.01
Determination of dough elasticity	Kieffer Dough & Gluten Extensibility Rig
Determination of dough stickiness	Chen-Hoseney Dough Stickiness Rig
Determination of dynamic rheological properties	Frequency and time sweep tests
Determination of steady rheological properties	Stress relaxation or creep recovery tests
Determination of protein network structure	DoMiQ procedure (Jekle and Becker 2011)

5. Motivation

During dough production, different kinds of physical stress factors act simultaneously on the forming dough. They all have impact on the later baking properties to a different extent. The temperature and the mechanical energy input are the kinds of strain during dough production that can be changed in order to keep the dough composition and the dough production time constant. The mechanical mixing power and the mixing temperature are both reciprocally related to the resulting mixing time. The effect of the dough mixing temperature on the dough rheological properties is well investigated. But the investigations only aimed on increasing the mixing temperatures. Generally, ready (warm) dough is exposed to a low fermentation temperature when aiming for long term fermentation. Although the impact of low fermentation temperatures is well described in terms of the development of the aroma profile and the rheological properties, the influence of low mixing temperatures as a kind of stress factor for the development of the dough rheology is hardly examined.

A lower mixing temperature and less thermal energy input demand for a longer mixing time and more input of mechanical energy in order to produce fully developed dough. Keeping the dough mixing time constant, changes in the kind of mechanical energy input ultimately lead to either underdeveloped or overmixed gluten. This may occur when the kind of mechanical energy is changed as the consequence of the introduction of a new kneader. The efficacy of mechanical energy transmission can be different afterwards. During dough mixing, the kneading elements of a mixer apply mechanical energy by extension, compression, and shear. The studies of Peighambardoust et al. (2004; 2006) give rise to the assumption that shearing as the single source of mechanical energy can be an efficient way in order to develop dough. Shearing the dough ingredients has the potential to decrease the dough mixing time. However, the input of shearing energy can be applied in different ways as there are various sorts of shearing geometries available. But their effect on the dough development characteristics and later dough properties is not examined.

The condition and the properties of dough are crucial for the final product quality. In industrial processes it is important that each batch results in a product with equal properties and equally high quality. From the scientific point of view, it is essential to understand the process of dough formation. Exact knowledge about the stress evolution of dough towards physical strains during dough mixing enables

to model the complete process and to understand wheat dough. It enables to predict the final dough properties and to develop more efficient mixing techniques. The knowledge about origin and modification of dough behavior is crucial for both, industry and science, in order to maintain or enhance dough properties.

This thesis aims on showing the influence of low dough mixing temperatures as the first physical stress factor on the dough development and the dough rheological properties. Cool dough exhibits a longer dough development time. A more efficient dough development technique will be introduced in order to account for that. This technique uses laboratory equipment in order to develop wheat dough only by shearing – this is the second physical stress factor. Cone and plate shearing geometries are used in order to transfer the mechanical energy into the forming dough. The efficacy of the shearing geometry and the rheological changes in the forming dough are discussed. Not only the shear mixing geometry but also the kind of shearing is examined. Therefore, continuous and stepwise shearing is compared. This thesis will show whether the new dough development technique is capable of delivering the information that can be retrieved from standard laboratory mixers. In the end, a new mixing technique will be delivered that is capable of handling small dough amounts and could unify dough mixing and dough examination in one step. It is therefore suitable for breeders and laboratories.

6. Results (Publications)

Rheological Properties of Wheat Dough upon Varying Mixing Temperature

Wheat dough behaves like a pressure sensitive adhesive (PSA) and its stickiness is a serious problem for dough handling and machinability. On the basis of its adhesiveness dough residues remain on machines and equipment and can spoil. Stress is provoked by the application of low mixing temperatures. This will have an influence on the dough development and could influence the rheological properties of the final wheat dough. Besides, lower mixing temperatures could possibly lead to less stickiness as it is the case for other PSAs.

Therefore, wheat flour and a constant amount of water were mixed at temperatures between 15 and 35 °C followed by rheological characterization at the respective temperatures. Dough was examined in terms of baking relevant properties like dough development time, extensibility and stickiness. Confocal laser scanning microscopy (CLSM) was used to visualize the constitution of the protein network.

Producing dough at low temperatures resulted in extended dough development times that were attributed to the decrease in the kinetics of chemical reactions. The extensibility until rupture increased since the temperature dependent elastic modulus decreased. The measured stickiness was unaffected by lower mixing temperatures but the subjectively experienced stickiness increased drastically. Dough stickiness showed to be highly dependent on the surface to which it adheres. Due to the selectivity in adhesion it was concluded that the thermal stress factor needs special attention in terms of dough handling and processing. The selective dough adhesion possibly altered the measured rheological properties. It was supposed that the measured values did not reflect the true stress state.

For this publication, the main author conceived the idea, developed the test setups and conducted all experiments. The author evaluated the results, wrote the publication, submitted it and was the active part in the reviewing and publication process.

Possibilities to derive empirical dough characteristics from fundamental rheology

Thermal strain strongly influences the rheological properties of wheat dough. Simultaneously, the stickiness or adhesiveness can become an obstacle for alteration-free measurements of dough rheological properties. The transfer of dough specimens from the kneader to the measuring device already induces small amounts of mechanical strain into the specimen. In the result, the measurements deliver slightly altered values. Very sticky dough will be altered more during transfer and the evaluation of rheological measurements can lead to misinterpretations of the results. Since most rheological methods base on shearing the specimen, it would be straightforward to produce the dough in the rheometer. This can help to evade the disadvantages that come along with sticky dough.

The article describes the possibilities of dough production, proofing and baking in a rotational rheometer. Based on the physical and mathematical relations, computations of dough rheological properties are presented. The rheological test setups are described that are necessary to produce wheat dough by shearing and to have it examined in the direct sequence in the same device.

For this publication, the main author conceived the idea and developed the framework. The author wrote the publication, submitted it and was the active part in the reviewing and publication process.

Development of wheat dough by means of shearing

During the transfer from the kneader to the measurement device the dough specimen is exposed to additional mechanical strain. Wheat dough which is produced at low temperatures is characterized by high adhesiveness and the transfer becomes more complicated. These circumstances increase the probability to alter the dough structure and dough rheological properties during the transfer. The measurements will deliver values that do not reflect the state of dough development. Dough will be developed in the measuring device in order to avoid alterations during transfer.

Wheat flour and water are subjected to a constant strain rate in a rotational rheometer in order to develop dough. The components are exposed to shear strains for different mixing times. The dough development is evaluated by CLSM and small amplitude oscillatory shear tests. The frequency dependent rheological values were used to compute the relaxation spectra of the dough specimen. All tests were performed with a plate and with a cone geometry and the results were compared to standard dough that was mixed in z-blade mixer.

The increase in dough consistency indicated that shear mixed and standard dough have the same dough development time. But evaluation of the CLSM micrographs proved that dough development of shear mixed dough sets in later. The CLSM showed that the gluten aligns and that gluten and starch separate during shear mixing. This occurred for both tested shearing geometries. The peaks in the relaxation spectra confirmed the differences in dough development that were visualized by the CLSM. The spectra were helpful to discriminate between developed and under- or overdeveloped dough.

It was shown that it is possible to produce dough in a rotational rheometer. The exposure of flour and water to continuous shear strain led to dough development. Excessive shearing led to the separation of gluten and starch. The plate geometry proved to be more advantageous for shear mixing as the variation in the measured values is lower than for the cone geometry. Dough development and subsequent dough characterization can be performed in one device but the application of continuous shear strain cannot be recommended.

The main author conceived the idea, developed the test setups and conducted 80 % of the experiments. The author evaluated the results, wrote and submitted the publication and was the active part in the reviewing and publication process.

Advances in the development of wheat dough and bread by means of shearing

The application of simple shear to flour and water in a conventional rheometer produces dough that is comparable to conventionally kneaded dough. Besides dough formation, continuous shearing leads to unwanted separation of starch and flour. In an enhanced shear process flour and water are produced by applying consecutive stress relaxation steps with alternating shear direction. Here, the mechanical mixing energy is applied stepwise. Again, the shear mixing process was conducted in a small shearing device that was attached to conventional rheometer. Each step was examined in terms of the fundamental rheological data. For each shearing step the dynamic rheological data was used to compute the relaxation spectrum. The overview of all stress relaxation spectra over the shear mixing time revealed that there is a point after which the rheological properties of shear mixed dough did not change. With additional support of confocal laser microscopy this point could be identified as the dough development time in shear mixing. It is in good agreement with the one of standard dough. Comparing the rheological data of developed shear mixed and conventionally mixed dough both resemble up to 94 % with a repeatability of up to 96 %. Thus, the settings for the advanced shear mixing process led to dough that has comparable rheological properties. Given that information, the resulting bread from shear mixed dough should have comparable properties to standard bread. Further tests, with six different flours confirmed the efficacy of the shear mixing method. Performing proofing and baking tests in the shearing device led to invalid information. The unpredictable behavior of the added yeast resulted in dough and bread with unsteady rheological properties. However, it was shown that the application of mechanical energy in the form of shearing is highly potent in developing wheat dough with a high quality gluten network and in a short time.

For this publication, the main author conceived the idea, developed the test setups, conducted app. $\frac{2}{3}$ of the experiments and supervised the standard baking trails. The author evaluated the results, wrote the publication, submitted it and was the active part in the reviewing and publication process.

Rheological Properties of Wheat Dough upon Varying Mixing Temperature

STEFAN TIETZE, MARIO JEKLE AND THOMAS BECKER, MÜNCHEN

Abstract

The objective of this study was to process wheat dough at different temperatures between 15 and 35 °C and to examine it in terms of changes in mixing characteristics, microstructure, rheological behavior as well as textural and structural properties. Dependent on temperature and accompanying slowing of chemical reactions cool dough of 15 °C partially requires more than 200 % of the development time of warm dough of 35 °C. Rheological tests

showed that ratio of viscous and elastic behavior of dough is slightly affected by temperature. Although oscillatory rheological tests attest more than 50 % higher stiffness of cool dough, the extension force was unaffected by temperature. Stickiness of dough was less at cooler temperatures whereas extensibility was increased considerably. Image analysis revealed that gluten network degradation occurs faster at higher mixing temperature.

Keywords: dough, temperature, CLSM, rheology

1. Introduction

Wheat dough is a complex structure which has been subjected to many studies. There are numerous publications that dealt with the influence of different ingredients on dough behavior in terms of rheology, machinability or final bread quality and others. Rheological tests can be performed by evaluating properties empirically by recording mixers, extensibility tests or related tests or fundamentally when using rheometers or the Rapid Visco Analyzer (RVA) (Jekle and Becker 2012b). Several scientists examined wheat dough made from wheat with different content in high molecular glutenin subunits (HMW-GS) and evaluated the mixing and dough characteristics like Uthayakumaran et al. (2003). They found out that dough rheological properties were closely related to glutenin composition and that HMW-

GS are the key component. Others gave additives to the recipe and examined their influence on mixing characteristics and final bread quality in terms of crumb structure and others (Biliaderis et al. 1995; Wang et al. 2002). The influence of environmental effects during mixing on dough and bread structure was also examined (Elmehdi et al. 2004). It was shown that mixing under vacuum results in finer but less pores in the final bread loaf whereas overpressure resulted in the opposite. Graveland et al. (1980) showed that breakdown of gluten was limited when mixing under nitrogen atmosphere instead of air. Mixing under differently composed atmospheres was also examined by Chin et al. (2005) who found that mixing under pure nitrogen atmosphere results in softer but also more sticky dough. Machinability mostly comprises stickiness and/or extensibility tests of dough. Regarding handling of dough both parameters are of

interest for industrial bakeries. An American group (Heddleson et al. 1994) dealt with stickiness behavior of wheat dough and related it to rheological properties. They revealed that stickiness becomes negligibly small when elastic modulus of dough is higher than 50 kPa. Others developed instruments for determining dough stickiness but also made progress in identifying a possible cause for wheat dough stickiness (Huang and Hosney 1999). However, processing and baking performance of wheat dough is and was of great interest to researchers and therefore it was examined intensively in the past.

Irrespective of variations in further processing, the essential step in the making of a baked product is the kneading process. The constitution of wheat dough is mostly determined in this step (Verheyen et al. 2012). During mixing wheat flour components and water pass four phases (Cauvain et al. 2007). Prior to hydration of particles they are distributed evenly. During hydration soluble constituents become dissolved, others like starch begin to swell. After the phase of pure hydration, gluten actually begins to develop (Jekle and Becker 2012b). Gluten development is considered as formation of intermolecular disulfide bonds between glutenin and gliadin protein fraction whereas glutenin contributes to elastic and gliadin to viscous properties of final dough rheology (Macritchie 1992; Uthayakumaran et al. 1999). Rheological properties but also dough firmness can be modified by adding dough improvers or ions in the form of different salts (Beck et al. 2012). Developed gluten can be considered as a particle network consisting of glutenin aggregates in the mesoscopic size range. The equilibrium reaction of disruption and dispersion of glutenin particles is an important step in dough development. When dough is overmixed the breakdown of the glutenin aggregates results also in the cleavage of disulfide bonds, making the glutenin subunits (GS) soluble in SDS. Another effect of this further breakdown of glutenin into GS is that during dough rest the dough may not regain viscoelasticity and re-assembly of the SDS insoluble gel proteins is incomplete (Don et al. 2003). This stage is also referred to as dough softening. All stages can be visualized in recording mixers more or less quantitatively. Ready mixed dough can be considered as foam where air is

incorporated in a matrix of soluble and partly dissolved and swollen constituents. The presence of formed gluten protein has the major impact on wheat dough structure. Consisting of glutenin and gliadin fraction, gluten is capable to form a film impermeable to gases which includes air and CO₂ and thus making risen loafs possible.

Next to input of mechanical energy during mixing, the thermal environment has substantial effect on dough and bread properties. It is reported that dough mixed at 16 °C results in higher loaf volume after fermentation at this temperature and finer crumb structure after baking (Başaran and Göçmen 2003). The influence of warmer mixing temperature or freezing of dough on the changes in dough properties and dough behavior are well known (Cuq et al. 2000; Jiang et al. 2008; Schofield et al. 1983). However, the changes or effects of cool mixing temperatures on dough properties are hardly explored. On the one hand, Başaran and Göçmen (2003) showed that cool temperature (16 °C) has strong effects on dough structure during dough formation. Although Mohammed (2011) examined wheat dough with the help of temperature sweeps the actual dough was always made at a fixed temperature. So it is still rather unknown to what extent low mixing temperature has influence on fundamental rheological properties of dough or on machinability of dough. This study was set out to examine the effect of mixing temperature on: dough development, resulting gluten structure, dough rheology and texture. The intention is to reveal advantages or disadvantages of low vs. higher mixing temperature. The results may be helpful to decide whether for certain applications, e.g. biscuits, bread, cookies, noodles, a low or high temperature dough processing should be preferred.

2. Materials and methods

2.1 Dough preparation and evaluation

Model wheat dough was processed on a lab-scale recording mixer (Doughlab, Perten, Germany) according to AACC Intl. method 54-21. 50 g of commercial wheat flour type 550 (Rosenmühle, Ergolding, Germany), with ash content 0.54 mg/100 g d.m. and protein content 11.56 % d.m., and distilled water and 1.75 % NaCl on flour basis corrected to 14 % flour moisture

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were fed to the bowl and mixed until respective dough development. The mixing bowl was tempered between 15 and 35 °C. The temperatures were set to 15, 17.5, 20, 22.5, 25, 30 and 35 °C. They were kept constant during the whole mixing time. Water dosage corresponded with the water amount necessary at 30 °C to achieve 500 BU which equals 28.35 g water or 56.7 % water absorption rate of the flour. The mixing process was surveyed by recording the torque. The dough properties were evaluated in terms of development time (min) and peak consistency (Nm). Each measurement was done in triplicate.

2.2 Stickiness measurement of dough

Stickiness tests were performed to put a number on the potential machinability of the dough. Standard Chen Hosoney test was applied to dough samples subsequent to mixing with a texture profile analyzer TA XT Plus (Stable Microsystems, Godalming, UK) and corresponding Chen Hosoney stickiness cell. Settings for test runs were saved to software TA Exponent Lite v4.0.13.0 which is to manage the measuring and evaluation procedure. Test speed and post-test speed were 0.5 and 10 mm s⁻¹, applied force was 0.4 N, trigger force was 0.05 N, contact time 0.1 s and return distance 4 mm. The peak force of adhesion needed to separate the probe from sample surface was recorded and is attributed as stickiness DS (mN). Work of adhesion AS (μJ) which resembles the area under the curve when plotting force vs. distance was calculated as well as cohesiveness CS (mm) which represents the distance to which dough adheres to the moving probe. Immediately after kneading, dough was inserted the measuring cell and then applied to test procedure. All tests were done in triplicate on three doughs.

2.3 Extensibility measurement of dough

Uniaxial dough measurement was performed to determine extensibility of dough. It was performed with a texture profile analyzer TA XT Plus (Stable Microsystems, Godalming, UK) and corresponding Kieffer extensibility rig. Elongation distance was 75 mm, trigger force 0.05 N, test speed 3.3 mm s⁻¹ and post-test speed 10 mm s⁻¹. Evaluated data contained tensile strain to rupture ϵ_{em} (R) and tensile force and

Young's modulus E (mPa), respectively. After mixing, 20 g of dough were fixed between grooved silicone plates which were prior lubricated with liquid paraffin to avoid drying and sticking to the form. The plates were compressed firmly to form strings and the dough had a rest of 40 min at 20 °C. By this procedure the dough sample was separated into several single dough strings. The resulting strings were subjected to measurement whereas tests were done in triplicate on three doughs.

2.4 Rheological measurements and setup

Rheological tests of dough samples were performed with an oscillation rheometer (AR-G2, TA Instruments, New Castle, USA) equipped with a peltier heating plate. A plain cross hatched steel plate geometry (to avoid slippage) with 40 mm diameter was used. The gap between geometry and heating plate was set to 2 mm. The dough sample was fixed between the two plates, excess dough was trimmed and the edge was covered with liquid paraffin to avoid drying during measurement. A thermal cover was used to prevent unwanted cooling and buildup of temperature gradients in the dough sample. Temperature was set to the according mixing temperature. Frequency sweep was performed in the linear viscoelastic region of dough hence frequency was varied between 0.1 and 10 Hz. Prior amplitude sweeps indicated that independent on mixing temperature strains smaller than 0.3 % ensure operating in the linear viscoelastic region of dough so that deformation was fixed at 0.1 %. Frequency sweep was evaluated in terms of storage modulus G' and loss modulus G'' as well as loss factor tanδ and complex shear modulus |G*| at a frequency of 1 Hz. For creep recovery test a shear stress of 50 Pa was applied. Creep time was 5 min and recovery time 15 min. A dough rest of 1 min in the measuring device was performed prior to each measurement. These settings are optimal to ensure long enough creep and retardation and to keep the test short. Creep recovery test was evaluated in terms of elastic (J_e), remaining viscous (J_v) and maximum compliance (J_{max}), zero shear viscosity (η₀), elastic shear modulus (G_e) and equilibrium compliance (J_e) which in this case is equal to J_e. All parameters can be easily gained from the Four-Parameter-Burgers-model:

$$J(t) = J_0 + J_1 (1 - \exp(-t/\lambda_1)) + t/\eta_0 \quad (1)$$

2.5 Confocal laser scanning microscopy (CLSM)

A confocal laser scanning microscope e-C1plus (Nikon, Düsseldorf; Germany) with a 60x oil immersion objective was used for visualization of dough structure. Dough for CLSM was prepared as described above in a 50 g DoughLab bowl at a mixing speed of 63 rpm. With scissors 2.3 g of dough were taken and transferred into a specimen shape (diameter 18 mm, height 0.8 mm). The examination method is in compliance to the method of Beck (Beck et al. 2010). For marking proteins, 10 μ l Rhodamin B, concentrated by 1:100.000 in distilled water, were transferred onto the dough surface and finally covered by a thin glass plate. Proteins were monitored as fluorescence images ($\lambda_{exc} = 543$ nm, $\lambda_{em} = 590$ nm) with 512 x 512 pixel resolution (212 x 212 μ m) in a constant z-position. A detailed scale is evident in each image. Pictures were only taken of dough mixed at 15 and 30 °C. In each case, five pictures were taken which were subjected to evaluation with software for image analysis.

2.6 Software image analysis

For image analysis the open source software ImageJ was used following DoMiQ (dough microstructure quantification) method of Jekle and Becker (2011). Pictures were converted into a binary black and white picture, dark and bright threshold pixels of sizes smaller than 2x2 were removed according to the method of Huang and Wang (1995). Images were analyzed in terms of protein shape and particle properties, respectively – amount, average particle size $\bar{\phi}_A$ (mm^2), area fraction AF (%), and particle perimeter P (μ m) were analyzed.

2.7 Statistical analysis

For each set of data, statistics software Graphpad Prism 5 (Graphpad Software Inc., La Jolla, CA, USA) was conducted for evaluation of regression models by which nonlinear regression was used. If applied confidence interval was usually set to 95 %. Unless not mentioned otherwise all measurements were done in triplicate.

3. Results and Discussion

3.1 Empirical Rheology

For all tests dough was prepared with a recording z blade mixer and mixing graphs were analyzed in terms of dough or flour relevant values like dough development time.

Prior to dough preparation for TPA, rheometer and CLSM, respectively, the flour parameters have been determined (Fig. 1). As a result of lower mixing temperatures the time to achieve developed dough (corresponding to 500 BU = 1 Nm) increased. Next to hydration of flour particles, the development of dough relies on the formation of the gluten network which itself relies mainly on the formation of intermolecular disulfides bonds between gluten filaments. Finally this leads to the formation of gluten strands which are distributed three-dimensionally throughout the wheat dough. According to the hyperaggregation model mixing represents the second stage on a mesoscopic level in which glutenin polymers form larger aggregates. This occurs due to entanglement, the formation of stabilizing intermolecular disulfide bonds but also by hydrogen bonding between the glutenin polymers (Hamer and van Vliet 2000). When the temperature during mixing is raised, the chemical processes of hydration and formation of disulfide bonds is accelerated (Schofield et al. 1983). Hereby different peak development times of dough can be explained in which the highest consistency reached during mixing refers to the point of optimum gluten development. Compared to 30 °C, an increase in mixing time from 2 to 5 min occurred when

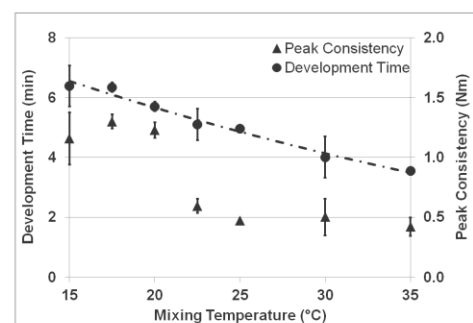


Figure 1: Illustration of wheat dough development time and peak consistency in dependence on different mixing temperatures ($x \pm$ s. d.; $n = 3$).

