

The importance and impact of Starch Damage and evolution of measuring methods

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1. Starch

Starch represents 67-68% of whole grain wheat and between 78-82% of the flour produced after milling. Composed of amylose (26-28%) and amylopectine (72-74%), starch is the main polysaccharide reserve of superior plants (Feillet 2000). Its long glucose chains become tangled forming spherical granules with a size between 20-25 μm (starch A) or 2-10 μm (starch B).

Indispensable for a plant's life, starch is also indispensable for many processed products. Starch is one of food's most important functional polymers because of its gelling, viscosity and water retention capabilities.

The semi-crystalline structure of the starch granule gives it similar characteristics to other solid particles, thus it can be damaged by mechanical operations. According to Viot (1992), regardless of mill type, 5 to 12% of starch granules are damaged during the milling process. The importance of damaged starch in the bread making process is considerable and generally twofold. Damaged starch absorbs 2 to 4 times its weight in water as compared to 0.4 by native starch. Damaged starch granules are also subject to preferential attack by some specific enzymes (one is β -amylases). Some of these enzymes are incapable of attacking an intact native starch granule.

The term "Starch Damage" is somewhat of a misnomer as the word "damage" implies it is something to be avoided. In fact, starch damage should be optimized as it has both positive and negative effects on bread quality. As mentioned, damaged starch has much greater water retention capacity; however, too much starch damage leads to sticky dough, strong proofing, and undesirable red crust color. The optimum

starch damage value varies by the usage of the flour, and is greatly dependent upon the flour protein content, the alpha-amylase activity, and the kind of bread making process used.

2. Milling

2.1. Industrial

During milling, some starch granules are mechanically damaged. According to Dubois (1949) the largest granules are subject to greater damage. He also shows that the granule exhibits elastic properties that lead to different types of damage such as cracks and breaks (**Figure 1**).

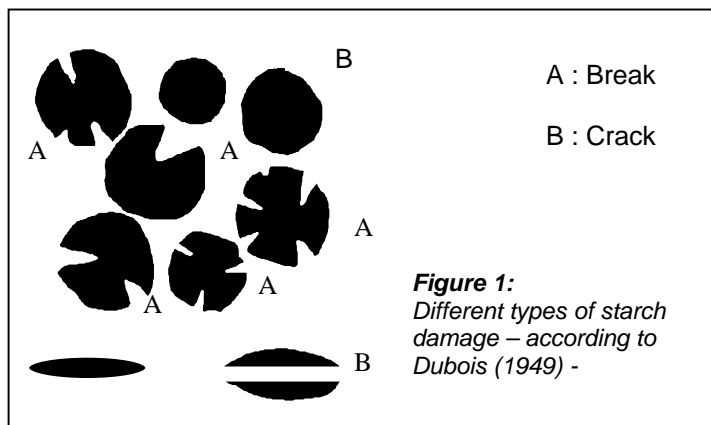


Figure 1:
Different types of starch damage – according to Dubois (1949) -

According to Dubois, it is necessary to distinguish two factors which lead to damaged starch:

- The surface factor corresponding to the scratching effect by the surface of grooved roller mill.
- The internal factor appearing during the reduction phase when granules are broken or flattened.

The more important the mechanical work, the greater the starch damage production.

Claude Willm (1977) provides more details about milling factors that lead to greater starch damage. He points out an

increase in starch damage from the front of the mill at the last middling reduction. A significant increase is also seen while going through smooth rolls. Willm multiplies the rate of damaged starch by the percentage of flour of the passing and sees that grinding leads to only 20% of total damage and that the majority of the damage is produced by the front end reduction and sizing reduction.

Willm then adjusts different roll parameters to study their impact on starch damage production. He notes that tightening the rolls, increasing the rate of feed, increasing the pressure exerted on smooth rolls, and decreases in roller speed¹, all lead to an increase in the level of starch damage.

Both authors note the important impact of grain hardness - the more resistant to milling², the greater the starch damage. This "hardness" can be partly modified when preparing the wheat. Particular attention is given to the moisture conditioning of wheat and the tempering time.

From these studies, it is possible to list ways to increase or decrease starch damage at the mill level (**Figure 2**). The miller can affect the starch damage content of flours through wheat choice, grain preparation and the mill set-up and adjustments.

2.2. Pilot Mills

The goal of a laboratory pilot mill is to produce a flour similar to a flour produced in an industrial mill - from both the biochemical and functional point of view. It is most important that the lab produced flour is representative of the original grain with regards to characteristics such as protein, ash, enzymes, starch damage, etc. It is necessary to obtain both damage types (crack and break) while using a laboratory pilot mill. With this in mind, a laboratory pilot mill must be equipped with both grooved and smooth rolls. A standard wheat conditioning protocol should also be

¹ Providing to tighten enough the rolls.