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operating at 20 °C and lower. Operating in cooler ambient, development time of dough was about 2.5 fold higher. There is no linear relationship between peak development time and mixing temperature. Moreover, the warm and the cool mixing regime each exhibited a span of time in which mixing time were quite constant (Fig. 1). The sudden change in mixing time can be attributed to the development of the gluten network. At higher temperatures, end of hydration phase almost overlaps with peak development of the gluten network. This general difference in development time and dough consistency is visualized in Fig. 2. However, peak consistency is clearly negatively correlated to mixing temperature. The coolest dough at 15 °C exhibited a 1.6-fold higher resistance than standard dough at 30 °C (1.00 ± 0.17 Nm). The consistency of dough at lower temperature is increased so that displacement of dough by the mixing blades requires more energy and thus higher torques are generated. At 15 °C, hydration and gluten development phase can be clearly distinguished due to prolonged reaction times. The first maximum relates to blending and full hydration of flour particles whereas the second maximum indicates the complete development of the gluten. With lower temperatures the mobility of water is decreased and hydration is expected to be slower. It is the same for gluten network formation (Hébrard et al. 2003) and in detail the formation of covalent disulfide bonds which are the basis of gluten aggregation but also other related processes occur at lower reaction rates. Since processes at lower temperature are retarded dough stability is higher for cool dough and softening is less, in general. Dough breakdown or softening of dough occurs due

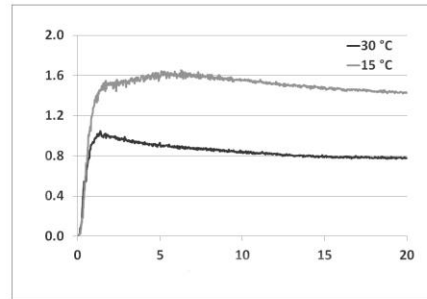


Figure 2: Illustration of the comparison of the course of the mixing curves for wheat dough at standard (30 °C) and at the coolest mixing temperature (15 °C) ($x \pm s. d.$; $n = 3$).

to a shift off the equilibrium of formation and breakdown of disulfide bonds towards breakdown in which glutathione cleaves disulfide bonds, occupies them and thereby weakens the gluten network. Glutathione is flour immanent or can be released by added yeast cells. Next to that also excessive input of mechanical energy can contribute to gluten breakdown. On the one hand, mechanical energy is essential for the development of the gluten network during wheat dough processing. Without mechanical energy the flour particles are only present in their hydrated state without having formed any disulfide bonds as they are present in fully developed gluten as it was presented when dealing with zero-developed dough (Campos et al. 1997). On the other hand, when applying mechanical energy beyond the point of optimum dough development, the surplus energy contributes to the separation of the formed gluten network. The network

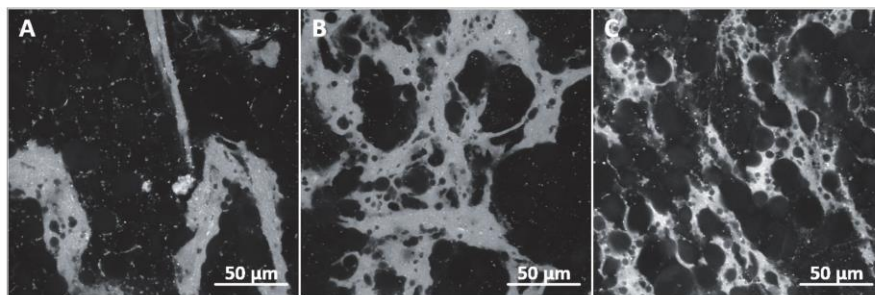


Figure 3: CLSM micrographs of dough mixed at different temperatures and different stages of development. A) dough mixed at 15 °C at the stage of hydration phase; B) dough mixed at 15 °C at the stage of full gluten development; C) dough mixed at 30 °C at the stage of full gluten development.

which consists of glutenin macropolymers (GMP) is degraded to smaller, SDS-soluble glutenin macropolymer strands (Skerritt et al. 1999). These strands are more mobile in dough and thus the dough is less resistant towards deformation in the mixer. By that, the dough loses parts of its capability to retain gas and recovery of former viscoelastic properties is limited.

3.2 Visualization of dough structure

As seen with the mixing characteristics of cool and standard dough, cool dough exhibits slower dough development. By this behavior visualization of different states in dough development is possible. The samples were subjected to a confocal laser scanning microscope (CLSM). By dyeing certain specific components of dough, it is possible to specifically highlight only starch or proteins e.g. With the CLSM three different dough samples were examined (see Fig. 3): dough A was mixed at 15 °C until end of hydration phase, dough B was mixed at 15 °C until peak mixing time and dough C was mixed at 30 °C until peak mixing time. Since with 30 °C end of hydration phase and peak mixing time merge into one peak, only this peak could be examined. These images are to show basic differences in cool and warm mixed dough. In Fig. 3-A, the gluten structure (indicated blue) of dough mixed at 15 °C to completed hydration phase is visualized. A gluten network has not developed yet; instead, thicker protein strands are detectable. Fig. 3-B shows dough at 15 °C where the gluten network is fully developed. The protein molecules formed an irregularly shaped network with randomly oriented filaments throughout the dough. At 30

°C (Fig. 3-C), the formed gluten network was also widely spread throughout the dough but in contrast to 15 °C filaments were thinner but also more fragmented. Dough at 30 °C is easier to deform and stretch and therefore filaments are thinner and maybe partly disrupted.

Differences between mixing temperature and the stage of mixing become clearer after image processing and analysis of pictures taken with the CLSM. The values are shown in Table 1. Comparing the finished hydration step (A) and gluten development step at 15 °C (B) the area fraction (AF) of particles increased by 62 % and average particle area (\bar{A}) increased by 36 % meaning that employing more mixing energy into the dough leads single particles to join and to form a network. In contrast to single protein strands this interlinked network cannot avoid mixing motion easily and thus is stretched. This is also confirmed by particle count (ΣP) which decreased during further mixing by about 20 % from 42.9 to 34.3 single particles. During gluten development, the protein perimeter (P) increased from 56.9 to 72.6 μm and 28 %, respectively. This suggests a change from more globular shape to stretched filaments but also to increased serration. It is confirmed by an increase of the perimeter with simultaneous increase of particle area. However, input of mixing energy is also accounted for disaggregation of gluten even before dough is completely mixed to final peak development (Don et al. 2003; Skerritt et al. 1999). This is not the case for dough mixed at 15 °C.

Comparison of fully developed dough mixed at 15 (B) vs. 30 °C (C) shows that the average ΣP increased by

Sample		A – 15 °C after finished hydration	B – 15 °C after dough development	C – 30 °C after dough development
Count	(-)	42.9	34.3	90.3
Total Area	(μm^2)	8919	14459	10909
Average Size	(μm^2)	343.1	465.2	144.4
Area Fraction	(%)	21.9	35.4	26.7
Perimeter	(μm)	56.9	72.6	35.8

Table 1: Results from image analysis of the CLSM micrographs ($n = 9$)

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over 150 % at higher temperature, from 34.3 to 90.3. The additional input of thermal energy next to mechanical energy due to mixing action supports a decrease in DA of 69 % (from 465.2 to 144.4 μm^2) and also a decrease in average P from 72.6 to 35.8 μm (50 %). The average size of protein particles decreased thus agglomerates were separated into more but smaller fragments. This is also confirmed by an almost unchanged AF comparing fully developed dough B and C. Although heat promotes formation of intermolecular disulfide bonds it is more likely that the process of gluten breakdown is accelerated and slowed re-assembly of gluten, respectively. According to Don et al. (2005), breakdown sets in when mixing beyond peak development which also means that overmixing pushes glutenin breakdown beyond the ability of the gluten gel to recover during dough rest.

3.3 Oscillatory testing of dough

Oscillatory tests are useful to examine the dynamic response of viscoelastic material towards sinusoidal deformation. Within the range of tests, frequency sweep tests were made in which frequency was increased from 0.1 to 10 Hz. Based on the mathematical relationship, frequency dependent behavior of dough showed increasing storage or elastic modulus G' , loss modulus G'' and complex modulus $|G^*|$ over increasing frequency (data not shown) as it is typical for dough when examined in the linear viscoelastic area (Uthayakumaran et al. 2002). The development of dynamic rheological behavior in dependence on temperature is shown in Fig. 4.

By trend, the ratio between viscous and elastic modulus (loss factor $\tan\delta$) varied only slightly over mixing temperature whereas the highest was with the lowest temperature. Overall, it ranged between 0.43 and 0.40 which is in agreement with findings of Uthayakumaran (1999) but can be regarded as decreasing which means that in dependence on temperature the elastic and viscous nature of dough is affected to that extent that the elastic proportion is increasing with warmer dough. There are at least significant decreases in $\tan\delta$ when comparing 15°C-dough with all dough warmer than 22.5 °C ($p < 0.01$). When operating at higher T proteins' thermal motion is increased. Thereby it is possible that residues containing glutamine come

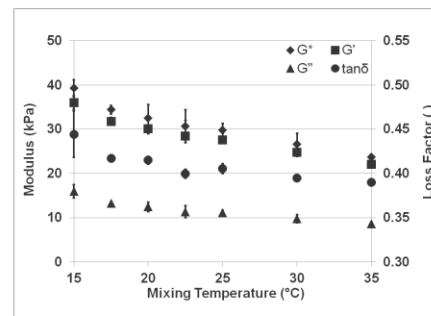


Figure 4: Dependence of rheological moduli and loss factor on mixing temperature. Values displayed for 10 Hz ($x \pm s. d.$; $n = 3$).

closer to be able to form further non-covalent bonds by which also the size of the GMP increases (Lefebvre et al. 1993). Considering the glutenin as an entangled polymer more hydrogen bonds between glutenin now contribute to an increase in the elastic component of dough since more bonds stabilize the gluten network. At low temperatures the chance for formation additional non-covalent bonds is reduced so that dough behaves more viscous. Within the range of temperature the course of $\tan\delta$ behaves in double reciprocal manner ($r^2 = 0.76$) in which $\tan\delta$ correlates negatively with mixing temperature.

Dough softness at 1 Hz represented by complex modulus $|G^*|$ decreased by 39.8 % with higher mixing temperature that is due to less rigidity of polymer chains in dough meaning that deformation and evading action of molecules is facilitated. This is controversial since the potential of interactions between polymers is increased. However, also molecule slipperiness is increased due to simple viscosity decrease which is the dominating effect in this case. Since overall mixing action during rheological measurements is limited the probability of the formation of new intermolecular bonds is low. This is in agreement with findings about zero developed dough where it is said that it demands for input of mechanical energy to have a gluten network developed (Hamer and van Vliet 2000). For the dependence of G' and G'' on temperature exponential equations according to the general Arrhenius equation can be fitted ($r^2 = 72.19$ and $r^2 = 74.91$) whereby dough is considered as a liquid in this case:

$$G'(T) = 14.70 \cdot \exp(17494/RT) \quad (2)$$

$$G''(T) = 0.41 \cdot \exp(23786/RT) \quad (3)$$

In these equations T represents mixing temperature in K and R the gas constant. In all cases, elastic modulus of dough (G') preponderated over loss modulus (G'') representing higher elastic than viscous behavior and showing that dough behaves as distinctive viscoelastic material.

3.5 Dough behavior in creep tests

In addition to oscillation tests, creep tests were made to reveal the response of dough towards constant stress or strain rate which can be considered as simulation of processes with constant shear stress like dough sheeting. From that point, results from creep and oscillation test are only directly comparable when creep time goes towards zero and oscillation frequency goes towards infinity. Although the results will not be exactly identical, there can be similarities in rheological behavior.

Having evaluated the mixing curves it can be seen that dough consistency was negatively dependent on temperature. This trend can also be applied when examining the zero shear viscosity which is shown amongst others in table 2. The impact of temperature is generally increasing. Lowering mixing temperature from 35 °C to 15 °C zero shear viscosity increased by more than 50 %. The temperature effect on damping performance of viscoelastic materials has already been modeled and it could have been shown that the damping performance is reduced with increasing temperature which results in less energy needed for deformation (Tsai 1994). Applied to wheat dough, this means that

viscosity is reduced in general. In detail, at the level of the gluten proteins, it is gliadin component that is responsible for the viscous character of dough (Khatkar et al. 1995) and thus the one which will be influenced in its behavior due to temperature change. Higher viscosities as for low temperatures have the advantage of granting more stability to air bubbles in the dough, standing higher gas pressures in the dough and thus higher possible loaf volumes after fermentation and baking (Başaran and Göçmen 2003). Elastic deformation J_e and elastic compliance, respectively, increases with temperature. In the Burgers model purely elastic deformation is represented by a spring element. As it is for most materials and also dough, the underlying spring constant (G_0) decreases with increasing temperature so that elastic deformation is facilitated which in turn results in greater deformation but also reformation of dough after molding or sheeting. Due to increased temperature the partial degradation of the gluten network is inevitably further progressed or has at least begun so that the cohesive forces between entangled particles are reduced but secondary interactions of protein particles due to higher particle surface increased. By this, smaller local networks by them are capable to deflect faster and to comply easier. As for elastic and also viscous deformation, viscoelastic deformation is also easier and occurs faster at warmer mixing T as it is indicated by a decreasing retardation time (λ_1) over temperature. It can be resumed that cooler temperature results in firmer dough on the one hand but on the other hand it results in dough which is able to stand higher stresses without degradation of gluten network as could be seen with the CLSM micrographs.

Temperature (°C)	η_0 (Pa s)	G_0 (Pa)	λ_1 (s)	J_e (1/Pa)	J_{max} (1/Pa)	J_c (1/Pa)	J_v (1/Pa)
15.0	1.13E+06	2.12E+04	6.69	1.18E-04	7.98E-06	4.71E-05	1.22E-02
17.5	1.09E+06	1.91E+04	6.05	1.22E-04	8.34E-06	5.24E-05	9.43E-03
20.0	1.04E+06	1.80E+04	5.91	1.33E-04	8.89E-06	5.55E-05	7.71E-03
22.5	1.05E+06	1.70E+04	5.58	1.23E-04	8.71E-06	5.87E-05	1.09E-02
25.0	1.02E+06	1.72E+04	5.63	1.23E-04	9.48E-06	5.81E-05	8.50E-03
30.0	8.67E+05	1.49E+04	5.08	1.32E-04	1.01E-05	6.72E-05	1.28E-02
35.0	7.37E+05	1.33E+04	5.10	1.48E-04	1.17E-05	7.52E-05	1.77E-02

Table 2: Parameters evaluated by a four parameter Burgers model for rheometer creep tests ($n = 3$)

3.6 Texture Analysis

Texture analysis of dough was split into extensibility and stickiness test. The respective results are displayed in Fig. 5. Extensional test revealed ambivalent behavior of dough in dependence on temperature. In general, ϵ^R decreased the warmer the dough was mixed. Overall, tensile strain decreased from 11.5 to 8.9 (-23 %). Comparable observations were also made by Kieffer et al. (1998). Explaining gluten behavior with the "loop and train" model (Belton 1999) in which viscosity is relying on loops and elasticity relies on trains between polymer strands, one can conclude that at low temperatures only few trains exist. Mixing at warmer temperature accelerates protein bonding which can lead to formation of more intermolecular bonds so that the size of eventual loops is reduced. Extending these small loops results in lower extensibility before dough strings disrupt. Operating in the microscopic range, Jekle and Becker (2012a) assumed that differences in extensibility of dough are due to differently charged parts in the protein strands and thus resulting in different states of aggregation. Resulting varying water uptake causes slippage of gluten strands and in the end extensibility. They observed this phenomenon when operating at varying pH-values of wheat dough.

Young's modulus E showed only small fluctuations over the range of measured mixing T of dough which means that in the applied range no other types of bonds between molecules are affected as there are also ionic and hydrogen bonds involved when it comes to gluten formation in dough (Wieser 2007). Having mixed at warmer temperatures than 30 °C, E of dough increases significantly from former 6.5 mPa to 8.8 mPa (+35 %). It can be assumed that gluten strength above 30 °C is higher due to further formation of more non-covalent bonds between protein molecules as they also determine dough extension properties. On the one hand this strengthened network can stand higher stresses (increased E) but on the other hand it is less extensible (decreased ϵ^R). These outcomes are in contrast to simple dough mixing experiments or rheological testing (see above) where dough became softer and easier to deform when mixed at higher temperatures. It gives rise to the assumption that the applied strain in tensional direc-

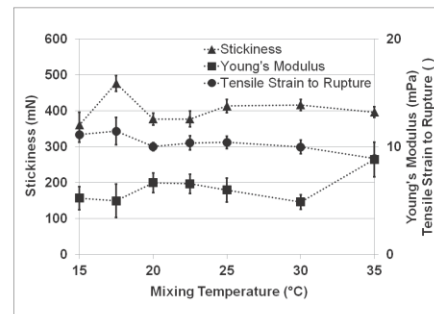


Figure 5: Obtained data for tensile force, extensibility, stickiness of wheat dough ($x \pm s. d.$; $n = 9$).

tion causes stresses inside dough to exhibit so called strain hardening. Kokelaar et al. (1996) examined this phenomenon in dough from different wheat cultivars intensively and concluded that the more pronounced strain hardening the higher is the later baking quality in terms of loaf volume and crumb properties. With strain hardening a persistent film between gas cells in dough is preserved which is of importance during fermentation and oven rise to prevent film/gluten rupture and thus coalescence of gas bubbles.

Similar to tensile force, stickiness of dough samples was mostly unaffected and showed no clear dependence on mixing temperature. A correlation between mixing temperature and dough stickiness behavior does not exist. In the course of measurements the stickiness ranged between 360 and 480 mN. Since wheat dough is considered a pressure-sensitive adhesive (PSA) it is said that the viscosity causing component is responsible for the sticky or tackifying behavior of dough (Heddleson et al. 1994). Although gliadin is attributed as viscosity causing component in dough a carbohydrate could have been identified that is mainly responsible for stickiness of wheat dough. It consists of 71 anhydroglucose units with an attached trans ferulic acid moiety (Huang and Hosney 1999). This makes an approximate molar mass of 13,000 gmol⁻¹ so that this will likely be the cause for stickiness. Nevertheless, other carbohydrates deriving from starch degradation can cause stickiness as well as it would do a sucrose solution. In general, stickiness is dependent on temperature since it increases the closer one operates near to the glass transition temperature (T_g)

of the respective material (Slade and Levine 1995). The T_G of dough is around 30 °C. Since stickiness is hardly differing due to the mixing temperatures one can assume that the chosen temperature regime is far from T_G of the stickiness causing carbohydrate. Otherwise there should have been a distinct difference in stickiness.

Adhesion can be defined as failure in cohesion and vice versa. According to the Dahlquist criterion (Heddeson et al. 1993), stickiness in terms of cohesion and adhesion of PSAs is almost insignificant when elastic modulus G' is near 50 kPa and non-existing when G' is above that threshold. The highest obtained value for G' of here examined dough was 36 kPa at 15 °C compared to 22 kPa at 35 °C. With the examined dough samples, indeed G' increased with cooler temperature but dough adhesion in the sense of stickiness values was not affected to the expected extent. Moreover, stickiness remained quite constant over the observed range of temperature. Although storage modulus of bread crumb is about 5 kPa, stickiness should not be a problem for baked goods as they are not considered as PSA. It is rather a problem for dough handling and machinability when dough is too sticky as it is the case for warm mixed dough.

Cohesiveness and work of adhesion behaved positively linear to each other ($r^2 = 0.985$) in which work of adhesion dominated over cohesiveness. Both showed decreasing behavior in dependence on mixing temperature but at 15 °C dough exhibited an unexpected drop (data not shown). It can be assumed that at 15 °C the gluten network is completely developed but solubles in flour are still partly undissolved. At 17.5 °C these insolubles can become dissolved and contribute to cohesive potential which might be a factor in work of adhesion. However, dynamic scanning calorimetry of dough did not help to underpin this speculation.

4. Conclusion

The influence of different mixing temperatures on dough properties was examined by rheological, microscopic and textural analysis.

Empirical and fundamental rheological procedures indicate that dough processed at cool temperatures

is less favored for bread making since dough promises less loaf volume after baking. In contrast, textural examination, in detail tensile stressing, indicated the opposite. Young's modulus is higher at warmer temperatures by which one can assume smaller loaf volumes. Since cool dough needs more time for full development its application is not without taking disadvantages. As seen in tensile testing warmer dough on the other side exhibits the wanted strain hardening to a greater extent which is favorable for loaf volume but shows more stickiness which is problematic in dough handling. Choosing the correct mixing temperature can be sophisticated – both, coolest and warm dough promise higher loaf volumes but dough development kinetics vary drastically. Both doughs demand for different handling and treatment due to different physical properties. It has to be up to the baker which pro-

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cess is favored since next to loaf volume and dough handling aroma is the next decisive factor in bread quality.

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Review

Possibilities to derive empirical dough characteristics from fundamental rheology



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ABSTRACT

Background: The determination of dough properties is essential for the estimation of dough processing, dough handling behavior and future bread properties. Several methods are available for the analysis of these values. These include empirical rheological methods like torque recording during mixing, extensibility measurement or fundamental rheological methods. All have in common that the dough specimen needs to be transferred from one device to another. This leads to an additional incorporation of mechanical energy and by that to an alteration of the dough structure. As a result, the measurement data can be defective.

Scope and approach: This review describes the working principles of the traditional empirical methods and shows how the additional energy input can be avoided. In order to avoid alteration of data different measurement techniques are discussed that can be performed in one device and that deliver correct information about the dough properties.

Key findings and conclusions: Instead of common correlations, real physical and mathematical connections and links are shown in order to derive the values of the classical dough testing methods by fundamental rheological measuring techniques. These equations are the base for a successful data conversion between empirical and fundamental rheological methods. The reliable data conversion is crucial for a successfully working measurement technique that can be performed in a single conventional rheometer. This eliminates unwanted data alteration and assures proper machine settings for dough handling.

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1. Introduction

Over the decades several characteristics and measuring systems were developed to judge baking performance from dough properties. These systems describe dough development characteristics, dough handling properties and the following processing steps like proofing and baking. Knowledge of these dough characteristics is helpful to estimate properties of the final bread. Bread properties mostly comprise bread volume, crumb texture and up to a certain degree also sensorial attributes. For each tool, specific dough attributes are measured and correlated with bread attributes. In most cases, the correlations are quite high due to the underlying biochemical and physical mechanisms. On the other side, certain aspects of dough behavior and bread properties were correlated

that have no obvious relationship like bread volume and values from oscillatory shear tests (Dobraszczyk & Morgenstern, 2003).

In classical dough evaluation, empirical rheological methods are widely used for characterization. In these methods, shear, compression and extension as the basic types of deformation occur simultaneously (Charalambides, Wanigasooriya, Williams, Goh, & Chakrabarti, 2006). The most important empirical rheological methods are the Farinograph, the Extensograph, the Rheofermentometer and also standardized baking tests for wheat flour/dough. The Farinograph and comparable recording mixers work well for the determination of the optimum mixing time or the detection of mixing tolerances. Both methods allow the prediction of bread volume as part of the baking quality (Konopka, Fornal, Abramczyk, Rothkaehl, & Rotkiewicz, 2004; Oliver & Allen, 1992). The Extensograph measures the stretchability of dough which is a prerequisite for high bread volumes. In most cases it showed high correlation with the baking volume (Horvat, Magdić, Šimić, Dvojković, & Drezner, 2008; Janssen, van Vliet, & Vereijken, 1996;

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Ktenioudaki, Butler, & Gallagher, 2010). Dough stretchability and gas retaining capacity are crucial for the final bread volume. They can be determined with the Rheofermentometer (Banu, Stoescu, Ionescu, & Aprodu, 2011; Hadnadev, Pojić, Hadnadev, & Torbica, 2011; Huang, Kim, Li, & Rayas-Duarte, 2008). All empirical methods have in common that the sample is exposed to high settings in deformation, temperature, pressure, time or energy input. In most cases, this comes along with a destruction of the sample or an alteration of the structure since they were developed for the simulation of the usage, the handling or the consumption of the intermediate or the final product which indeed undergoes changes in reality. On the other hand, there are the fundamental rheological methods. Only one of the basic types of deformation is applied during the measurement. The advantages that come along with fundamental rheological methods are easy computation of related physical properties, easy handling, robustness and non-destructivity. Small samples are used to avoid inertia phenomena and the samples are protected against alterations like drying out. These methods are very common in science but not in cereal industry. A direct comparison and correlation of empirical and fundamental methods can lead to erroneous conclusions. This results in a reduced efficacy in predicting dough or bread properties and successful correlations may have only occurred by chance (Autio, Flander, Kinnunen, & Heinonen, 2001). The link between a correct prediction of bread properties and fundamental rheological methods is missing.

This review is settled in a yet undiscovered field of science. It has the aim to show the most common methods that are used in the cereal and baking industry for the estimation of baking quality. It will also comprehend how the underlying working and measuring principles can be translated to fundamental rheological tests. For this purpose, the fundamental rheological tests are considered to be performed by means of shear rheometry. The missing link in form of the mathematical derivation from empirical to fundamental rheological methods is the key aspect of this review and will be outlined for a better overview. This review is organized into several parts. Each part deals with a processing step during bread production. These steps include dough formation, dough characterization in terms of stickiness and extensibility and finally proofing and baking. It is also intended to demonstrate to what extent results from fundamental rheological measurements can be converted to corresponding values from empirical tests. This can enhance the prediction accuracy of fundamental rheological methods and give suggestions for appropriate tests which could lead to reasonable interpretation.

2. Rheometer basics – standards in dough rheometry

In cereal science rheometers have been used intensively to study the behavior of dough at certain stress states or to have an insight in changes due to varying ingredients. Weipert demonstrated this topic comprehensively and illustrated the applied strains and strain rates during dough processing (see also Fig. 1) (Weipert, 1990, 2006). The rheometer enables testing in either non-destructive or destructive regions of the material. It is possible to conduct dynamic or transient testing depending on the respective region of interest. Dynamic testing allows the study of a process that occurs at high speed. These tests comprise oscillatory tests with varying frequency or shear rate (frequency sweep) or varying amplitude or strain (deformation sweep). Sweep tests with varying shear stress or temperature are also possible. Transient testing allows the observation of changes occurring at low speeds. Transient tests can be either driven by a constant stress (creep tests) or constant strain (stress test). Dough is a viscoelastic material and hence depending on creep or stress tests which are stress and strain

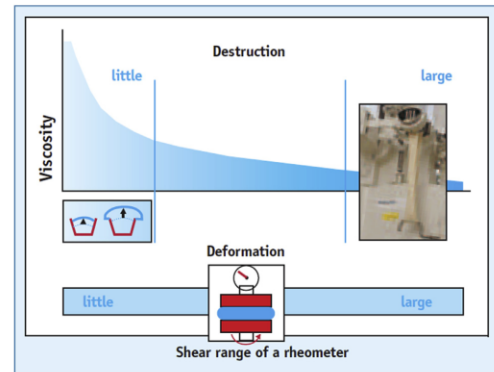


Fig. 1. Stress strain curves of wheat flour doughs with different dough properties recorded with a rotational viscometer (left) and a viscosity curve showing "yield point" and "shear thinning" (right) (Weipert, 2006).

driven, respectively, the Kelvin-Voigt and the Maxwell model are applied. Fig. 2 displays the differences in both basic models for viscoelasticity.

Although extrinsically appearing as a solid dough acts like a viscoelastic liquid when it is exposed to a sudden constant deformation. In general, the recorded decrease in stress or modulus of dough can be written in the form of an exponential function:

$$\frac{\sigma(t)}{\gamma} = G(t) = \sum_{i=1}^n G_i e^{-\frac{t}{\tau_i}} \quad (1)$$

$$G(t) = \int_{-\infty}^{+\infty} H(\tau) e^{-\frac{t}{\tau}} d\tau \quad (2)$$

With the shear stress σ , the shear modulus $G(t)$ at time t , the shear modulus of each Maxwellian element G_i , the corresponding relaxation time of each Maxwellian element $\tau_i = \eta_i/G_i$ and the strain γ . When plotting G_i over τ_i the discrete relaxation spectrum can be visualized. It is characteristic for each material. For approximation of the continuous relaxation spectrum $H(\tau)$ the discrete relaxation spectrum is used as it is mathematically easier to access. The spectrum can be also gathered from dynamical tests. Then the strain is applied in sinusoidal manner and the resulting shear modulus is displayed as the complex shear modulus $|G^*| = ((G')^2 + (G'')^2)^{0.5}$. Typical values for G^* are in the order of 10^1 kPa but G' , G'' and thus G^* depend on water content, temperature, air inclusions or on cultivar and thus gluten network strength. Due to viscoelasticity a phase shift occurs during oscillation between given sinusoidal displacement and resulting strain. This phase shift δ is used for calculation of the loss factor $\tan \delta = G''/G'$ which is usually between 0.3 and 0.5 for fully developed wheat dough (Weipert, 1990). In this equation G' is the storage modulus and represents the elastic part which is in phase with the strain during oscillation. On the other hand, G'' is the loss modulus which represents the viscous part that is out of phase. Performing frequency sweeps the relaxation spectrum $H(\tau)$ can be extracted from the following relationships:

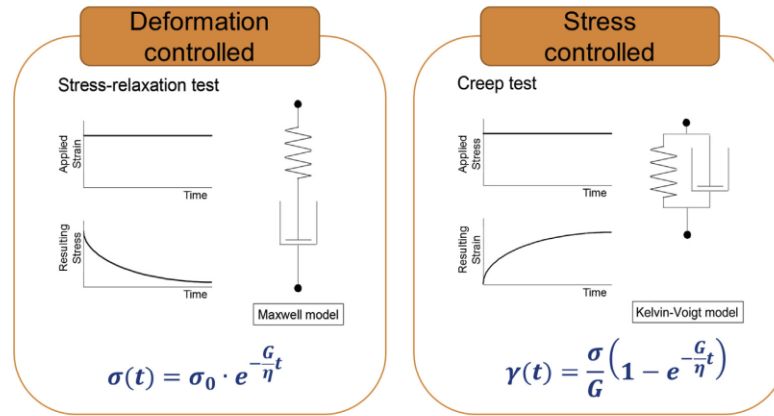


Fig. 2. Illustration of viscoelasticity in terms of the Maxwell (left) and Kelvin-Voigt model (right) (γ – strain, σ – stress, G – shear modulus, J – compliance).

$$G'(\omega) = G_e + \int_0^\infty H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (3)$$

$$G''(\omega) = \int_0^\infty H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d\tau \quad (4)$$

with the equilibrium modulus G_e at zero frequency. For liquids G_e is zero and for solids it is greater than zero. In stress testing with constantly applied strain dough is considered a viscoelastic liquid. For creep tests where stress is constantly applied dough is considered a viscoelastic solid. From these tests is possible to compute a retardation spectrum $L(\lambda)$ similar to the related relaxation spectrum $H(\tau)$. Actually, wheat dough is unable to return completely. Therefore additional terms were added for satisfaction. This leads to the Burgers model which consists of one Maxwell model and several Kelvin-Voigt models in series. The recorded compliance J can be written as

$$\frac{\gamma(t)}{\sigma} = J(t) = J_0 + \sum_{i=1}^n J_i \cdot \left(1 - e^{-\frac{t}{\lambda_i}}\right) + \frac{t}{\eta_0} \quad (5)$$

$$J(t) = J_0 + \int_{-\infty}^{+\infty} L(\lambda) \left[J_i \cdot \left(1 - e^{-\frac{t}{\lambda_i}}\right) \right] d\lambda + \frac{t}{\eta_0} \quad (6)$$

with the instantaneous elastic compliance J_0 at time, the shear compliance $J(t)$, the contribution to compliance of each Kelvin-Voigt element J_i , the corresponding retardation time of each element $\lambda_i = \eta/G$ and the zero shear viscosity η_0 . The following equations govern the determination of the retardation spectrum from dynamical tests:

$$J'(\omega) = J_0 + \int_0^\infty L(\lambda) \frac{1}{1 + \omega^2 \lambda^2} d\lambda \quad (7)$$

$$J''(\omega) = \frac{1}{\omega \eta_0} + \int_0^\infty L(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} d\lambda \quad (8)$$

The spectra $H(\tau)$ and $L(\lambda)$ cannot be read directly from the equations that describe the behavior in dynamic or transient testing. Equation (2) and the Kelvin-Voigt part of Equation (6) are a Fredholm integral of the first kind:

$$g(s) = \int_a^b K(s,t) f(t) dt, \quad a \leq s \leq b \quad (9)$$

In this integral, $K(s,t)$ is the kernel $e^{-t/s}$, $g(s)$ is the measured signal and $f(t)$ is the unknown solution which is the wanted spectrum. Solving this integral is an ill-posed problem. The solution is very sensitive towards experimental noise and a large number of relaxation/retardation times. Different methods were developed to overcome ill-posedness and to compute the spectrum from data deriving from either transient or dynamical tests (M. Alcoutlabi & Martinez-Vega, 1998; Mataz Alcoutlabi & Martinez-Vega, 2003; Baumgaertel & Winter 1989; Brabec, Rögl, & Schausberger, 1997; Hansen, 1992; Honerkamp & Weese, 1990, 1993; Kaschta & Schwarzl, 1994; Malkin, 2006; Malkin & Kuznetsov, 2000; Stadler & Bailly, 2009). The foundation of some algorithms is a least-squares-fit to Equations (3) and (4) or (7) and (8). They differ in whether τ_i or λ_i are fix or being determined by the algorithm. Another approach is the fitting of integral or differential fractional equations. Other successful algorithms base on the usage of advanced nonlinear regularization methods. The available procedures were discussed and it was concluded that they are comparable in their accuracy. This qualifies each of them for computation of the spectra for dough. In case of $G(t)$ the spectrum displays the distribution of relaxation times τ_i and the ratio to which the respective G_i contribute to the total G . Physical interpretation is obvious but molecular interpretation is difficult. Wheat dough which exhibits short relaxation times contains mostly elastic and solidifying molecular structural components. On the other hand, long relaxation times can be interpreted as softening structures dominated by viscous flow. In polymer science the relaxation or retardation spectra can also be used to check for monodisperse or polydisperse molecular weight distributions (Cassagnau, Montfort, Marin, & Monge, 1993; Li, Dobraszczyk, & Schofield, 2003; C.; Liu, He, Ruymbeke, Keunings, & Bailly, 2006; Thimm, Friedrich, Marth, & Honerkamp, 1999). The spectra allow a deeper insight in the molecular structure of gluten or wheat dough which was demonstrated for hydrated gluten samples (Kontogiorgos & Dahunsi,

2014; Kontogiorgos & Kasapis, 2010; Kontogiorgos, Jiang, & Kasapis, 2009). The continuous spectra $H(\tau)$ and $L(\lambda)$ are an essential term in the equations of $G(t)$ and $J(t)$. They are also needed for interconversion between $G(t)$ and $J(t)$ and thus between transient and dynamical tests. This would enable the computation of data of a transient test from the data that are derived from a dynamical test and vice versa. Various methods were developed to interconvert the spectra from either transient or dynamical data sets (Baumgaertel & Winter 1989, 1992; Dooling, Buckley, & Hinduja, 1997; Y. Liu, 2001; Malkin & Masalova, 2001; Tschoegl & Emri, 1992, 1993). They all showed sufficient accuracy and computing effort.

In general, the relaxation or retardation spectra are the foundation for rheological characterization since all rheological quantities can be more or less directly derived from them. An interconversion of data from short time tests can give a potential estimation for the long time behavior of dough and vice versa.

3. Dough formation and rheology

The aim of this review is to identify the link between empirical and fundamental dough rheological measurements. For dough formation the mixing step is the essential processing step. Dough formation is the process in which flour, water, yeast, salt and other ingredients are thoroughly mixed and kneaded to result in a solid but viscoelastic foam-like dough. Flour and dough mixing properties are usually assessed from small-scale laboratory mixers with an attached unit to record the torque. Different flour or dough characteristics are derived from its graph. The time until the maximum torque is reached is characterized as dough development time. Bread from fully developed dough shows higher volume than undermixed dough (Amemiya & Menjivar, 1992; Roels, Cleemput, Vandewalle, Nys, & Delcour, 1993). For wheat dough the development time is dependent on the mixer type, the rpm, the temperature, gluten quality, additives and others and can therefore vary widely. In the laboratory mixers torque gives the only information about the dough status. Considering a rheometer test setup where flour and water are sheared with a constant shear rate, fully developed dough should exhibit a maximum shear stress or viscosity in the rheometer. During normal kneading different mechanical actions take place and contribute to dough development – compression, extension and shear. In a rheometer shear would be the only source of mechanical energy contributing to dough formation. Although he did not develop dough by shearing Weipert (1990) was able to record fundamental dough rheology completely during proofing and baking in one device. Schluentz, Steffe, and Ng (2000) sheared a flour-water mixture in a conventional rheometer for a given deformation of 180° but failed to produce dough since dough escaped the geometry gap. Shearing in a cylinder could be a possibility in order to prevent dough from escaping the gap given that the moving geometry does not get in contact with the cylinder wall. More recent experiments in a shear device showed that dough formation is possible by simply shearing flour and water between the gap of a rotating cone-cone geometry (Peighambardoust, Fallah, Hamer, & van der Goot, 2010; Peighambardoust, van Brenk, van der Goot, Hamer, & Boom, 2007; Peighambardoust, van der Goot, Hamer, & Boom, 2004). It was also stated that due to different migration dynamics a separation of gluten and starch sets in after a certain time of shearing. In order to determine dough development it is appropriate to compare the shear stress curve from the shearing device and the torque curve from the z-blade mixer until the point of gluten-starch separation. Within this period of time the courses of both curves should be theoretically congruent. Zalm and co-workers compared dough from a z-blade mixer with dough from the

mentioned cone-cone shearing device (Zalm, Goot, & Boom, 2009, 2010) but it is not correct to directly compare their mixing curves. They manually premixed flour and water and gave the premix in the gap of the shearing device. Manual premixing applies an unknown amount of mechanical energy into the dough which is difficult to quantify. The shear mixing curve is influenced to an unknown degree which means that the dough development time cannot be determined accurately. The advantage of a cone-cone shearing device is that it can form dough that is ready for further rheological characterization. On the other hand, this kind of shearing device is not commercially available and is designed for scientific approaches. A method for simultaneous shear-mixing of dough and detection of the optimum dough development time is the use of the method for the determination of the critical gel point/time. This point can indicate finished polymer (gluten) crosslinking (De Rosa, Mours, & Winter 1997; Izuka, Winter, & Hashimoto, 1992; Trevor S. K.; Ng, McKinley, & Ewoldt, 2011). For the presented procedure consecutive frequency sweeps with frequencies between 1 and 100 rad/s were conducted. From Fig. 3 can be seen that data was rearranged into different sets of equal frequencies. For all these new data sets $\tan \delta$ was plotted over time. The critical gel time was determined from the intersection of all curves. With this method the optimum dough mixing time could be indicated which relies on the reaction between glutenin and gliadin molecules (Wieser, 2007). However, reliable results will only be achieved when the sweep test are performed in the linear viscoelastic region of dough. This means that frequency sweeps have to be conducted at strains smaller than app. 0.1%. It is questionable if mixing of ingredients or even dough development will set in due to a lack of sufficient mechanical energy input due to too small strains. This method is inappropriate for shear mixing but it can be conducted after a proper shear mixing step. Nevertheless, it is possible to produce dough by application of constant shear and dough development can be read from the course of the shear stress curve. There is a high risk to falsify data by excessive shearing due to shear thinning behavior of dough and occurring gluten starch separation in optimally shear mixed dough. A simultaneous and also complete dough characterization would then be hardly achievable. The strain rate for dough shear mixing must be high enough that dough will be developed in adequate time so that shear banding does not occur.

Besides indicating the optimum mixing time, the recording mixers are used to determine the water amount that is necessary to produce dough of optimum consistency. The change in water dosage leads to a change in dough stiffness and thus to a change in torque and shear stress. Concerning fundamental rheometry, another possibility would be to detect an optimum between elastic

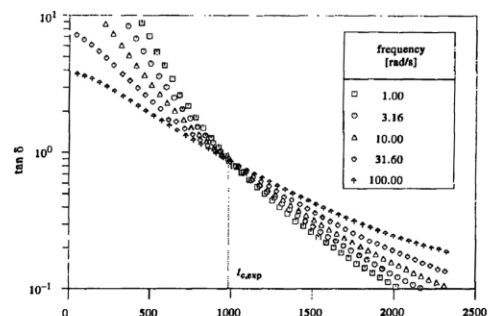


Fig. 3. Indication of the critical gel point (De Rosa et al., 1997).

and viscous part of the viscoelastic dough. Increasing the water content in dough leads to a higher degree in liquefaction and decreasing the water content to a higher degree in solidification. Liquids are characterized by viscous behavior whereas solids exhibit predominantly elastic behavior. Performing oscillatory testing in the rheometer the viscous and the elastic part and their respective contribution to viscoelastic behavior can be identified. Considering optimally mixed dough, it exhibits a certain consistency or complex shear modulus G^* . Changes in the water dosage would result in a shift in the ratio between viscous (G'') and elastic part (G') (Equation. (10)). This ratio needs to be in a certain range in order to provide for an acceptable baking result (Autio et al., 2001; Mirsaedghazi, Emam-Djomeh, & Mousavi, 2008). Dough which is highly viscous is incapable of sufficient rising during proofing whereas dough that is very elastic does not achieve a wanted volume since it is restrained in expansion by too strong contraction. The measure for that is the loss factor $\tan\delta$ which is determined by oscillatory testing. In these tests, G' and G'' also contribute to overall dough consistency that is described by complex shear modulus G^* . It is reported that changes in the water content of dough can be recognized by observing $\tan\delta$ (Jekle & Becker, 2011; Martling, Mulvaney, & Cohen, 2004; Upadhyay, Ghosal, & Mehra, 2012). By increasing the water amount in dough an increase in $\tan\delta$ was detected. The flow behavior of dough in dependence on the water ratio can be modelled with power law equations. The flow properties can be followed by changes in the flow index and the overall viscosity (Lefebvre & Mahmoudi, 2007; Masi, Cavella, & Sepe, 1998). However, they mentioned that in case of insufficient water G' and G'' develop inconstantly which results in an irregular relationship to water content. Water contributes to plasticization of proteins and is bonded by them. Faubion and Hosney (1990) confirmed that it is not freely available to affect neither the viscous nor the elastic part. Other authors also found no significant relationship between water content of dough and $\tan\delta$ (Berland & Launay, 1995; Létang, Piau, & Verdier, 1999; Skendi, Papageorgiou, & Biliaderis, 2010) but their test setups covered a too small bandwidth of water contents. Significant changes in these areas could not have been detected. In conclusion, $\tan\delta$ can be used from dynamical tests performed in the linear viscoelastic region of dough in order to estimate the correct water addition to flour. However, for a reliable determination of the water content master curves or charts for known $\tan\delta$ -correlations are needed – but these will be unique for each wheat cultivar. Nevertheless, plotting the shear stress and standard data evaluation are useful for the determination of the dough development time.

4. Dough stickiness and rheology

Dough exhibits different degrees in stickiness that depend on temperature and flour inherent components. For proper handling or conveying, a low or non-sticky surface is desired. It appears difficult to derive a relation between rheology and stickiness since there are no standardized measurements available. Each stickiness test is based on its own principle but to a certain extent relates to interactions of adhesion and cohesion. To determine stickiness of dough Chen and Hosney invented a measuring device (Chen & Hosney, 1995). A flat probe is pressed on top of a standardized curve-shaped dough surface area and withdrawn after a short resting period. The force for withdrawal is correlated to stickiness. In other methods a flat dough sample is brought in contact with a probe which is either withdrawn or peeled off from the dough surface. From a force-distance plot the peak force is related to adhesive strength or stickiness and the total work for complete withdrawal or peeling is considered as the work of adhesion (W_a). It is known that stickiness of each material is dependent on the

surface energy of the material with which it is in contact. In contrast to plastics metals have a high-energy surface that causes higher stickiness or adhesion to dough (Ghorbel & Launay, 2014; Hosney & Smewing, 1999). Although being termed a rheological method, a direct link to the viscoelastic dough properties is missing. Even Heddleson and coworkers showed no direct link but they could confirm the Dahlquist criterion. It says that stickiness disappears when the elastic modulus G' is greater than 10^2 kPa. They also found that the wheat dough stickiness is correlated to $\tan\delta$. This means that an increased stickiness can be recognized by an increased viscosity (Heddleson, Hamann, & Lineback, 1993).

The work of adhesion as a measure for stickiness is related to surface tension which in turn is related to surface rheological properties. In order to change the shape but not the area of a surface the viscosity is the opposing force. The surface tension is the opposing force when changing the area of a surface while its shape remains unchanged (Bos & van Vliet, 2001). Although emerging in different physical context attempts were made to directly link work of adhesion to rheological properties. Tests were done by examining the adhesive and rheological properties of a polymer matrix filled with silica polymer powder (Shang, Williams, & Söderholm, 1995) and the following relationship was found:

$$\frac{G'_c}{G'_p} = C \cdot \exp\left(-\frac{K_G}{W_a}\right) \quad (10)$$

G'_c and G'_p are the storage moduli of the composite and the polymer, C and K_G are constants and W_a is the work of adhesion. For dough W_a is dependent on the temperature, the moisture content and the separation rate and therefore is between 1 and 10 mJ (Heddleson, Hamann, Lineback, & Slade, 1994). Although a phenomenological correlation between shear data and adhesion could have been shown, this relation does not rely on basic physical relations. W_a itself can be defined as:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (11)$$

Here γ_1 and γ_2 are the surface tensions of the respective materials brought in contact and γ_{12} is the resulting interfacial surface tension for which Bloksma says is around 100 mJ/m² (Bloksma, 1980). For quantification of stickiness phenomena it appears necessary to determine both surface and interfacial tension. Based on Kendall (1971) a method is derived to calculate W_a from standard rheometer shear tests. Considering the peeling off of a circular disc from a flat gelatin sample, the change in specimen thickness δ is calculated by the following equation:

$$\delta = \frac{P(1 - \nu^2)}{2Er} \quad (12)$$

with E the elastic modulus, r the radius of the specimen, P the force trying to remove the disc from the specimen and ν the Poisson's ratio of the specimen. It is known that a force trying to bend a beam is the same like the force trying to shear the beam. By that it leads to $P = F_{\text{shear}}$. Bending of a beam occurs when trying to peel off the disc from the sticky specimen. It follows that:

$$F = \frac{2Er\delta}{(1 - \nu^2)} \quad (13)$$

Here F would be the shear force that acts when deflecting the disc by deformation δ and in the end Kendall's derivation leads to:

$$F^2 = \frac{8\pi}{(1-p^2)} E\gamma_{12}r^3 \quad (14)$$

With this equation a force-strain graph can be plotted from which W_0 can be extracted. The contribution of the surface tensions γ_1 and γ_2 can be easily determined with standard procedures but the contribution of γ_{12} is difficult to measure. Considering two immiscible liquids an empirical equation was derived which describes the relation between surface tension and viscosity (Ghatee, Zare, Zolghadr, & Moosavi, 2010):

$$\ln \gamma_{12} = \ln a + b\eta^{-0.3} \quad (15)$$

In this equation a and b are constants and η the viscosity of the surrounding liquid. However, this equation is only valid for liquids and not for viscoelastic materials like dough. The equation above showed empirical correlations but lacked of physical connections. An advanced relation between rheology and surface properties was demonstrated by Gramespacher and Meissner (1992). They showed that the interfacial tension between two compounded polymers (polysterene and poly(methylmethacrylate)) in a melt can be calculated from dynamical rheological tests. According to their findings the interfacial tension can be determined as proposed earlier by Scholz, Froelich, and Muller (1989):

$$G''(\omega) = \eta \frac{(\omega^3\tau_1\tau_2 - \omega)}{1 - \omega^2\tau_1^2} = \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1}\right) \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + \omega\eta \frac{\tau_2}{\tau_1} \quad (16)$$

$$\eta = \eta_{matrix} \left[1 + \Phi \frac{5k+2}{2(k+1)} + \Phi^2 \frac{5(5k+2)^2}{8(k+1)^2}\right] \quad (17)$$

$$gk = \frac{\eta_{dispersed\ phase}}{\eta_{matrix}} \quad (18)$$

$$\tau_0 = \frac{\eta_{matrix}R}{\gamma_{12}} \frac{(19k+16)(2k+3)}{40(k+1)} \quad (19)$$

$$\tau_1 = \tau_0 \left[1 + \Phi \frac{5(19k+16)}{4(k+1)(2k+3)}\right] \quad (20)$$

$$\tau_2 = \tau_0 \left[1 + \Phi \frac{3(19k+16)}{4(k+1)(2k+3)}\right] \quad (21)$$

In these equations γ_{12} is the interfacial tension, R is the radius of the embedded granules of the dispersed phase, τ_i are the relaxation times, η the zero shear viscosity, ω the angular frequency and G'' the loss modulus. However this model is restricted. It is assumed that both interacting materials have the same zero shear viscosity. This is not true for dough, the contained starch and gluten phase or the contacting metal of the rheometer geometry. Also both interacting materials are supposed to behave like a Newtonian liquid which is not applicable for both gluten and starch. Moreover the relaxation spectrum is necessary for the determination of the characteristic relaxation time τ_0 . It relates to a distinct peak in the spectrum that only appears when the blend is measured and not the single material. Gluten exhibits several peaks in its relaxation spectrum (Kontogiorgos & Kasapis, 2010). Therefore it is difficult to identify an additional distinct peak when dough is analyzed as a mixture of hydrated gluten and starch granules. Nevertheless, if it is possible to determine a distinct characteristic relaxation time τ_0 it is also possible to calculate the wanted interfacial tension γ_{12} . Considering published values for dough viscosity ($\eta_{matrix} \approx 28$ kPa), relaxation times of dough and gluten ($\tau_0 \approx 0.022$ and $\tau_1 \approx 0.02$ s), average

starch granule diameter ($R \approx 20$ μm) and gluten ratio in dough ($\Phi_{gluten} \approx 0.0625$) (Barak, Mudgil, & Khatkar, 2013; Keentok, Newberry, Gras, Bekes, & Tanner, 2002; Kontogiorgos & Dahunsi, 2014) the computed interfacial tension is 610 mJ/m^2 . Although the values for the parameters are from different flour and dough samples the order of γ_{12} is in agreement with the 100 mJ/m^2 proposed by Bloksma (Bloksma, 1980).

Values for the stickiness or the interfacial tension can be derived from the presented approaches. The needed Young's modulus in Kendall's approach (Equation (14)) can be computed from the shear modulus by stress relaxation tests. The procedure of Gramespacher and Meissner (1992) was proved to be applicable to viscoelastic composites like dough.

5. Extensibility and rheology

For further dough processing it is essential to know the extensional properties of dough. High extensibility is a prerequisite for high volumes of the processed bread which is a desired attribute. At the same time, high bread volume results in high crumb porosity which in turn causes a soft crumb texture as a second important attribute.

Quantification of extensibility is typically conducted with the Extensograph or with comparable test setups like a Texture Profile Analyzer (TPA). In both cases, a piece of dough with defined measurements is stretched until rupture and the recorded normal force gives information about dough firmness and stretchability. The maximum stretchability is reached in the moment of rupture. The total work needed for stretching is recorded and serves as a measure for dough strength. In an Alveograph a sheet of dough is inflated to form a bubble until it bursts. The interpretation of the resulting graph of force or pressure is similar.

The problem with these procedures is that the determination of extensibility and the elastic modulus or Young's modulus per se is only valid when uniaxial deformation tests are performed. This implies a constant cross section area of the sample during the measurement. This is approximately true for infinitesimal small extensions. In the applied testing machines the dough strings are thinned out during extension by which an accurate determination of the elastic modulus becomes impossible. A second obstacle for correct determination of the elastic modulus is strain hardening of dough when undergoing high deformations with strain rates above 0.001 s^{-1} (Amjid et al., 2013; Kouassi, Muresan, Gnangui, Mudura, & Kouame, 2014; Sroan, Bean, & MacRitchie, 2009). In wheat dough the gluten proteins build a three-dimensional network or film throughout the dough with embedded starch granules. The gluten proteins are more or less raveled. Extension unravels the proteins until they are fully elongated. Beyond the point of unraveling, the gluten network is disrupted which consumes more energy than unraveling and straightening the protein filaments (Belton, 1999; Kindelspire, Glover, Caffé-Tremil, & Krishnan, 2015; Shewry, Halford, Belton, & Tatham, 2002). Depending on flour type straining of dough shall not be greater than 130–180% to avoid strain hardening and to avoid dough rupture at strains greater than 1300–2000% (Amemiya & Menjivar, 1992; Dobraszczyk & Roberts, 1994; Hicks, See, & Ekwebelam, 2011). When exposing polymers to high strains Hyun, Kim, Ahn, and Lee (2002) described four different types of strain hardening but in general, shear and extensibility tests are conducted at low rates. For accurate calculation of the tensile properties and the corresponding Young's modulus uniaxial tests with infinitesimal small deformations have to be conducted. The Young's modulus E can be determined by either drag or squeeze testing and is defined as follows:

$$E = \frac{\sigma}{\epsilon} \quad (22)$$

Here σ is the tensile stress and ϵ the extensional strain. Dough behaves viscoelastic instead of purely elastic. By that, dough may show creep behavior during compressive or tensile testing. For that purpose correction methods have been developed (Ngan, Wang, Tang, & Sze, 2005) which need to be applied at first. The determination of E is only valid in the linear viscoelastic region and implies deformation rates around $10^{-2} - 10^{-3} \text{ s}^{-1}$ (Dobraszczyk & Roberts, 1994; Mohammed, Tarleton, Charalambides, & Williams, 2013; Trevor S.K.; Ng, McKinley, & Padmanabhan, 2007). By considering corrections E can be derived from other tests setups. With a given bulk modulus K from compression testing it is possible to determine the Young's modulus with the following equation:

$$E = 3K \cdot (1 - 2\nu) \quad (23)$$

in which ν is the Poisson's ratio. E can be also calculated from the known shear modulus G or shear stress τ and applied strain γ :

$$E = 2G \cdot (1 + \nu) = 2 \frac{\tau}{\gamma} \cdot (1 + \nu) \quad (24)$$

These relations are only valid for linear elastic, isotropic materials for which ν is 0.5. Dough at rest or under small deformation can be considered as an isotropic material. With the assumption of dough being elastic it could be proven that wheat dough is incompressible and has an even higher bulk modulus than water (C. Wang, Dai, & Tanner, 2006). This makes it easy to determine the needed Poisson's ratio which is 0.5 so that $E = 3G$. It was also stated that this assumption is only valid for dough with few air inclusions like normal dough which has porosity values between 7 and 16% (G. Bellido, Scanlon, Page, & Hallgrímsson, 2006; Shehzad et al., 2010). Dough in the fermentation stage cannot be interpreted this way due to increased porosity. Admittedly, dough doesn't behave elastic but viscoelastic. Therefore, the Poisson's ratio needs to be determined additionally.

Extensibility in terms of elastic modulus can be determined by shear measurements. These tests need to be conducted in the linear viscoelastic region to avoid the slightest impact of strain hardening. The maximum possible dough stretchability cannot be determined since rupture of dough cannot be observed in non-destructive small deformation shear measurements.

6. Proofing and rheology

During proofing the yeast is producing CO_2 continuously. The formed CO_2 diffuses through the dough and collects in the bubble reservoirs that were created during mixing. As a result the whole dough expands. But not all the formed gas is stored in the dough due to upward migration of gas bubbles and release of gas at the dough top surface. The time until gas begins to escape from dough is an important indicator for dough stability and gas retaining capacity. The more gas can be retained the higher loaves can rise. These properties can be determined with a Rheofermentometer. It consists of a heated and sealed chamber where the dough proofs and gains height. The gain in height in a cylindrical vessel can be recorded and escaping CO_2 can be measured at the exhaust at the bottom of the vessel.

Transferring these requirements means that the rheometer must be capable to quantify the escaped gas fraction. Also the rheometer needs to determine the dough volume or at least the volume increase during proofing. Assuming that in the rheometer the dough is trapped between the upper rheometer geometry and the bottom plate the expansion of incompressible dough would

occur only in radial direction. Bellido, Scanlon, and Page (2009) forced this for determination of the gas fraction of dough during proofing in a sealed chamber. Further, assuming dough is also hindered from radial expansion by a cylinder wall the normal force exerted to the then locked upper rheometer geometry increases. Since a gap between upper geometry and cylinder wall remains normal force increases until equilibrium of gas production and gas release from dough is achieved. In optimally mixed dough, the entrapped portion of gas is higher than the portion that is released. So it is likely that dough will additionally escape through the thin gap between side wall and upper plate and will collect on top of the upper plate. These arbitrarily forming additional dough surfaces between rheometer geometry and dough cannot be considered reliably during shear measurements. Unlocking the upper plate would result in an increase in the rheometer gap which can be recorded similarly to the Rheofermentometer. Also in this case it is likely that dough will escape at the edges of the rheometer geometry. Sealing the gap between geometry and cylinder side wall will cause additional friction that alters the data. These alterations to the rheometer would result in a similar measuring device like the Rheofermentometer and real rheological measurements are not possible anymore. Creating a comparable measurement system to the Rheofermentometer also undermines the purpose of this review.

For liquids it is possible to calculate a solvent viscosity from the known viscosities of each component. Using superposition of rheological data the respective concentrations of viscoelastic solutions could have been determined (Choppe, Puaud, Nicolai, & Benyahia, 2010). In turn, considering dough as a mixture of hydrated viscoelastic gluten with embedded starch granules and additionally embedded gas bubbles an approximation of gas formation could still be possible. Therefore, the change in viscosity over proofing time has to be recorded. But occurring shear thinning could falsify data. In dependence on gas content of dough the viscosity will change. Although the gas development in dough of up to $0.66 \text{ ml}/(\text{min} \cdot \text{g yeast})$ is generally known (Chiotellis & Campbell, 2003; Luchian & Canja, 2010), a master function for gas content-viscosity is still needed for correct determination of the included gas. Another approach could be the evaluation of time sweep tests. During proofing the dough consistency decreases due to an increasing volume fraction. With respect to a shift in the linear viscoelastic region this causes a decrease in G^* and an increase in $\tan \delta$ which indicates a higher viscous than elastic ratio (Salvador, Sanz, & Fiszman, 2006; Verheyen, Jekle, & Becker, 2014). This whole approach is similar to the proposed determination of water content in dough. In this case, rising dough escaping from the rheometer gap might falsify the G^* -value but $\tan \delta$ shall be unaffected since only the ratio of viscosity to elasticity would be of interest. When $d(\tan \delta)/dt = 0$ the maximum in gas retention capacity of dough should be reached. From this approach, the maximum fermentation time until gas release can be determined but still the resulting dough volume remains undetermined. There are possibilities to correlate the dough density which is related to dough volume to rheological data (Verheyen et al., 2014) but since dough density changes during fermentation correct rheological characterization is very difficult. In addition, the initial density before fermentation is unknown and must be determined with other procedures than the rheometer. Furthermore, there still remain differences between properties of the measured dough and the actual dough status.

7. Baking and rheology

Baking constitutes the final step in dough processing. During baking thermal energy is transferred to dough which gains volume

again due to thermal expansion of the included gas bubbles. Simultaneously, the gluten structure denatures and forms a frame for starch granules which gelatinize and solidify during baking (Barak et al., 2013; Keetels, Visser, van Vliet, Jurgens, & Walstra, 1996; Scanlon & Zghal, 2001). In the end, the dough is converted into bread exhibiting a more or less crunchy crust and a sponge-like soft crumb. Applying the process of baking to a rheometer means to perform a temperature ramp while applying small deformation oscillating shear measurements for being able to follow the dough transformation process. Dough rises due to the temperature increase during baking and the accompanying gas expansion by which the total volume increases. This has to be considered for simultaneous gathering of rheological properties. Here the problem is comparable to the process of proofing as outlined above. Fixing the gap size would result in radial expansion of dough and increase of the normal force exerted to the rheometer geometry. As the diameter of dough specimen in the gap increases during baking a reliable measurement of rheological properties cannot be guaranteed anymore – neither for transient nor for dynamical tests. A correction of the gap size according to an increasing normal force exerted to the rheometer geometry could probably overcome this problem in combination with limiting radial expansion of the forming bread. The increase in baking volume could be determined from the change in gap size.

Primary property for bread quality assessment is the bread volume. Other quality attributes comprise visual appearance, odor and taste. Comparable to dough stickiness the work of adhesion W_a is the key for the determination of crumb texture parameters like hardness, cohesiveness or chewiness (Brady & Mayer, 1985). By plotting the force F from Equation (14) over time the graph for the assessment of the crumb quality can be derived. Despite of texture and volume the other attributes are difficult or even impossible to quantify by shear measurements in a rheometer. Compared to dough in the proofing stage, the gas is not embedded anymore but has formed a network of pores that are interlinked up to 99% (S. Wang, Austin, & Bell, 2011). Through this network of pores the ambient air could flow unhindered. As a result the porosity deriving from fermentation will have an indirect effect on the softness or consistency of the crumb. It is the constitution of the matrix of denatured protein and gelatinized starch that is responsible for rheological behavior of bread crumb

(Lagrain, Wilderjans, Glorieux, & Delcour, 2012; Zghal, Scanlon, & Sapirstein, 2002). The porosity will affect the final thickness of pore cell walls and by that the subjective perception of crumb softness. It will also affect the size of the surface area on which forces from the rheometer will act. The formation of the crumb matrix depends on flour properties, and the settings during mixing and proofing as well as during baking. Considering constant dough recipes but different fermentation times and thus variable dough porosity, these differences should be recognizable in rheological measurements of the bread crumb after baking. From the differences in rheological data at least correlations to porosity can be made. Another possibility could be similar to the determination of extensibility with the Young's modulus as a measure for crumb softness. However, the pore structure itself could only be estimated indirectly from Young's modulus. Considering only few gas inclusions in the former dough, the crumb matrix would in general exhibit higher wall thicknesses. This would result in a higher Young's modulus, meaning a firmer crumb but total quantification of pores or even pore size distribution would not be possible. With the knowledge of the Young's Modulus it can further be possible to calculate different crumb properties like critical stresses to buckling of crumb pores and others which were reviewed by Liu and Scanlon (2003). Another way to have information about the developing pore structure can be a combination of a rheometer with an attached CLSM (confocal laser scanning microscope). A CLSM is capable of scanning dough structures three-dimensionally up to a certain depth. By this, the formed crust can be passed without destruction and an insight in the crumb structure can be gained. Here, quantification of pores can be made and the amount of pores can be extrapolated to the total bread volume. This approach does not really base on rheological measurements but is based on simultaneous use of different techniques.

Total characterization of bread or crumb structure is not possible by shear measurements only. Bread volume determination by adjusting normal forces can be out of the capabilities of some rheometers. Visual, gustatorial and olfactorial testing are also impossible to realize with a rheometer. Properties and structure of the pores could be estimated or correlated from crumb softness measurements or CLSM imaging. At least for determination of crumb softness the proposed method can be applied for measuring dough extensibility.

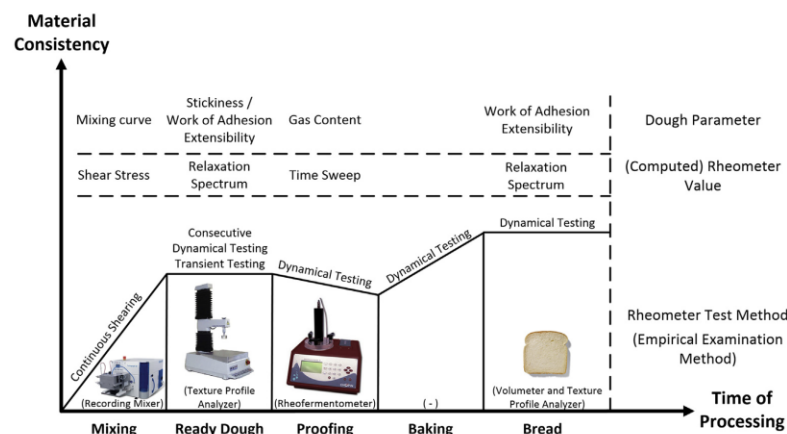


Fig. 4. Illustration of the classical dough evaluation methods used during the course of processing standard wheat bread and the rheometer test methods for their replacement.

8. Conclusion

Empirical rheological methods are widely in use for dough characterization. During their use it is likely that additional mechanical energy is incorporated into the dough specimen when transferring them from one measuring device to another. In order to avoid alteration of data by unwanted energy input, the dough needs to be produced, processed and examined in a device that is capable of performing all tests without transfer of the specimen. This review aimed on showing the possibilities how this can be accomplished by means of rheometry. It was shown to what extent results from empirical rheological methods can be displayed by fundamental rheological methods. Therefore conversion methods were proposed and discussed for each step of dough processing. An illustrative summary is given in Fig. 4. The common empirical method is shown along with the fundamental rheological method that is necessary for the computation of dough properties.

For characterization of dough development recording kneaders are often used. Comparable results can be extracted from shearing flour and water in the rheometer. Previous experiments showed that it is possible to form dough by simple shear. Rheological characterization still appears to be sophisticated since separation of starch and gluten occurs due to shearing for a certain span of time. Irrespective of that, methods for flour and dough properties like water absorption were proposed and discussed.

Extensibility of dough is crucial as it determines the final bread volume. It was shown that it is possible to determine extensibility of dough from rheometer data. Accurate data conversion can be achieved by incorporation of the relaxation spectrum. Further it was shown that relaxation spectra can be derived from retardation spectra and that they can be extracted from dynamical or transient rheological tests. For determination of dough stickiness rheological tests can deliver only partial insight. It is the interfacial surface tension of dough and the contacting measurement device that is still missing and cannot be derived from rheological data. The fermentation characteristics and final volume of dough can only be estimated roughly from rheological tests since rising dough constricts rheological measurements. That is the same case for evaluating final bread properties. At least, crumb softness could be determined by shear measurements. Other bread specific attributes can only be estimated or correlated from other measurements.

More accurate characterization of dough can be achieved if changes in the rheometer setup are made. This can include a possibility to determine the gas that escapes the dough during fermentation. Then a differentiation between poor yeast activity and poor gas retention capacity can be made. In general, a conversion of rheological data is helpful to estimate empirical rheological properties since these are well established and enable estimation of final bread quality.

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Development of wheat dough by means of shearing



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ABSTRACT

Wheat dough is transferred from the mixer to the rheometer in order to perform rheological measurements. During this step additional energy is inserted in the dough by stretching or squeezing, which causes an alteration of the gluten network. To avoid an unwanted additional energy input water and flour were mixed directly in a rheometer. The rheological data of reference dough and shearmixed dough were compared for correlations. The dough consistency during shear mixing was similar to the standard mixing method but the dough breakdown occurred faster. Relaxation spectra and the visualization of microstructure revealed that the gluten network development did not coincide with the indicated dough development of the consistency curve. A rheometer is capable of producing dough which is comparable to the standard procedure. The correlation of rheological properties between standard and shear mixed dough is of medium strength but the basics for a short dough characterization method were established.

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1. Introduction

Fully developed wheat dough is characterized by a three-dimensional gluten network with evenly distributed gas nuclei and embedded starch granules. The gluten network is highly crosslinked and spread throughout the dough (Jekle and Becker, 2011; McCann and Day, 2013). This enables a high retention of gas which is produced during proofing. The gas containment results in a high baking volume and an appealing crumb texture (Dowell et al., 2008; Hrušková et al., 2006; Wikström and Bohlin, 1996). Changes in the gluten network constitution or microstructure directly affect the physical dough properties and thus the baking quality (Naeem et al., 2002; Wieser, 2007).

The network is formed from glutenin and gliadin protein fractions only by the input of mechanical energy (Jekle and Becker, 2015). Mixing is the essential step during dough formation where mechanical energy is transferred from the kneading elements to the forming dough. Peighambardoust et al. (2006a) showed that a mechanical energy input of app. 30 kJ/kg is required to form an optimum wheat dough. Depending on the mixer and flour type the energy input can be up to 100 kJ/kg (Rao et al., 2000; Zheng et al., 2000). The needed mechanical energy comprises tension, compression and/or shear.

Kneaders with spiral hooks incorporate mechanical energy mostly by tension and compression (Connelly and Kokini, 2006a; b; Connelly and Kokini, 2007). Whereas the rotating blades of high speed mixers provide predominantly shear for the production of dough. Schluentz et al. (2000) were the first who applied shear as the only source of mechanical energy to an undeveloped dough sample. Other authors experimented with shear and were successful in forming a gluten network (Peighambardoust et al., 2007, 2004; 2005, 2006b; van der Goot et al., 2008). Wheat flour and water were sheared and the material resulted in a texture comparable to wheat dough. However, the rheological characterization was conducted in a separate rheometer. It means in that particular case that the material was stressed additionally and that its structures were altered prior to the measurements. This could have led to falsified rheological data and therefore to a misjudgment of the possible baking performance.

The aim of this study was to establish a fast laboratory test where dough is produced only by shearing. Dough preparation and dough characterization was conducted in the same apparatus to avoid a transfer. The test setup was evaluated in terms of mixing speed and efficacy of different mixing geometries. All of the results were compared to dough prepared by the standard doughLAB method (AACCI 54–70.01). Another goal was to characterize the different wheat dough development states during shear mixing. This included visualization of the dough's microstructure by confocal laser scanning microscopy (CLSM) to get a deeper insight in the process of shear induced dough development.

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2. Materials and methods

All experiments were conducted at constant 30 °C and were done in triplicate.

2.1. Z-blade mixer settings

The standard dough was produced on a lab-scale recording z-blade mixer (doughLAB, Perten, Germany). 50 g of wheat flour type 550 (Rosenmühle, Ergolding, Germany) and 30.4 ml distilled water were mixed according to AACCI method 54–70.01. The dough consistency reached a maximum torque of 1 Nm during mixing. At this point the dough was optimally mixed and the gluten network was fully developed.

2.2. Shear mixing settings

Shear mixed wheat dough was produced in an AR-G2 rheometer equipped with a non-serrated cone (1°) or plate geometry each with a diameter of 40 mm (TA Instruments, New Castle, USA). The mixing vessel was a cylinder with an inner diameter of 40.1 mm 199 mg flour were distributed flat and evenly on the cylinder bottom. 121 µl of distilled water were pipetted droplet-wise on seven different positions onto the flour; one droplet in the middle and six droplets circular around the center. The gap between rheometer geometry and cylinder bottom was set to 500 µm. The resulting dough was examined every 60 s after mixing for a total of 360 s.

2.3. Rheological characterization

DoughLAB samples were examined with the AR-G2 rheometer equipped with a steel plate geometry with a diameter of 40 mm. The gap between the probe and the bottom plate was set to 2 mm. Excess dough was trimmed and the edge was covered with liquid paraffin to avoid drying. For shear mixing the gap and geometry remained unchanged and no oil was used. Frequency sweep tests were performed in the linear viscoelastic region at a deformation of 0.1%. The lower and upper frequency limits were 0.1 and 100 Hz. A dough rest of 60 s was allowed before measuring. Frequency, storage modulus (G') and loss modulus (G'') were used to compute the relaxation spectra for further interpretation. This was performed by using the Matlab routine *contspec* from the freely available *ReSpect* package (Shanbhag, 2013).

2.4. Confocal laser scanning microscopy

A confocal laser scanning microscope e-C1plus (Nikon, Düsseldorf, Germany) with a 60× oil immersion objective was used for the visualization of the dough structure. The examination method was in compliance with the method of Beck et al. (2011). The dough samples were transferred into a specimen shape. 10 µl Rhodamin B (diluted 1:100,000) were pipetted onto the dough surface to mark the proteins. The dough was covered with a glass plate and the proteins were observed as fluorescence micrographs ($\lambda_{\text{ext}} = 543$ nm, $\lambda_{\text{em}} = 590$ nm) in a constant z-position.

2.5. Image analysis

For the image analysis the open source software ImageJ was used following the dough microstructure quantification method (DoMiQ) of Jekle and Becker (2011). Micrographs were converted into binary black and white pictures, threshold pixels smaller than 2×2 were removed and a filter was applied according to Huang and Wang (1995). 10 micrographs were taken from each dough

sample and analyzed in terms of protein particle size and particle aspect ratio. The aspect ratio is defined as the quotient of width by length of the protein particle.

2.6. Statistical evaluation

GraphPad Prism 5 software (GraphPad Software, Inc., La Jolla, CA, USA) was used for the analysis of variance, fitting regression equations and the determination of significant variations in the resulting values.

3. Results and discussion

3.1. Evaluation of shear mixing settings

First of all, the settings for the rheometer and the geometries had to be identified in order to produce dough in a rheometer. The gap size was determined regarding to the density of dough (~ 1100 kg/m³) (Ktenioudaki et al., 2009; Soleimani Pour-Damanab et al., 2011), bulk flour (~ 500 kg/m³) and the used amount of flour and water. The result was 230 µm, which was enlarged to 500 µm. This precaution was intended to avoid that material was squeezed out of the gap. Another reason is that it prevented falsified measurements caused by crushed starch granules (Schirmer et al., 2013; Wilson et al., 2006).

Secondly, the shear rate or the shear mixing speed had to be determined. Experiments with different shear rates between 10 and 100 s⁻¹ were performed in the rheometer. The results were evaluated with respect to the dough development time (DDT). In a standard mixing process the maximum peak in the torque-time graph is interpreted as the DDT. At this point the dough is in the optimum state for further processing and will yield the highest baking quality (Dobraszczyk and Salmanowicz, 2008; Kahraman et al., 2008). The shear tests ran for a total of 360 s. As shown in Fig. 1a the optimum DDT decreased by increasing the shear rate. Even the lowest shear rates did not exceed development times over 93 ± 43 s. In comparison to that, the doughLAB dough was optimally mixed after 149 ± 29 s.

Dismounting the shearing geometry revealed that for shear rates between 10 and 40 s⁻¹, no dough production had occurred. A flour-water slurry was present where flour particles were wetted and agglomerated on the bottom. The drag flow in the gap must have been too weak and the energy input too low to provide for a sufficient dough development. Peighambari et al. (2006b) produced developed dough at this speed with the difference that the author had sheared up to 45 min. At a rate of 50 s⁻¹ the material formed an intermediate between slurry and dough. For rates of 60 and 70 s⁻¹ the material in the rheometer gap exhibited the typical dough-like texture. Shear rates above 70 s⁻¹ did not lead to dough formation. Instead, the material was dragged out of the rheometer gap due to an imbalance of centripetal and centrifugal force. Flour and wetted flour flakes accumulated at the edges and were pushed upwards the cylinder wall. These results and the evaluation of the peak in the plotted torque graph during shear mixing showed that: (1) a minimum shear rate is necessary to form dough in an acceptable time; (2) a critical shear rate should not be exceeded to avoid discharging the material out of the rheometer gap; and (3) in contrast to standard mixing, a maximum peak in the torque-time graph had no informative value about the actual state of dough development (compare Fig. 2). Therefore, the specific mechanical energy (SME) input was evaluated for the determination of the dough development and the optimum shear rate. Equation (1) allowed the computation of the needed shear rate for the shear mixing process

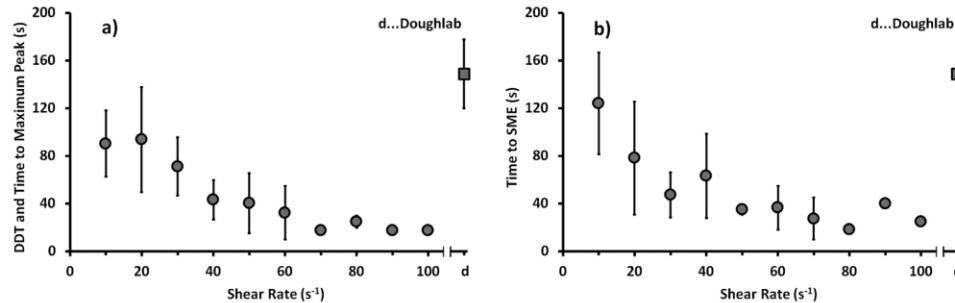


Fig. 1. (a) Time during shear mixing at different shear rates until maximum peak in dough consistency curve is reached. (b) Time during shear mixing at different shear rates to equal specific mechanical energy (SME) that is necessary to produce doughLAB dough.

$$SME = \frac{\omega}{m} \cdot \int M_d dt \quad (1)$$

where m is the dough mass, M_d is the torque, t is the mixing time and ω is the angular velocity. With an appropriate shear rate (angular velocity) and a target SME value from the doughLAB, it is possible to determine the dough development time of shear mixing. Considering the actual dough weight in the doughLAB that is sheared between the mixing blades and the walls the target SME value was about 1368 ± 83 kJ/kg. This was in reasonable agreement with Peighambari et al. (2004). They incorporated mechanical energy being of the order of 10^3 kJ/kg. However the evaluation of the shear rate on the basis of the SME (see Fig. 1b) did not confirm the observations from the previous section. At low shear rates the optimum dough development was indicated although a flour-water slurry had formed. For shear rates over 70 s^{-1} the SME value was useless since most of the material was discharged. Only at medium shear rates the resulted SME had an informative value. The optimum shear mixing time was equal to 37 ± 18 s or 28 ± 18 s for medium shear rates of 60 or 70 s^{-1} .

In conclusion, the gap was set to $500 \mu\text{m}$ and an average shear rate of 65 s^{-1} was used. This shear rate equaled an angular velocity of 0.75 rad/s which was used for both cone and plate geometries. The shear mixing times were set to 60, 120, 180, 240, 300 and 360 s for the following experiments. Fig. 2 illustrates the rheometer and the doughLAB mixing curve. The rheometer curve had its peak after

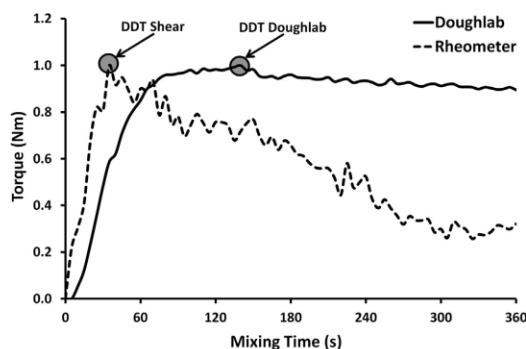


Fig. 2. Typical dough mixing curves from doughLAB (—) and dough shear mixed in the rheometer (at 60 s^{-1}) (---). Values of shear mixed dough were rescaled.

about 35 s, whereas the standard dough had a DDT of 149 s. The shear mixed dough reached an early mixing optimum. After that the dough lost gradually in consistency and faster than the standard dough. The differences in the dough development were examined with CLSM micrographs of the gluten network.

3.2. CLSM characterization of dough

The CLSM characterization of dough was conducted with the cone and the plate geometry. Then CLSM micrographs were taken in order to visualize the changes in gluten network structure induced by shear mixing. In Fig. 3 the development of the protein network is demonstrated in dependence of the shear mixing time. After the first 60 s the proteins were distributed incoherently throughout the forming dough matrix. At 120 s small protein or gluten strands began to aggregate and form small networks. After 180 s the network increased and inclusions of starch granules and air were detected. At 240 s the gluten network was spread widely and more air inclusions were present. An optimum development can be marked at 240 or 300 s of shear mixing. After 360 s an alignment of gluten molecules and air inclusions along the shear direction was observed. This is in agreement to the findings of Peighambari et al. (2006b), who discovered this orientation and referred to it as shear-banding. The authors also stated that excessive shearing leads to gluten-starch separation Peighambari et al. (2006a). This was also observed for both geometries when exceeding 600 s of shear mixing. By comparing the mixing curves from Fig. 2 with the CLSM micrographs, it seemed that the decrease in dough consistency after 60 s was not related to gluten degradation. Moreover, the decrease is probably related to gluten orientation along the direction of shear. On the other hand, the orientation of glutenin polymers was associated with a strain hardening effect, this being essential to assure gas cell intactness (Dobraszczyk and Roberts, 1994; Van Vliet et al., 1992). This explains the successful entrapment of gas cells within the matrix. Otherwise, the lack of oxygen as the actuator of gluten crosslinking would lead to a less stable and less extensible gluten network (Belitz et al., 1986; Miller and Hosenev, 1999).

The results from software particle analysis of the CLSM micrographs are demonstrated in Fig. 4. Shear mixing with the cone geometry for 60 s resulted in average gluten particle sizes of $240 \pm 87 \mu\text{m}^2$. During the ongoing shearing up to 900 s the particle size did not vary significantly. The size ranged between 226 and $331 \mu\text{m}^2$. The dependence of the aspect ratio (AR) of gluten particle vs. mixing time was similar to that of the particle size. After 60 s the AR was 0.86 ± 0.1 and remained about constant for longer shearing. Excessive shearing led to an AR of 0.65 ± 0.1 . This indicated that the

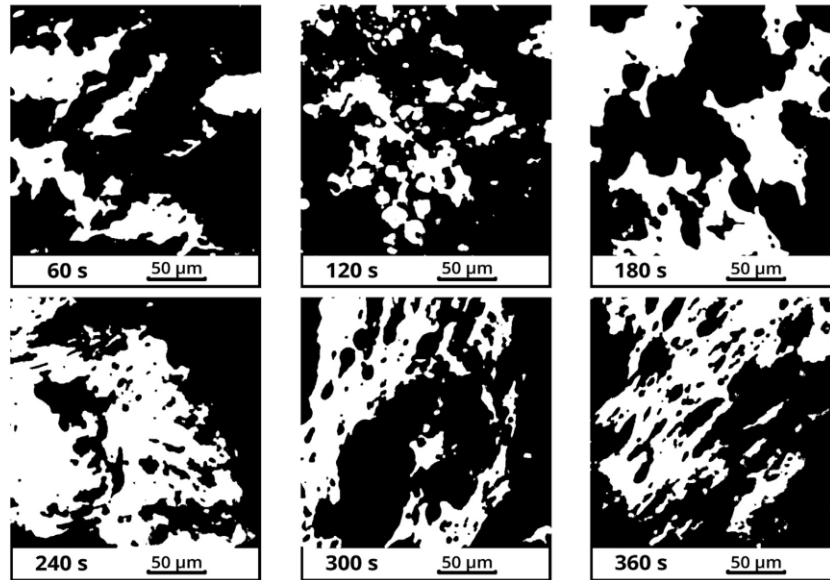


Fig. 3. CLSM micrographs of wheat dough processed in the rheometer and illustration of gluten development (white) in dependence on shearing time.

particles were more stretched due to the prolonged shear mixing. The plate geometry achieved gluten particle sizes of $400 \pm 110 \mu\text{m}^2$ after 60 s. Shearing for additional 60 s led to a decrease in the particle size ($296 \pm 47 \mu\text{m}^2$). A continuous shearing for a total of 900 s led to no further significant changes, the gluten particle sizes ranging from 245 to $283 \mu\text{m}^2$. In agreement with Zalm et al. (2010), the high standard deviation gave rise to the assumption that gluten-starch separation set in after about 600 s. Very small and large gluten patches were present. On the contrary, dough that was mixed for 900 s in the doughLAB reached an average gluten particle size of $590 \mu\text{m}^2$; quite higher than that achieved with both of the used shear mixing geometries. It is assumed that the smaller particle size from shear mixing occurred because of less protein interaction. Bekard et al. (2011) conducted experiments at higher shear rates but they reported that shearing of proteins leads to their elongation. It exposes former intramolecular domains by which the proteins are able to accumulate. In this case a longer

shearing time would have led to more protein-protein interactions but the risk of forming protein aggregates would have also been increased.

The AR showed a similar but inverse trend in comparison to the protein particle size. After 60 s the AR was 0.71 ± 0.1 and increased insignificantly afterwards. The rise after 120 s indicated that the gluten particles were almost equally extended in x- and y-direction rather than the initial elliptic shape. For mixing times increasing from 120 to 360 s the AR did not vary significantly and ranged between 0.85 and 0.80. After shearing for a total of 900 s AR decreased significantly to 0.41 ± 0.11 . This indicated that the particles were more stretched and probably aligned in the shear direction due to excessive shearing. The time for dough development cannot be determined from the AR. The CLSM micrograph evaluation of both geometries exhibited comparable AR's. The plate geometry showed a more consistent course in the particle size compared to the standard method. The particles migrated more or

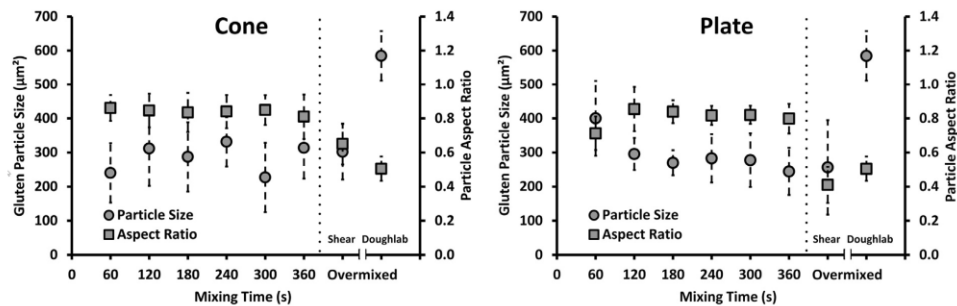


Fig. 4. Average gluten particle size development (●) and gluten aspect ratio (■) during mixing in the rheometer as a function of mixing time and in comparison to doughLAB dough.

less unhindered towards the center between the plates. This reduced the intermixing of the dough components and caused an alignment of gluten.

3.3. Rheological characterization of dough

For the rheological characterization frequency sweep tests were conducted directly after shear mixing. Fig. 5 shows the development of the complex shear modulus G^* and the loss factor $\tan\delta$ at $f = 1$ Hz for the cone and plate probes. The G^* -curve exhibited a maximum value at 120 s even if such a maximum value was equal to 1255 ± 133 or 251 ± 105 kPa for the cone or plate geometry, respectively. The trend of the curves resembled that of the standard mixing curve (compare Fig. 2). The results of the maxima are contrary to the findings in Sections 3.1 and 3.2. After 120 s of shear mixing a flour-water-slurry only had formed and proceeding led to the decrease of G^* . In contrast to the standard dough the decrease in G^* was not an indicator for a beginning gluten degradation (Létang et al., 1999; Zheng et al., 2000). The CLSM measurements indicated a gluten network optimum after 300 s where the geometries exhibited a minimum in G^* . However, the cone geometry achieved higher G^* -values than the plate geometry. A comparison of the normal forces during shear mixing (data not shown) showed an explanation. In the beginning of shear mixing the flour-water mixtures yielded in similar properties for both geometries. By continuing shear mixing the developing dough exhibited the Weissenberg effect (Peighambaroust et al., 2008). The reason is that the cone geometry has a decreasing gap size towards the center. The developing gluten accumulated in the center which led to an increase in the normal forces. In addition to that, G^* became dependent on the dough volume because the bottom of the vessel was not covered completely. The loss factor ($\tan\delta$) on the contrary is independent on the dough volume. Fig. 4 shows that the trends of the curves are incoherent. Only values of $\tan\delta$ at 300 or 360 s are comparable with results from doughLAB dough (0.39 ± 0.01). At these times $\tan\delta$ was between 0.36 ± 0.09 and 0.34 ± 0.02 for the cone geometry and between 0.39 ± 0.10 and 0.30 ± 0.05 for the plate geometry.

For an exclusion of misleading rheological data and for further evaluation the frequency sweep test data were transformed into respective relaxation spectra. They allow an interpretation of the molecular structure like network formation or branching (Malkin, 2006). The Equations (2) and (3) illustrate the relationship between the elastic (G') and viscous component (G'') of dough and the relaxation spectrum $H(\tau)$.

$$G'(\omega) = \int_0^\infty \frac{H(\tau)(\omega^2\tau^2)}{1 + \omega^2\tau^2} d \ln \tau \tag{2}$$

$$G''(\omega) = \int_0^\infty \frac{H(\tau)\omega\tau}{1 + \omega^2\tau^2} d \ln \tau \tag{3}$$

It is known that relaxation spectra for wheat dough or gluten develop the most remarkable positive peak at relaxation times between 10^{-2} and 10^{-1} s (Kontogiorgos, 2010; Phan-Thien et al., 1997; Ramkumar et al., 1996). The computed spectra were analyzed with regard to these relaxation times and are presented in Fig. 6.

First, the spectrum of underdeveloped standard dough showed the highest peak at $7.1 \cdot 10^{-3}$ s. The location of the peak represents dominant viscous behavior. Continuing mixing until the point of optimum dough development showed several peaks. The most prominent peak at $6.7 \cdot 10^{-2}$ s was in the region of interest. The even distribution of peaks indicated a balance of viscous and elastic properties. A broad multimodal distribution of relaxation times signals that an optimally developed dough was produced and that the formed gluten macromolecules are of different molecule weight (Li et al., 2003). The overmixed reference dough developed a dominant peak shifted towards to the region of viscosity which indicates softened dough and fragmented gluten strands (Létang et al., 1999).

Second, shear mixing with the cone geometry for 60 s resulted in undermixed dough. The relaxation spectrum revealed one peak at $2.8 \cdot 10^{-1}$ s which indicated small elasticity. As stated before this could have been attributed to unhydrated starch granules which are dominating the elastic properties. The relaxation spectrum at the optimum mixing time at 300 s revealed two peaks. The first peak at $1.0 \cdot 10^{-1}$ s was the more prominent one and appeared in the viscous region. The second peak at $2.2 \cdot 10^0$ s indicated elasticity. It can be seen that less peaks appeared compared to standard dough which is a hint for less molecular weight dispersity (Jackson et al., 1994; Mao et al., 2000; Thimm et al., 1999). Overmixing the sample for 900 s resulted in a broader distribution of relaxation times. It indicates a larger molecular size distribution due to an extensive shearing. This is in agreement with Peighambaroust et al. (2008) and their conclusion that the glutenin macropolymer disrupts under excessive shear.

Finally, the plate geometry showed a dominant peak at $8.0 \cdot 10^{-2}$ s after 60 s which referred to a viscous dough. At this time the inhomogeneous distribution of shear rates that are inherent to that type of geometry decelerated the beginning of dough formation. Further shearing led to an optimally developed dough

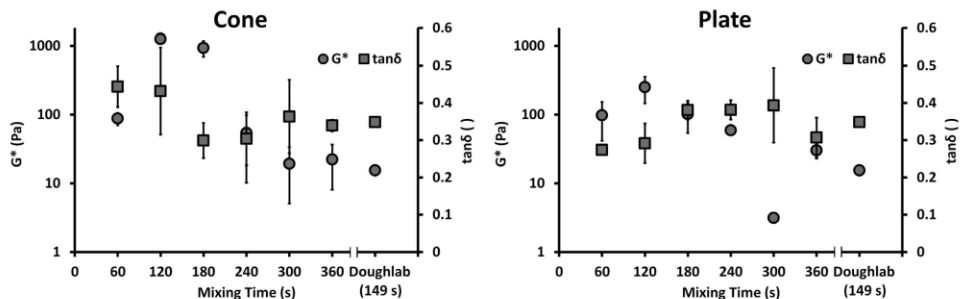


Fig. 5. Complex modulus G^* (●) and loss factor $\tan\delta$ (■) at $f = 1$ Hz against mixing time when using the cone and plate geometry in the rheometer mixing process.

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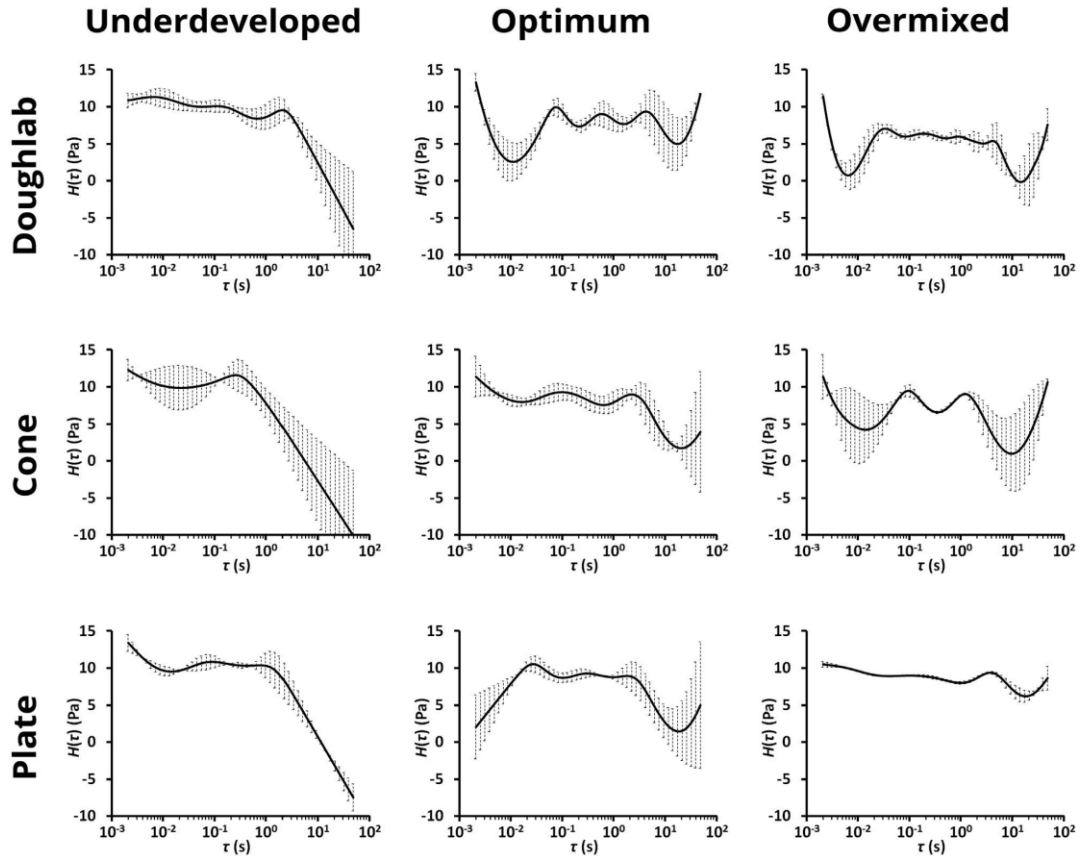


Fig. 6. Relaxation spectra for underdeveloped (60 s), optimum and overmixed (900 s) dough prepared with doughLAB, cone geometry and plate geometry.

showing three peaks ($2.9 \cdot 10^{-2}$, $2.8 \cdot 10^{-1}$ and $2.2 \cdot 10^0$ s), where the largest one was in the region of interest. The plate geometry caused several peaks indicating a high molecular diversity. The reason is an infinite spectrum of shear rates which are also exhibited by the reference method.

Comparing the cone and plate geometry it can be stated that both exhibited shear banding after overmixing, but it affected the final rheological properties in different ways. The gluten accumulated in the center and had more intense contact with the cone apex. Thus compressed gluten dominated the order of rheological properties and shape of the spectrum. The plate geometry had broader contact to the material over the total radius. Aggregated gluten in the center and accumulated starch in the outer rim contributed both to the rheological properties. This led to a spectrum similar to overmixed standard dough and to a smaller average percentage error (17.4%) than the cone geometry (22.6%) in comparison to the doughLAB spectrum.

3.4. Prediction of dough properties from shear mixing

Shear mixing showed that the produced dough had not the same rheological properties like the standard dough. The last test

was conducted to find a possibility to relate from rheological data of shear mixing to the standard method. NaCl was added at five different levels to the flour (0, 0.6, 1.2, 1.8, and 2.4%). This resulted in a variety of different doughs since it is known to significantly affect the rheological dough properties (Beck et al., 2012; Salvador et al., 2006). Considering the previous experiments, the plate geometry was used for proper mixing and flour, water and NaCl were shear mixed for 300 s. Additional samples at the point of underdevelopment were also examined for a possible early prediction of the final rheological dough properties. Fig. 7 shows the rescaled values for G' and G'' both for dough produced with the doughLAB and by shear mixing. The addition of NaCl caused a softening of dough. Dough mixed in the doughLAB lost 20–30% of its consistency whereas shear mixed dough lost more than 60%. The NaCl-induced contraction of gluten and the resulting release of water appeared to be promoted by shearing. However, the course of the curves remained equal. The addition of NaCl caused a steady decrease in both moduli and also in overall dough consistency as can be seen from Equation (4).

$$(G^*)^2 = \sqrt{(G')^2 + (G'')^2} \tag{4}$$

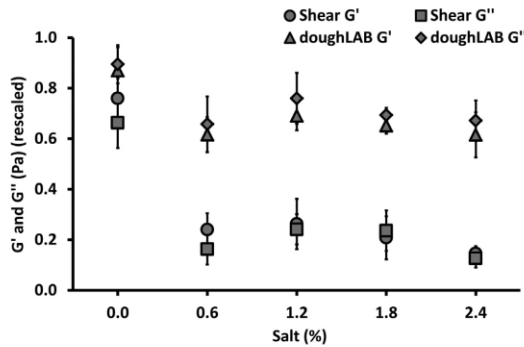


Fig. 7. G' and G'' at $f = 1$ Hz of shear mixed and doughLAB dough in dependence on the added NaCl amount.

The ANOVA of the data revealed that the addition of NaCl changed the rheological properties significantly ($p \leq 0.05$) for standard and shear mixed dough (data not shown). The curves of G'_{doughLAB} and G''_{doughLAB} over the NaCl concentration were considered as the expected values. The results were evaluated with respect to the correlation coefficient r and are summarized in Table 1. It shows that there are no significant correlations in the underdevelopment stage between the shear mixed and the reference dough. On the other hand, there is a significant correlation at optimum mixing times, which exists between G''_{shear} and both G'_{doughLAB} and G''_{doughLAB} . The correlation coefficient r was 0.72 and 0.59, which displayed a medium strength of linear correlation. These results indicate that G''_{shear} allows the prediction of standard dough properties to a certain degree under the condition that the shear mixed dough is in an optimum state of gluten development.

4. Conclusion

The findings demonstrate that shear mixing of flour and water in a rheometer produces developed dough. The plate geometry is preferable to the cone geometry since the gap size is larger and the movement of particles is supported. The use of mixing curves is not applicable because the dough aligns in the shear direction and a standard rheological characterization leads to misinterpretation. The CLSM and the relaxation spectra provide useful information about dough development and the optimum dough mixing time. However, the CLSM requires additional investments in time and laboratory work. The relaxation spectra cannot be read directly from the rheometer but can be easily computed with a PC.

The presented tests can be used to correlate characteristics, but its predictability is moderate and needs improvement. It is necessary to perform baking trials and more mixing experiments in order

Table 1 Comparison of correlation coefficients between optimally mixed doughLAB dough and shear mixed dough at two different mixing stages ($\alpha = 0.05$; * $p \leq 0.05$; ** $p \leq 0.01$; $n = 3$). Subscripts in brackets showing the standard error.

		Shear mixing			
		Underdeveloped dough		Developed dough	
		G' (6.8)	G'' (2.2)	G' (0.3)	G'' (0.1)
doughLAB	G' (2.9) G'' (0.8)	0.46 0.32	0.39 0.24	0.25 0.17	0.72** 0.59*

to correlate to the baking quality without the use of the doughLAB standard. Moreover, alternative shear techniques need to be tested with respect to the alignment of dough and the variability in standard rheological characterization. The presented shear mixing procedure can be considered as a pretrial and the results can be the base for future projects.

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Advances in the development of wheat dough and bread by means of shearing

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ABSTRACT

Wheat dough was produced in a rheometer by applying consecutive stress-relaxation steps with alternating direction of shear. A well-defined stress environment prevented separation of gluten and starch during shearing and allowed instantaneous determination of dough properties. Relaxation spectra of each relaxation step were used to determine the optimum dough development time. The spectra were correlated to rheological properties of standard dough that was mixed in a z-blade mixer. The correlation showed R^2 s between 0.82 and 0.96. The dough development time as indicated by the relaxation spectra was comparable to standard dough. The evaluation of CLSM micrographs confirmed the results from the spectra. Imitated proofing and baking in the rheometer delivered inconsistent results due to an uncontrollable system by yeast leavening. In the current stage the proposed microscale shear mixing (MSSM) technique can be a reliable method for the rapid evaluation of flour and dough properties.

1. Introduction

Fully developed wheat dough is characterized by a three-dimensional gluten network with evenly distributed gas nuclei and embedded starch granules. The gluten network is highly crosslinked and spread throughout the dough (Jekle and Becker, 2011a; McCann and Day, 2013). It enables a high retention of gas, a high baking volume after proofing and an appealing crumb texture (Dowell et al., 2008; Hrušková et al., 2006; Wikström and Bohlin, 1996). These properties are directly affected by the gluten network constitution which is established during dough mixing (Naeem et al., 2002; Wieser, 2007). The gluten network is formed when wheat flour and water are mixed and only when mechanical energy is applied (Jekle and Becker, 2015). Mechanical energy comprises tension, compression and/or shear and is transferred from the kneading elements to the forming dough. Kneaders with spiral hooks incorporate mechanical energy mostly by tension and compression (Connelly and Kokini, 2006a; b; Connelly and Kokini, 2007) whereas the rotating blades of high speed mixers provide predominantly shear for the production of dough. Depending on the mixer and flour type the energy input can be up to 100 kJ/kg (Rao et al., 2000; Zheng et al., 2000). Although the complete dough handling process in an extruder is not comparable to standard hook mixing, flour and water are predominantly sheared in the extruder in order to form dough. During processing the energy consumption of an extruder can

rise up to 1600 kJ/kg dependent on the process conditions (Matysiak et al., 2018; Osen et al., 2014). In the extruder mixing zone the mechanical energy input into dough barely exceeds 30 kJ/kg (Godavarti and Karwe, 1997). Peighambardoust et al. (2005) were the first to succeed in shear mixing dough in a special apparatus other than an extruder. Tietze et al. (2017) introduced a different method to shear mix dough in a conventional rheometer and by that dough could be examined in direct sequence. This eliminated the risk of incorporating unquantifiable additional stress into the dough specimen during transfer from kneader to rheometer which could lead to falsified results. It also produced dough in a well-defined stress environment. They showed that the formed dough structure is comparable to dough that was mixed in a z-blade mixer and that correlations of properties between both are possible. They computed the relaxation spectra and analyzed the peaks. The peaks in these mechanical spectra were in agreement with those from Kontogiorgos and Dahuni (2014) and also others showed that differences in dough composition and processing can be directly read from the mechanical spectra (Almusallam et al., 2016; Larrosa et al., 2015). However, Tietze et al. (2017) characterized dough after and not in the very moment of mixing. By that, the evaluated rheological dough properties could still be falsified due to a beginning dough relaxation between mixing and measuring. Another disadvantage is that their dough aligned in the direction of shear and that it tended towards unwanted gluten and starch separation. This

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prevented a reliable prediction of rheological properties and a formulation of a relation between stress field and rheological behavior.

The aim of this work was to improve the shear mixing technique that produces wheat dough in a rheometer. The resulting dough has to be free from shear alignment as well as gluten and starch separation. The developed method aims to provide dough which has properties comparable to standard dough. The formation of dough will be achieved by application of consecutive stress-relaxation steps. The rheological properties will be computed from the resulting relaxation spectra of each relaxation step. In order to evaluate the possibility for a complete bread making process, shear mixing will be followed by two in-rheometer procedures that aim on imitating proofing and baking. The comparability with standard dough and the predictability of dough and bread properties will be tested on six different wheat flours. Finally, the new shear mixing method will deliver rheological data of dough simultaneously to the shear mixing process. The intermediate rheological data will be used to predict the rheological data of dough that is mixed by a conventional method.

2. Materials and methods

The development of the shear mixing technique was done with a commercially available all-purpose wheat flour type 405. The evaluation tests were performed with six different wheat flours “Bun”, “Cookie”, “Premium”, “Waffle”, “Wheat Type 550” and “Wheat Type 1050”. For their chemical composition, see Table 1. If not stated different all tests were done in triplicate.

2.1. Z-blade mixer settings

The dough was produced on a lab-scale recording z-blade mixer (doughLAB, Perten, Germany). 50 g of wheat flour and 30.4 ml distilled water were mixed according to AACCI method 54–70.01. Flour and water were mixed until optimum dough development. Dough produced with the z-blade mixer is further referred as to “standard”.

2.2. Shear mixing settings

Shear mixed wheat dough was produced in an AR-G2 rheometer equipped with a smooth plate geometry with a diameter of 40 mm (TA Instruments, New Castle, USA). The mixing vessel was a cylinder with an inner diameter of 40.1 mm 199 mg flour were distributed flat and evenly on the cylinder bottom. 121 μ l of distilled water were pipetted droplet-wise on seven different positions onto the flour; one droplet in the middle and six droplets circular around the center. The gap between rheometer geometry and flour was variable to maintain a constant normal force of 1 N. Shear mixing consisted of a flour-dependent amount of consecutive stress relaxation tests with alternating direction of deformation γ with $\dot{\gamma} = 0.75$ rad. The relaxation time for each step was 2 s. Every odd numbered strain cycle was of the order 1γ . Every even numbered strain cycle was of order -2γ . For the evaluation of the shear mixing technique, dough was shear for a total of 720 s.

2.3. Imitation of proofing and baking

The standard dough was proofed for 60 min in a proofing chamber at constant 30 °C and a relative humidity of 90%. The 500-g-loaves

were proofed in a pan. The proofed loaves remained in the pan and were baked for 30 min at 220 °C in an oven. After cooling the bread volume was determined according to AACCI Method 10–16.01 and the crumb firmness was determined according to AACCI Method 74–09.01. Instead of water, each MSSM dough sample was prepared with a fresh 1% dried yeast suspension per flour weight. Mixing was followed by 60 min proofing in the fixed rheometer gap at constant 30 °C. In order to imitate baking the specimens were subjected to a temperature sweep following the temperature profile of real bread crumb during baking (Mack et al., 2013). This led to a temperature ramp consisting of heating for 1000 s with a rate of 3.98 °C/min followed by 250 s at a heating rate of 0.72 °C/min. The frequency was at constant 1 Hz and the deformation was 0.1% to ensure operating in the linear viscoelastic region. After baking and cooling to 30 °C a last relaxation test with $\gamma = 0.75$ rad and a duration of 3 s was performed. All trials were performed 12-fold.

2.4. Rheological characterization

Standard dough samples were examined with the AR-G2 rheometer equipped with a steel plate geometry with a diameter of 40 mm. The gap between the probe and the bottom plate was set to 2 mm. Excess dough was trimmed and the edge was covered with liquid paraffin to avoid drying. Frequency sweep tests were performed in the linear viscoelastic region at a deformation of 0.1%, the frequency limits were 0.1 and 100 Hz and a dough rest of 60 s was allowed before measuring. The dynamic rheological parameters (G^* , G' , G'' and $\tan\delta$) were evaluated at 1 Hz. Stickiness of standard dough samples was evaluated as work of adhesion (W_a) with a texture profile analyzer TA-XT Plus (Stable Microsystems, Godalming, UK) according to the method developed by Chen and Hosney (1995). The analyzer was equipped with a Chen-Hosney stickiness cell, test and post-test speed were 0.5 and 10 mm s⁻¹, applied force was 0.4 N, trigger force was 0.05 N, contact time 0.1 s and return distance 4 mm. A Kieffer extensibility rig was used to determine the shear modulus (G_0) with the texture profile analyzer. 20 g of dough were elongated for 75 mm. The trigger force was 0.05 N, test speed 3.3 mm s⁻¹ and post-test speed 10 mm s⁻¹. G_0 was computed from the resulting force-time data.

2.5. Confocal laser scanning microscopy and image analysis

A confocal laser scanning microscope e-C1plus (Nikon, Düsseldorf, Germany) with a 60 \times oil immersion objective was used for the visualization of the dough structure. The examination method was in compliance with the method of Beck et al. (2011). For the image analysis the open source software ImageJ was used following the dough microstructure quantification method (DoMiQ) of Jekle and Becker (2011a). 10 micrographs were taken from each standard and MSSM dough sample and analyzed in terms of protein particle size and particle aspect ratio.

2.6. Computation of the rheological properties of shear mixed dough

The relaxation spectra were computed following the procedure proposed by Kontogiorgos (2010) and the strain history due to consecutive steps was considered by applying Boltzmann superposition principle. G' , G'' , G_0 and W_a were computed from the relaxation spectra

Table 1
Content of fat, protein and starch of the used flours (n = 3).

	Bun	Cookie	Premium	Type 550	Type 1050	Waffle	All purpose flour
Fat	1.11 \pm 0.05	1.22 \pm 0.06	1.01 \pm 0.16	1.15 \pm 0.03	1.8 \pm 0.04	0.62 \pm 0.05	0.97 \pm 0.04
Protein	10.64 \pm 0.44	11.51 \pm 0.61	11.37 \pm 0.28	11.93 \pm 0.43	12.15 \pm 0.49	10.77 \pm 0.36	10.41 \pm 0.67
Starch	69.23 \pm 4.75	53.93 \pm 2.04	39.36 \pm 0.38	42.91 \pm 1.89	58.26 \pm 3.81	56.48 \pm 2.18	58.42 \pm 1.72

as proposed by Tietze et al. (2016). For the computation of W_a the Poisson's ratio ν was set to $\nu = 0.5$. The complex modulus G^* and the loss factor $\tan\delta$ were computed by following equations (1) and (2).

$$G^* = G' + iG'' \quad (1)$$

$$G''/G' = \tan \delta \quad (2)$$

The rheological values from the spectra and the statistical data were computed using the software MATLAB R2010b (The MathWorks, Inc., USA). The accuracy and precision were computed following equations (3) and (4) in which \bar{x} is the mean value and s the standard deviation.

$$Accuracy = \frac{\bar{x}_{Shear\ Mixing}}{\bar{x}_{Doughlab}} \cdot 100 \quad (3)$$

$$Precision = \left(1 - \frac{s_{Shear\ Mixing}}{\bar{x}_{Shear\ Mixing}}\right) \cdot 100 \quad (4)$$

2.7. Statistical evaluation

GraphPad Prism 5 software (GraphPad Software, Inc., La Jolla, CA, USA) was used for the analysis of variance, fitting regression equations and the determination of significant variations in the resulting values.

3. Results and discussion

3.1. Improvement of the shear mixing procedure

The preceding work showed that it is possible to develop dough by continuous shearing in a rheometer (Tietze et al., 2017). Yet, the method suffered under low correlation to the properties of standard dough which was attributed to the occurring shear alignment of dough polymers. In comparison to those results the new microscale shear mixing (MSSM) method should avoid orientation of the dough structure along the direction of shear, the separation of gluten and starch and it should deliver a high degree in the predictability of real dough properties. In order to achieve that, shear mixed MSSM dough was produced by applying consecutive alternating stress relaxation tests to flour and water. The shear mixing settings were judged by comparing real/standard dough produced in a doughLAB and shear mixed MSSM dough produced in the rheometer. Standard dough was subjected to rheological examination followed by three consecutive relaxation tests. The settings for the relaxation tests were the same as for the MSSM procedure. The shear mixed dough was sheared for the duration of the development time of standard dough. This test was performed 5-fold. Fig. 1 illustrates the relaxation behavior of both ready standard and shear mixed dough. The scattering in the curve for standard dough may result from the higher sample mass in the rheometer gap. The rearranging of particles in the gap was more obstructed as it was for shear mixed dough. However, the short term relaxation behavior of both kinds of dough appeared to be similar. The standard rheological data was compared with the computed rheological data from these relaxation spectra in terms of accuracy and precision (Table 2). The accuracy expresses how well the order of the results from the spectra of the MSSM process equals to those of standard dough. Except for W_a , the accuracy in producing the same order of the rheological values as for standard dough was between 69.01 and 93.93%. This showed that the MSSM results allowed a reasonable interpretation. On the other hand, the accuracy for W_a was very poor. The order of the values that derive from the Chen-Hosoney stickiness test (Chen and Hosoney, 1995) is very different to the order that derives from the relaxation spectra. A sensible transformation of Chen-Hosoney stickiness data is sophisticated due to the amount of boundary conditions and assumptions of unknown values. The precision ranged from 51.15 to 96.26% and expresses the reproducibility of the results. For the rheological parameters the precision showed very high values above 92% but $\tan\delta$ showed the

lowest accordance. Since $\tan\delta$ is calculated as the quotient of G'' and G' small deviations to opposed directions provokes even bigger deviations in $\tan\delta$. These results showed that it is allowed to draw conclusions from computed rheological data since they correspond well with standard wheat dough. The accuracy can be increased by adding an offset or by transforming the input values. However, the MSSM process can be prone to small deviations in the dough composition or dough distribution under the shearing geometry since very small specimens are used.

In order to determine the necessary amount of relaxation steps of fully developed MSSM dough the time-dependent position of the peaks in a relaxation time - modulus graph was observed. MSSM dough was shear mixed for 720 s. The resulting relaxation spectra for each step were plotted and compared with the spectra of fully developed standard dough (Fig. 2). The spectra of standard dough showed four different peaks. The prominent peaks were at $5.0 \cdot 10^{-3}$ s, $3.3 \cdot 10^{-2}$ s, $2.2 \cdot 10^{-1}$ s and $8.0 \cdot 10^{-1}$ s. These peaks were in close agreement with those from Kontogiorgos and Dahmsi (2014) who examined relaxation spectra of hydrated gluten. This concludes that the MSSM dough is of equal degree of dough development since even small deviations in the dough condition lead to noticeable changes in the dynamic rheological data and thus in the resulting spectra (Didier et al., 2016; Kouassi et al., 2014). In the beginning of the MSSM process (Fig. 2 bottom), the peaks were randomly distributed. According to the reptation model peaks at small relaxation times refer to small molecules that have a low contribution to molecular gluten entanglement (Pokrovskii, 2010). These small molecules have a molecular weight much smaller than the one of the actual entanglement. They can include gliadins or unbound LMW glutenin. After app. 150 s of shear mixing all peaks remained constant at relaxation times around $2.1 \cdot 10^{-3}$ s, $1.2 \cdot 10^{-2}$ s, $4.2 \cdot 10^{-2}$ s, $1.3 \cdot 10^{-1}$ s and $1.0 \cdot 10^0$ s. The positions of peaks did not change after that. The four rows of peaks at high relaxation times were in close range to those from standard dough. However, the first row of peaks of MSSM dough does not appear for standard dough. Probably, all peaks of MSSM dough have an offset in relaxation time of app. 0.2–0.3 s. The peak at $2.1 \cdot 10^{-3}$ s became visible only after applying this offset. It can be attributed to a generally higher degree in entanglement of proteins or in forming intermolecular bonds between gliadins and glutenins. Yet, the accessibility to oxygen during shear mixing is limited which would result in low intermolecular chain formation and a weak gluten network with less molecular interaction (Decamps et al., 2016; Sliwinski et al., 2004). However, it is known that shear mixing incorporates mechanical energy more efficiently than standard mixing (Peighambardoust et al., 2007; van der Goot et al., 2008). Compared to the standard dough procedure where the specific mechanical energy input (SME) was 9.56 ± 0.61 kJ/kg, the SME until dough development for shear mixed dough was 361 ± 16 kJ/kg. It was computed following the equation in a previous work (Tietze et al., 2017). However, it is a third of the amount which was needed for dough development in the continuous shear mixing process and it underlines the efficacy of the new shear mixing method. Probably this would have outbalanced the effect of missing oxygen. This becomes more plausible as the estimated dough development time of 150 s from the spectra is in good agreement with measured 144 s of standard dough. In each shear mixing step the time to allow dough to relax was short enough to prevent molecular disentanglement since peaks at relaxation times longer than 10^1 s were not observed (Rao et al., 2000).

In order to evaluate the shear mixing efficacy CLSM protein micrographs of MSSM dough and conventional dough were evaluated. Fig. 3 shows the CLSM micrographs for different shear mixing times up to 720 s of shearing. After 120 s a widely spread protein network developed. This state remained for 720 s of shearing. Opposed to continuous shear mixing (Tietze et al., 2017), a standard dough-like protein matrix has developed already after 120 s. A macroscopic inspection showed no flour-water slurry opposed to continuous shear mixing. There the dough development time was 480 s. The earlier development

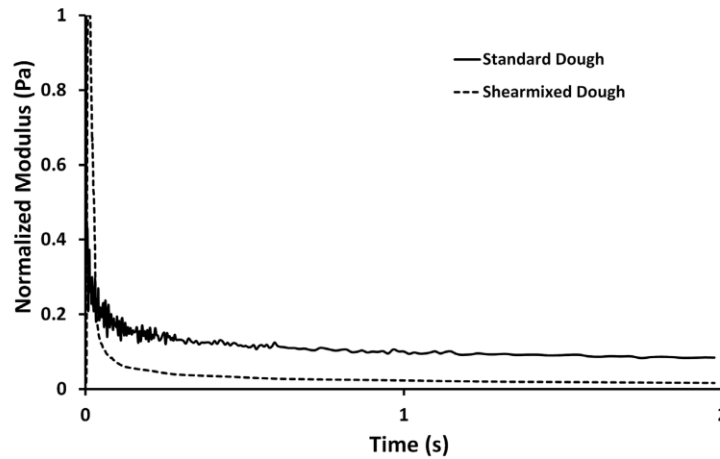


Fig. 1. Illustration of the shear modulus of standard and shearmixed dough over the course of relaxation time measured during the last relaxation step of a series of stress relaxation tests with alternating shear direction.

of MSSM dough can be attributed to the alternating direction of shearing. During continuous shearing the radial differences in the shear rate increased the chance that side chains of the polymers came close enough to form networks. Alternating shear directions support the redistribution of reactive molecules due to the change of axial forces. The chance that molecules interact or entangle is increased. The alternated shear mixing prevents alignment of molecules in shear direction and also prevents shear banding of starch and gluten, which would be visible as separation of starch from the gluten network. The particle analysis of the CLSM micrographs (Fig. 4) revealed that no significant change in protein particle aspect ratio occurred. The aspect ratio is defined as the quotient of width by length of the protein particle. It varied between 0.63 ± 0.05 and 0.56 ± 0.04 . Although the shape of protein particles suggests to be unaltered the particle size changed. In order to form the gluten network proteins have to get in contact with each other. This led to a protein particle size of $146 \pm 77 \mu\text{m}^2$ after 240 s of shear mixing but it showed no further significant increase although developed standard dough showed an average protein particle size of $361 \pm 80 \mu\text{m}^2$. However, the protein particle size after shear mixing is in agreement with findings from others (Bozkurt et al., 2014; Jekle and Becker, 2011b). A simple shear flow would result in an irreversible orientation of particles (Folgar and Tucker, 1984) as it was shown in the previous work (Tietze et al., 2017). Alternating shear directions would change the particle orientation due to compression and extension but particles may also be forced to rotate. This would result in measuring potentially smaller lateral cross-sections. Following an imaginary trend line for the development of the particle size would lead to the assumption that MSSM dough would be developed long after 720 s but it was already developed after 240 s. This discrepancy and by this the course of the particle size curve can be explained by protein reorganization after relaxation which was described by Don et al. (2005) or by Wang et al. (2015). It is possible that the short alternating

relaxation phases in the MSSM process were sufficient to support reorganization so that proteins could form bigger networks during ongoing shear mixing. Due to “relaxation zones” on top of the forming dough in a z-blade mixer the degree in protein reorganization will be higher and thus will be the particle size. On the other hand, Peighambardoust et al. (2005) did not observe protein disruption but shear banding accompanied by protein aggregation after shear mixing and developing dough. This is another approach in explaining further increasing protein particle sizes. However, the MSSM process did not lead to their described starch and gluten separation even after 720 s of shearing. However, the particle sizes imply that MSSM dough would be developed prior to 240 s and that the minimum in the particle size graph would indicate overmixing of shear mixed dough.

The point of optimum mixing time or the point of overmixing could not be clearly determined from CLSM micrograph evaluation. The relaxation spectra indicated no further rheological changes after app. 240 s of shear mixing. It can be concluded that overmixing and gluten fragmentation did not occur and that the shear mixing optimum has been reached when the peaks finished drifting after 150 s. The rheological properties can be computed with good accuracy from the relaxation spectra. The MSSM process is capable of producing wheat dough with properties comparable to standard dough. The rheological properties can be read directly from the relaxation spectra. The point of optimum mixing can be easily determined from the relaxation spectra since the peaks stop drifting. The rheological properties of dough can be determined from every single mixing step. Thus, overmixing can be neglected.

3.2. Validation with six different flours

The developed MSSM process and the evaluation of the relaxation spectra in the previous chapter showed good correlations to standard

Table 2 Results of the comparison between the rheological data of standard and MSSM wheat dough that were measured and that were computed from relaxation spectra.

	G*	tand	G'	G''	G0	Wa
	Pa		Pa	Pa	Pa	J
Accuracy (%)	87.59 ± 11.32	78.74 ± 8.57	85.80 ± 16.67	93.93 ± 12.27	69.01 ± 12.85	0.01 ± 0.00
Precision (%)	93.68	51.15	93.09	96.26	92.06	65.93

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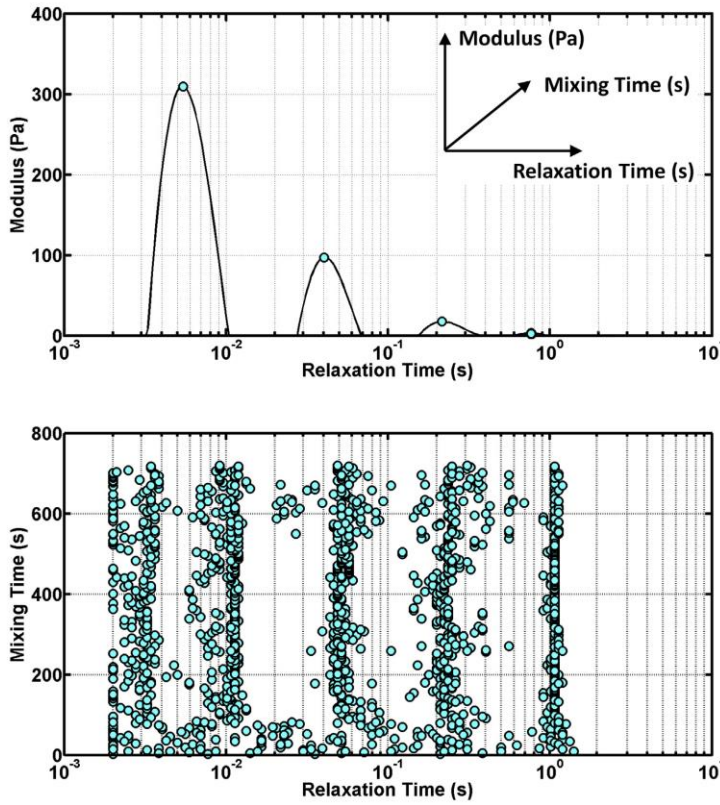


Fig. 2. (top) X-Z-view of the relaxation spectra of fully developed standard wheat dough. (Bottom) X-Y-view of a 3D-plot showing the development of the maximum peaks in the relaxation spectra of MSSM wheat dough in dependence on mixing time (bottom). Markers (●) indicate the local maximum peaks in each spectrum (n = 5).

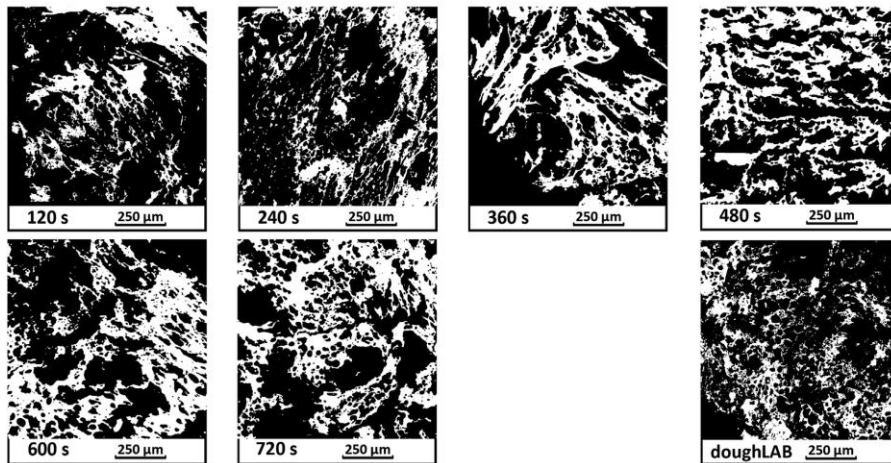


Fig. 3. CLSM micrographs of wheat dough processed in the rheometer and illustration of protein distribution (white) in dependence on shearing time. The declaration “doughLAB” refers to as fully developed standard wheat dough mixed in a doughLAB. Each micrograph is composed by 3x3 micrographs that were stitched together.

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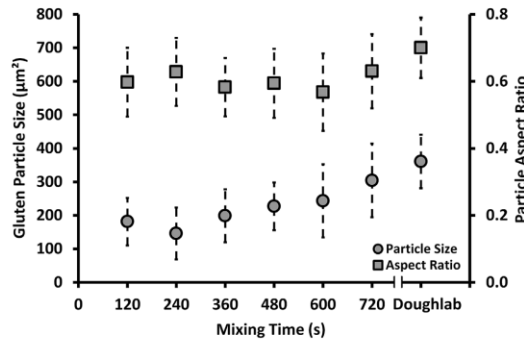


Fig. 4. Average protein particle size development (▲) and protein particle aspect ratio (●) during shear mixing of wheat dough in the rheometer as a function of mixing time.

dough. In the following, six different flours were analyzed in order to validate the MSSM process. Each type of flour was subjected to the MSSM procedure for 720 s. From the resulting relaxation spectra the optimum mixing time and the needed amount of alternating shear mixing steps were determined. The results of the correlation between standard and MSSM dough both with fully developed gluten network are shown in Table 3. The 6-in-1 model incorporates the type of flour as the varying parameter. The normalized root mean square error (NRMSE) indicates the deviation from the measured values of the respective standard dough and the according MSSM dough. The 6-in-1 model for dough without yeast showed good correlations for all parameters. R² ranged between 0.62 and 0.89. The sum of errors was between 207.06 and 174.01%. The single flours deviated strongly in G₀ as the sum of errors was 388.70%. Despite of that, the regression model allowed a good prediction since R² was 0.68 and the deviations amongst the G₀-values were close to each other. Others were able to predict dough properties with an error of 3–4% (Ruan et al., 1995) by using neuronal networks in order to predict dough mixing characteristics. But they only used torque data from the kneader and related it to empirical rheological values. The torque of a big kneader is probably less prone to small changes in the dough constitution than the rheometer. Others used fundamental rheological data for the prediction of dough properties and achieved agreements of 70% (Michel et al., 2017) and with a success rate of 65% others identified the ultrasound attenuation coefficient to be the best predictor for dough rheological properties (Peressini et al., 2017). Compared to those results, a good prediction of dough rheological data was possible in this study.

In order to evaluate the possibility to predict properties of final baked goods yeast was added to each of the six flours. These MSSM dough samples were subjected to proofing and an imitating baking

process. The results of the new 6-in-1 model and the error % are shown in Table 4. The reference method for stickiness basically delivers values in a different unit and of different order. A conversion of the values to fit W_a was not possible. In contrast to dough produced without yeast the coefficient of determination for the combined model of all six flours was not higher than 0.06. This showed that there were no correlations. Additionally, the sums of errors were generally higher than for dough produced without yeast. Comparing the crumb of standard and MSSM bread showed the same results (see Table 5). R² was not higher than 0.17 and the NRMSE reached values of the order of 10¹⁷. The high errors can be attributed to the irregular distribution and growth of the gas cells. The cells segregated to the top of the dough sample and burst when the gas pressure exceeded the maximum gas holding capacity or burst due to the sudden deformation of the relaxation step. The gas escaped the rheometer gap and at the contact surface of the rheometer geometry a random amount of dough remained in contact. The error in the computed rheological values reflected these circumstances. It can be also concluded that the yeast is the influencing factor. Verheyen et al. (2015) showed that dead yeast cells release free –SH groups which destabilized the gluten network. Living yeast cells instead produce succinic acid. It is known to stiffen dough and to reduce dough stability (Jayaram et al., 2014). This makes dough more susceptible towards mechanical stress. Proofing in the rheometer led to a further destabilization of the gluten network around the expanded gas cells. Since no crumb has formed during the imitating baking process the destabilized gas cell walls dried out. This made them stiff, brittle and resulted in high crumb consistencies. Another aspect can also be an unbalanced CO₂ production during proofing. The yeast was dosed as a suspension together with the water. Due to the asexual reproduction form of budding the used yeast *Saccharomyces cerevisiae* has formed heavily dividable conglomerates in the suspension. Although the suspension was shaken vigorously prior to dosing, the chance of pipetting conglomerates is high and has an even greater impact on the small dough sample during proofing. This led to an increased CO₂ production, larger gas cells and more susceptible cell walls. Under these circumstances a sensible evaluation of the baking properties is not possible.

4. Conclusion

The purpose of the new shear mixing technique was to evaluate dough properties from the relaxation spectra during mixing, to produce bread on a microscale and to evaluate its properties. The new shear mixing technique consists of a series of consecutive relaxation tests with alternating shear direction. The extraction and evaluation of the relaxation spectra of each shear mixing step enables to determine the dough rheological properties simultaneously to mixing. The CLSM evaluation proved the point of optimum dough development as indicated by the relaxation spectra. The computed dough rheological properties of MSSM dough were in good correlation to standard dough properties.

Proofing and baking of MSSM dough showed inconsistent results.

Table 3

Coefficient of determination (R²) between fully developed standard and MSSM wheat dough of the combined 6-in-1 model and deviation between the measured values for each standard and MSSM dough expressed as NRMSE. Dough samples were produced without yeast.

Type of Flour	G*	tanδ	G'	G''	G ₀	W _a	Sum of Errors
R ² 6-in-1 model	0.77	0.79	0.62	0.89	0.68	0.37	–
NRMSE (%)							
Bun	51.43	17.72	52.69	44.81	49.04	n/a	215.69
Cookie	25.63	23.57	26.97	20.74	71.73	n/a	168.64
Premium	31.61	55.09	34.85	23.83	64.45	n/a	209.84
Type 550	28.77	27.45	29.17	34.77	64.75	n/a	184.91
Type 1050	39.71	103.55	46.41	24.7	74.71	n/a	289.09
Waffle	29.9	51.43	33.06	25.16	64.01	n/a	203.56
Sum of Errors	207.06	278.81	223.15	174.01	388.7	–	

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Table 4

Coefficient of determination (R^2) between fully developed standard and MSSM wheat dough of the combined 6-in-1 model and deviation between the measured values for each standard and MSSM dough expressed as NRMSE. Dough samples were produced with yeast.

	Type of Flour	G*	tan δ	G'	G''	G0	Wa	Sum of Errors
	R^2 6-in-1 model	0.01	0.04	0.02	0.04	0.06	0.06	–
NRMSE (%)	Bun	122.33	226.71	65.27	334.01	155.41	n/a	903.73
	Cookie	38.92	217.16	55.75	87.27	58.79	n/a	457.88
	Premium	30.1	132.4	43.3	53.16	81.98	n/a	340.94
	Type 550	281.11	208.1	139.96	634.16	147.53	n/a	1410.86
	Type 1050	43.77	210.07	24.95	133.82	66.68	n/a	479.29
	Waffle	132.26	162.74	78	279.71	158.14	n/a	810.87
	Sum of Errors	648.49	1157.18	407.24	1522.13	668.53	–	–

Table 5

Coefficient of determination (R^2) between standard and MSSM wheat bread crumb of the combined 6-in-1 model and deviation between the measured values for each standard and MSSM bread crumb expressed as NRMSE. Dough samples were produced with yeast.

	Type of Flour	G*	tan δ	G'	G''	Go	Wa	Sum of Errors
	R^2 6-in-1 model	0.13	0.17	0.13	0.15	n/a	n/a	–
NRMSE (%)	Bun	1.19E+05	4.78E+01	1.19E+05	1.20E+05	n/a	n/a	3.57E+05
	Cookie	1.02E+16	7.94E+02	7.22E+15	4.29E+16	n/a	n/a	6.03E+16
	Premium	7.36E+11	6.20E+02	6.29E+11	2.43E+12	n/a	n/a	3.79E+12
	Type 550	3.32E+12	5.96E+02	1.53E+12	1.70E+13	n/a	n/a	2.18E+13
	Type 1050	5.95E+08	9.27E+02	2.93E+08	3.34E+09	n/a	n/a	4.23E+09
	Waffle	7.45E+16	9.89E+02	6.08E+16	2.45E+17	n/a	n/a	3.80E+17
	Sum of Errors	8.48E+16	3.97E+03	6.80E+16	2.88E+17	–	–	–

For MSSM dough the yeast undermined a successful correlation with standard dough/bread samples. Instead of yeast it would be advantageous to use chemical leavenings that contain no gluten-weakening agents and that can be dosed more precisely. However, when solving the yeast problem the MSSM technique will be a time and material saving dough evaluation technique with a good estimation of rheological properties.

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7. Discussion

This work showed the influence of two different physical stress factors on the rheological properties of dough. On the one hand, low mixing temperatures were examined. On the other hand there was pure shear as the only deformation and only source of mechanical energy during dough mixing. The measured rheological properties were obtained by empirical and fundamental rheological methods since both are widely used in bakery and cereal science.

7.1. Thermal stress

Exposing to thermal strain showed that the rheological properties depend strongly on the dough mixing temperature. Lowering the mixing temperature led to a reciprocal decrease in the mixing time and dough development time. At 15 °C, the mixing time was doubled compared to 35 °C. It is known that the reaction kinetics at lower temperatures are decreased which becomes more evident when following the equation for second-order chemical kinetics:

$$v = k \cdot c(\text{glutenin}) \cdot c(\text{gliadin}) \quad 7.1$$

with the concentration c of glutenin and gliadin and the reaction rate constant k which in turn is given by the Arrhenius equation

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}} \quad 7.2$$

Here, E_a is the activation energy, R the gas constant, T the temperature and A the pre-exponential factor from chemical kinetics. The reaction rate constant k will decrease with lower temperatures as will the reaction kinetics. Following the rules of thermal expansion, the volume of a material is decreased. The material is contracted while its density and consistency are increased which is in contrast to the experiments performed by Rosell and Collar (2009). They set the dough consistency to a constant level by adjusting the added amount of water. In the present work, the water-flour ratio and the dough recipe were constant over the time. Although Rosell and Collar (2009) measured a decreased elasticity of dough at low temperatures, the constant amount of water in the present work resulted in a higher elasticity, indicated as tensile strain to rupture. When exposed to low temperatures material contracts and extension becomes more restricted as can be seen by a higher Young's Modulus. The rise in the strain until rupture can be attributed to the molecular motion. Small molecules change their position within a certain area around it. When the temperature is increased, the motion of the

molecule is faster and the area of mobility is expanded. Following the course of Young's Modulus with temperature implies a decreased extensibility at low temperatures. But wheat dough exhibits the opposite behavior. Lowering the mixing and dough temperature resulted in an increased extensibility. Figure 16 illustrates the possible mechanism.

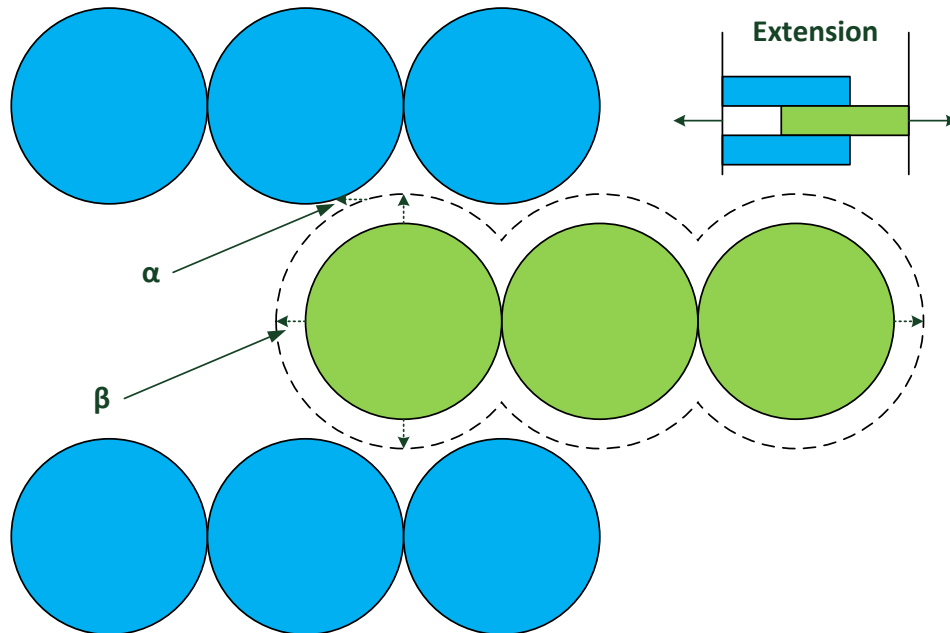


Figure 16: Simplified illustration of the extension of gluten molecules and their Brownian motion with α the possible maximum extensibility before collision with other molecules and β the temperature dependent space of the Brownian motion.

During extension of dough, the gluten macropolymers are dragged along each other. On the molecular basis and at low temperatures, the dimension of the Brownian motion of the molecules is smaller and thus the entangled protein strands can slide easier along each other at 15 °C compared to 35 °C. The course of Young's Modulus is in accordance with Sadd (2009) and Schiavi et al. (2016) who showed that it is negatively correlated with temperature. The same correlation is valid for the viscosity of fluids and thus the viscosity of dough which is expressed by the Williams-Landel-Ferry model:

$$\eta(T) = \eta_0 \exp\left(\frac{-k_1(T - T_g)}{k_2 + T - T_g}\right) \quad 7.3$$

In this equation T_g is the glass transition temperature of the polymer melt and k_1 and k_2 are constants that will be determined empirically from the experimental data. A rough estimation leads to the following: according to Wang et al. (2016) k_1 and k_2 can be set to 17.44 and 51.6, respectively. Extrapolating the measured zero shear viscosity η_0 to app. 2.0 MPas will result in a computed viscosity of 826 Pas at 15 °C. This exceeds the values from the experiments as the discrepancy between

measured and computed viscosity is more than 70.000 %. But wheat dough is neither purely viscous nor purely elastic – it is viscoelastic which derives from gluten (Belton 2012). In order to fulfill the equation, η_0 of dough must be of the order 10^9 which comes close to materials like glass or asphalt concrete. This leads to the conclusion that the viscoelastic stress response of dough to temperature cannot be simply computed with the WLF equation. Moreover, the calculation of k_1 and k_2 needs to be adapted to fit the properties of viscoelastic wheat dough.

Besides differences in the fundamental rheological properties, dough mixed at low temperature exhibited differences in the handling properties. The stickiness measured with a Chen-Hoseney stickiness cell indicated no temperature dependence but the actual handling properties and the machinability of the dough samples from low and warm mixing temperatures were different. Cool dough exhibited a subjectively higher stickiness towards human skin, the steel mixing bowl and other surfaces compared to warm dough. This phenomenon was neither described by Başaran and Göçmen (2003) nor by Rosell and Collar (2009) who also experimented with cool dough. The difference is that they adapted the water in the recipe to reach a fixed dough consistency after mixing at the respective low temperatures. In the present experiments, the water content and the recipe were kept constant. The surplus in free water in the dough provoked water extractable pentosans to take up more water as described by Wang et al. (2002) and thus resulted in stickier dough. According to Chen and Hoseney (1995) and Labat et al. (2000), these pentosans and especially their bound ferulic acid are responsible for dough stickiness. Heddleson et al. (1993; 1994) developed the Dahlquist criterion which gives information about the possible adhesiveness or stickiness of dough. The authors stated that the storage modulus G' needs to be larger than 10^5 Pa so that dough won't exhibit stickiness or failure in cohesiveness. In fact, G' of cool dough was $3.59 \cdot 10^4 \pm 0.13 \cdot 10^4$ Pa and non-stickiness was not given by the Dahlquist criterion. As expected, the course of the G' -curve indicates an increase in G' with lower temperature. Following the trend line for G' and following the Dahlquist criterion, implied that dough will exhibit no stickiness below -34.1 °C. Despite of the mathematical point of view, this is also reasonable from the thermodynamic point of view since the glass transition temperature of dough is at app. -30 °C as reported by Räsänen et al. (1998). They also reported that the water in dough freezes at -10 °C which affects the stickiness causing ferulic acid. As it is not dissolved at these temperatures, dough will probably exhibit no stickiness irrespective of the Dahlquist criterion.

From the CLSM micrographs of the cold mixed dough can be seen that the gluten was fully developed. The dough stickiness suggests that excess water is present in dough which was not taken up completely by the flour components. From native starch granules it is known that their water retention capacity is reduced with decreasing temperature (Li and Yeh 2001) although the rate of hydration of starch is higher than for protein (Larsen 1964). Independent on the competition for water by the flour components, the overall viscosity of dough is also reduced. This leads to the conclusion that the decreased viscosity at low temperatures is based on both, a general decrease due to the temperature itself as expressed by the Arrhenius equation (eq. 7.2) and based on still unbound water in dough. At the end, the stickiness problem could be solved by replacing the starch in flour with damaged starch as it is capable of taking up five times more water than native starch as proposed by Hébrard et al. (2003). Although pentosans are able to take up even more water, it is likely that the content of the accompanying and stickiness causing ferulic acid will rise. Irrespective of that, it can be assumed that the dough volume after proofing is higher than for mixing at normal temperature. Incorporating more mixing energy into dough due to longer necessary mixing times will increase its gas volume fraction right after mixing (Chin and Campbell 2005b). The gain in volume can be increased when dough is mixed at 15 °C and proofed at 30 °C. The thermal expansion of gas will contribute to 5 % more dough volume.

Wheat dough exposed to low mixing temperatures as the thermal strain exhibits an increased consistency while its degree in viscoelasticity is unaffected. On one side, cool mixed dough proves to be more resistant towards physical load which is expressed in an increased extensibility until rupture. On the other side, it exhibits a higher adhesiveness that is likely to affect its machinability. The demand for a longer dough development time can be balanced out by chances of a higher dough volume after proofing.

It was shown that cool mixing temperatures have strong effects on the rheological properties but also on the texture of dough. Both, the dough development time and the stickiness increased. To counteract longer mixing times, the mixing power needs to be increased. This in turn, will increase the dissipated amount of energy and the necessity for active cooling during mixing arises since the dough temperature after mixing could be too high and proteins could be damaged. Thus, a more efficient way of incorporating mechanical energy into dough is necessary in order to produce cool dough in acceptable time.

7.2. Shear stress

In standard dough kneaders, different kinds of mechanical energy are applied to the forming dough of which extension, compression and shear are the dominating forces. Pure shearing was chosen as the only source of mechanical energy in order to examine the influence of the mechanical strain on dough. Shear forces can be applied in a continuous form, the necessary effort for equipment is low and the evaluation methods for shear are well established. As shown by Peighambardoust et al. (2004) it is possible to produce dough by shearing. They used a specially designed shearing device in which the actual dough mixing occurred in the gap between two coni. Opposed to that, in this work a commercially available rheometer was used for conducting the shear and dough mixing experiments.

With respect to shear energy, the first objective was to identify which kind of shearing lead will lead to dough with properties that are comparable to dough that is mixed in a standard z-blade kneader. For that purpose, two different geometries were used on the rheometer. The resulting mixing zone in the rheometer consisted of a plate or cone geometry both in combination with a flat bottom. The plate geometry enabled to observe the influence of a constant mixing gap and the influence of a radially increasing strain rate. With the cone geometry it was possible to observe the influence of the opposite: a radially constant strain rate which derives from the radially increasing gap.

Both geometries qualified for the production of wheat dough and the development of a gluten network which is comparable to dough that was produced in a standard z-blade kneader. Moreover, it was demonstrated that it is possible to produce very small amounts of dough which permits the developed method to be also applicable for analytical purposes. The examination of the produced dough samples showed that the dough development times for both geometries were in close agreement with that of dough that was mixed in recording z-blade mixer at 30 °C. This dough will further be referred to as standard dough. The investigation of the gluten network with a CLSM showed that the developed gluten network of both shearing geometries resembles that of standard dough. This shear mixing process was observed for several minutes and samples were taken every minute. Discrepancies were detected between the course of the dough consistency curve during shear mixing and the structure of the gluten network at distinct points in time. The consistency-over-time curve indicated a fully developed gluten network after two

minutes of shearing. Opposed to that, the micrographs from the CLSM indicated loosely connected protein filaments which had no similarity to the protein network of standard wheat dough. Further shearing beyond the point of indicated dough development from the consistency curve led to an observable increase in protein network aggregation and connectivity. Opposed to standard kneading, this concludes that the consistency curve cannot be used for the determination of the dough development time. The rheological characterization showed that shear mixed dough had the properties of standard dough after five minutes of constant shearing. These findings were independent on the used shearing geometry.

Irrespective of that, Peighambardoust et al. (2010) found that shearing may damage gluten more than standard kneading where both extensive and shearing forces act simultaneously. According to the CLSM micrographs and the measured rheological properties, this could not be confirmed. Their reported damages can be possibly attributed to their applied shear mixing times of 25 minutes. As a similarity, the CLSM micrographs indicated that an alignment of the shear mixed dough occurred. The continuous shearing led to a radial orientation of dough and a separation of dough into a starch enriched inner and a starch depleted outer zone as it was already observed by Peighambardoust et al. (2008). This shows that starch granules tend to migrate to areas with high shear rates and that the migration is independent on the shear geometry.

A serrated bottom or top geometry can be used in order to prevent gluten and starch from segregation and to prevent dough from alignment. But in that case not only shear forces would be applied. Instead also compressive and extensive forces will be applied to material that is in the grooves. The kneading process would then be more related to standard process. Compressive forces will exert at the front faces and extension act at the back faces of the grooves. Shear forces will only be exerted on the top and side faces of the bumps. On the one hand, with these assumptions and the geometric dimensions of the serrations it is possible to determine the ratio of shear of the total amount of shear mixing energy. On the other hand, compression and extension are also applied which makes it difficult to determine the contribution of each force to dough development. The same is valid for standard z-blade mixing where there is not only single compression, tension or shear (compare Figure 17). Each of these kinds of deformation contributes to another extent.

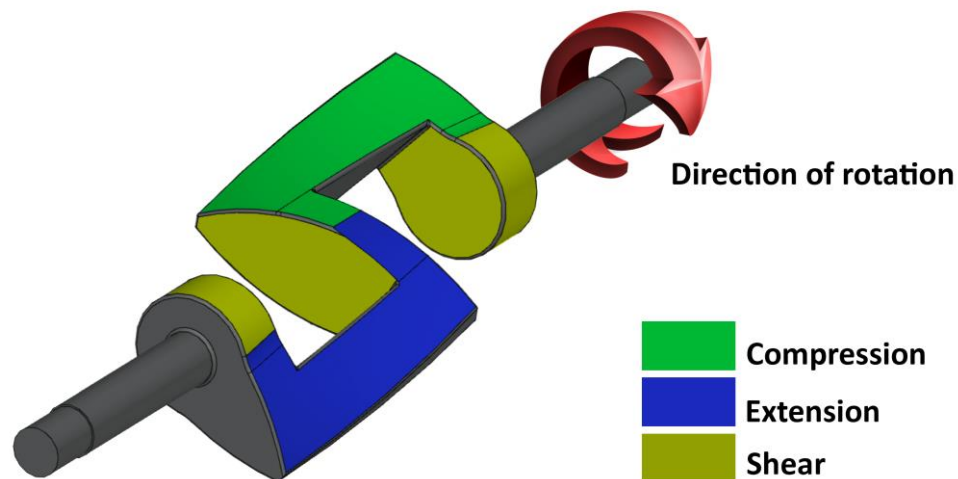


Figure 17: Simplification of the dominating acting deformations compression, extension and shear on the material in a mixer equipped with a rotating z-blade mixing hook (original image by santhosh (2015)).

At first sight due to the rotational motion of the mixing blades, compression forces are exerted to those parts of the dough specimen that are orientated perpendicular to the mixing plane and in the direction of the rotation of the mixing blades. Shear forces are exerted in the gap between the mixing bowl and the mixing blades – but also on the mixing blades when dough is forced to the sides of the mixing plane. On second sight, although the blue faces in figure 17 exert normal forces, they also cause movement of dough in- and outwards by which shear forces are exerted. Actually, each force acts on every plane of the mixing blade in each direction. The resulting stresses are expressed in the stress tensor (compare equation 3.3). As mixed dough may also contain air nuclei it is a compressible material. The overall stress tensor is then composed of both a hydrostatic and the deviatoric tensor σ_h and σ_d where σ_h only contains the normal stresses:

$$\sigma = \sigma_h + \sigma_d = \begin{bmatrix} \sigma_h & 0 & 0 \\ 0 & \sigma_h & 0 \\ 0 & 0 & \sigma_h \end{bmatrix} + \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad 7.4$$

Extensional forces may act when dough adheres to the surfaces of the mixing blades. As for most dough the adhesive forces dominate over the cohesive forces. The dough is stretched until rupture may occur. The Poisson's ratio of wheat dough is 0.46 (Charalambides et al. 2002). It shows that dough increases its volume when exposed to extension and decreases its volume when exposed to compression. In the mixing bowl, the effect of both deformations will balance out. Applying empirical methods for the determination of the elastic modulus may arise problems. Using the common procedure for the determination of the extensibility, a dough string is simply stretched at constant speed and the resulting force-time graph is

evaluated. Not only the volume of the dough string increases but the extension of the dough string is a biaxial deformation by which the string will show nonlinear thinning as demonstrated by Chakrabarti-Bell et al. (2010). In case the development of the stretching profile would be known the problem could be compensated. However, the fact that dough tends to strain hardening undermines the evaluation. Thinner dough parts will exhibit higher stresses when being extended and the resulting stress information of the whole sample is falsified, as there is no homogenous stress distribution in the sample. Instead, using the given information of a rheometer from shear tests, it is possible to derive information that is usually assessed by extension tests. Another important feature of shear mixing dough is that it is possible to extract the relaxation spectra. These can be used successfully to relate from shear mixed dough to the rheological data of standard dough and possibly further to bakery relevant properties. Some might be directly obtained during shear mixing and others would need additional tests. Although the empirical methods are closely related to real processes in the industry, it is difficult to derive scientifically based conclusions from them. The measuring units are arbitrary and can only be approximated to SI units. In addition, it is sophisticated to relate from a test with one kind of deformation (shear mixing) to a test where different kinds of deformation (z-blade mixing) are acting simultaneously.

However, exposing flour and water to shear leads to dough properties that are comparable to standard dough. Shear mixing is an efficient way of incorporating mechanical energy into dough and to develop a functional gluten network. However, the efficiency of shear mixing suffers from dough alignment in the direction of shear and from gluten-starch separation. The dough development in shear mixing is independent on the used plate or cone geometry. There is no measurable influence of gradients in the shear rate or gradients in the rheometer gap on the rheological properties of shear mixed dough. However, the plate geometry is preferred as it is likely that the mobility of flour particles is less restricted compared to the cone geometry.

Shear mixing flour and water by applying a constant shear rate leads to the formation of dough. However, the resulting dough is aligned in the direction of shear. Thus, the rheological characterization can be altered. In order to overcome the alignment of dough, another shear technique was introduced. Instead of applying a constant shear rate to the forming dough, consecutive stress relaxation tests with alternating shear direction were used. The alternating shear direction

prevents the dough from aligning and supports the actual mixing action in the rheometer gap. For the new technique which is referred to as microscale shear mixing (MSSM), there was no mixing curve directly accessible. Instead, since each mixing step consisted of a relaxation step, the relaxation spectrum of each step was computed and compared with the spectrum of fully developed standard dough. When the positions of the maxima and minima are in closest agreement, the shear mixed dough is considered fully developed. Since each relaxation step lasted 2 s, a series of several hundred spectra were combined in one overview. The shifting of the respective peaks could be followed easily. The spectrum of fully developed wheat dough is well known and has four distinct peaks at certain relaxation times as it was also shown by Kontogiorgos and Dahunsi (2014). With the equations presented by Tietze et al. (2016), it was possible to compute the rheological data out of the relaxation spectra. It was demonstrated that the MSSM process leads to dough that has similar rheological data like the standard dough. Depending on the respective rheological value, the accuracy between MSSM and standard dough was up to 93 % and the precision was up to 96 %. This shows that the evaluation of the relaxation spectra delivers rheological values which are very close to that from the standard rheometer software. However, the rheological spectra were evaluated and the rheological data was computed under the assumption that the relaxation process was performed with small strains which consider the linear viscoelastic region of wheat dough. In fact, the strain in the relaxation steps was 12 and -24 or 0.75 and -1.5 rad, respectively. The linear viscoelastic region is at strains smaller than 0.1. The spectra of relaxations with large strains can show peaks at slightly shorter relaxation times as demonstrated by Mckenna and Zapas (1986). However the accuracy of the computed rheological data would be less but the precision will still be high. A correction factor could be introduced to compensate for the differences. Although the intention of applying large strains was primarily to develop wheat dough the computation of rheological data from the spectra is of major importance, as well. Ng et al. (2011) conducted large strain oscillation experiments with gluten dough. They generated the dynamic rheological data by Fourier decomposition of the obtained stress data since part of the information (~12 %) lies within the harmonics of higher order and accounts for the nonlinear viscoelastic behavior at large strains. With Fourier decomposition equation 3.20 will then develop to

$$\sigma = \sum_{n=1}^N G_n' \gamma_0 \cdot \sin(n\omega t) + G_n'' \gamma_0 \cdot \cos(n\omega t) \quad 7.5$$

for which experiments at several different strains have to be conducted. But there is no necessity for additional experiments or mathematical efforts. First, in the MSSM procedure relaxation experiments were performed instead of oscillation experiments. Second, the summation of residual stress after each relaxation step was considered and third, the additional information of the higher harmonics is included in the spectra. Thus, the computation of an overall G' or G'' from the spectra already considers the contribution of each Fourier harmonic. However, the degree in the contribution of the harmonics will remain unknown.

The computation of the relaxation spectra is of high importance. All deviations in the goodness of fit between the standard and MSSM procedure rely on it. Greater deviations in the computed data will result in misleading information and misinterpretation. Other scientist conducted long term experiments with several hours of relaxation. For developing dough, this procedure is counterproductive. No real time information about the dough development would be gathered. If it is of interest, relaxation tests at higher temperatures can be performed as done by Kontogiorgos and Dahunsi (2014). By application of time-temperature superposition, a more accurate insight in the long term relaxation process and the decrease in stress during alternating shear directions can be obtained. However, the necessary increase in temperature is limited since the dough protein would denature at too high temperatures. Thus, also the insight into long term behavior will be limited.

Extracting the rheological data from the spectra enabled to compare the data with those of standard dough. After the MSSM procedure the shear mixed dough exhibited stress on a similar scale. Precision and accuracy between standard and MSSM dough were over 90 %. Therefore, it is straightforward to also apply the MSSM procedure to other flour types or to relate to future baking properties. Changing the flour type resulted in rheological data that came close to the data of the respective standard dough. However, the extraction of the relaxation spectra and the computation of the respective rheological data showed that the extraction method of the spectra is not universally applicable. The congruence of data was lower as it was for data gained with all-purpose flour, in the first. The error-% for the rheological values was between 17.72 and 103.55 % when evaluating each flour type on its own. Combining all examined flour types in one model resulted in overall coefficients of determination between 0.62 and 0.89 (excluding work of

adhesion). This demonstrates that the method of computing the rheological data out of relaxation spectra is close in representing the actual rheological data of real dough. The bandwidth in flour types and their different rheological data account for a scaling of data and for an increase in predictability. However, the predictability from MSSM dough to real leavened dough and baked bread is decreased. The difference in the examined subjects is too high and the rheological properties are too different from each other. The same is for “shear baked” bread and the low predictability to real bread. It can be attributed to the fact that during proofing the softest and thus largest gas bubbles with the thinnest cell walls accumulate at the top of the specimen. During baking in the rheometer these walls solidify but they cannot withstand the shear forces that act during measurement. The real bread instead when measured in the rheometer is not exposed to possibly destructive shear actions. The pores of the bread crumb are ideally developed and stable. However, during “shear baking” the surface of the specimen consists of solid dough. This accounts for local increases in the consistency but the predictability on the other hand is strongly decreased.

It was demonstrated that thermal strain has influence on the rheological properties of wheat dough. It has influence when increasing and when decreasing the temperature. Wheat dough which was processed at low temperatures exhibited a higher extensibility which can be helpful in achieving higher dough volumes after proofing. The dough mixing process at low temperatures affected the rheological properties but also revealed dough alterations that would remain undetected when cooling dough that was processed at warm temperatures. On the one side, the stickiness of cool mixed dough has increased as it can lower the machinability. It is possible to compensate for the increased stickiness but this would mean to apply additional chemical strain by reducing the water amount in the dough recipe as did others. But this would also reduce the advantage of the increased extensibility. On the other side, when mixing at low temperatures there may occur changes on the molecular basis that have a positive influence on the dough or the resulting product. However, they cannot be detected rheologically.

In order to compensate for the increased dough development time that comes along with a reduced mixing temperature it would be necessary to increase the mixing power. In turn, this will demand for higher cooling efforts. Thus, a more efficient way of incorporating the necessary energy for dough development was established. Applying shear strain in a continuous shearing process led to the

formation of dough that is comparable to dough which is made by common kneaders. Opposed to the latter one where extension and compression occur to a high degree, shear strain was the only source for mechanical energy. It was shown that the necessary mechanical energy for dough development is reduced compared to the common process. However, continuous shear mixing leads to the separation of starch and gluten in dough. Instead of continuous shearing, the stepwise application of stress relaxation tests also led to dough development. Opposed to common mixing, the specific mechanical energy input for dough development is reduced to one third and no starch-gluten separation occurs. Since consecutive stress relaxation tests are applied for dough development a simultaneous determination of the rheological dough data is possible. This is achieved by the computation and evaluation of the relaxation spectra of each mixing step. The computed rheological data from the relaxation spectra correlates well with the properties of dough that is produced with the common kneading process. Thus, this shear mixing method is qualified for the examination of small flour quantities and for laboratory purposes. The shear mixing method is also qualified for the examination of cool mixed dough since the dough can be characterized within the shearing device and the increased stickiness has no hindering effect anymore.

8. References

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