² Anglo-Saxon "Hardness".

followed. Monti (1998) suggests a method to drive experimental milling which characterises the flour produced in terms of

Damaged starch granules are more easily accessible to enzymes and hydration speed is increased. This

which doesn't have the chewing characteristics typical of this sort of bread. A relation has been established between the bread-making note of these breads and starch damage of flours (Quail 1996).

To increase starch damage.	To reduce starch damage.
<ul style="list-style-type: none"> • Strongly tighten the rolls. • Increase the layer compactness. • Feeding an unfavourable alimentation. • Decrease the flake disrupter efficiency. • Close the flour sieves at the front of the mill. • Favour the production of flack and straight run middling. • Choose hard type of wheat. 	<ul style="list-style-type: none"> • Avoid excessive tighten. • Reduce the product layer compactness. • If you agree to increase ash content use grooved rolls. • Choose efficient flake disrupters.

Figure 2: Measures which influence the production of damaged starch during milling. According to Willm (1977).

granule size, ash, and starch damage. Helen Allen (1996) mentions a study using starch damage measurement during passages as a reference to verify that the quality of the milling on a Bühler laboratory mill is correct. In this case it is indispensable to have a simple and rapid measuring tool for starch damage.

3. Influence on final products

Starch damage during milling operations will have a strong influence on most dough and baking processes.

3.1. Aerated breads

Aerated breads such as baguettes and pan breads are very sensitive to starch damage. Regardless of bread type, many parameters have an important influence on processing dough and baking bread. Of particular importance are starch damage, protein content, protein quality, and amylase activity. It is possible to significantly improve the baking quality of strong, glassy berry wheat - often rich in "long" chained gluten (i.e. protein), by increasing the rate of damaged starch.

Damaged starch notably improves the hydration potential of the flour. However, this water can be released by the mechanical mixing leading to sticky dough that can't be handled or processed.

sensitivity to hydration is the cause of three principal phenomena:

- The crust coloration will be much more intense (caramelization and Maillard's reaction).
- Texture of dough and crumb is stickier due to excessive starch hydration.
- The volume of bread can be improved providing that the retention of fermentation gas is controlled. If not, dough becomes porous and can lose volume while inside the oven.

3.2. Arabic flat breads

Flat breads are mainly composed of flour, water, salt, and yeast. Hard, un-sprouted (Falling Number > 250) wheat, with average protein content (10-13% on d.m.) is most commonly used for these types of products.

Compared to aerated bread, the optimal consistency for flat breads is more firm. Hydration is reduced to obtain good handling properties necessary during sheeting of dough. Water addition depends on protein content, starch damage, and flour bran content (extraction rate).

Low water absorption reduces the yield in dough and produces dry bread with low mouth feel quality. Beyond 65% water absorption Quail et al. (1991) estimate that doughs are difficult to manipulate and produce fragile bread

3.3. Biscuits/Cookies/Crackers

Starch damage has a notable influence on biscuit criteria (shortness, size, density...). In general, biscuit processes require flours with low starch damage content (particularly to reduce water lost during baking thereby reducing cook times).

3.4. Noodles

The characteristics of a good flour for noodle production depend on the kind of noodle and local preferences. Very often, these flours have low extraction rates and low ash content. Characteristics of all these products are described in the book "Pasta and Noodle technology" (AACC, 1996) to which we will be referred.

Among important criteria, one will note proteins (which influence the product firmness), colour (consumers want white products), absence of high amylase activity and granule size (< 180 µm). Granule size should not be too fine as it increases risks of starch damage which has a negative impact on the final product.

High levels of damaged starch increase baking time, decrease water penetration inside the product, and cause higher loss of product during cooking. All these elements give the final product a sticky texture and a very bad mouth feel quality. Starch damage, when excessive, is also the cause of a browner product colour which is undesirable to the consumer.

3.5. Durum wheat

3.5.1. In the bread making process

Although the principal use of durum wheat is the production of pasta, some regions of the world (Near and Middle East, North Africa, South Italy....) use durum wheat for bread making. Lindhal and Eliasson (1992) have compared durum and soft wheat. They found that dough with similar rheological responses could be obtained from flours with differing protein content

simply by modifying particle size distribution and starch damage level.

3.5.2. For pasta production

The contribution of starch to the dough rheological properties of pasta is much less studied than effects of gluten. Although, some studies show that the starch granule surface condition has an important effect on dough responses. Particle size influences the likelihood of water linking with the starch or with the protein structure.

water absorption capacity, dough extensibility, and viscosity. When starch damage increases and particle size decreases, the tortilla becomes less able to stretch and much firmer. Wang and Flores (1999) demonstrate that the folding³ capacity of a tortilla depends very much on protein content, water absorption and starch damage. Authors conclude that to make a good tortilla, starch damage should not be too high and particle size not too fine.

This bibliographic study shows that, whatever the final product, starch damage is an important criteria. It is

solution and red congo) enable one to differentiate very easily damaged and native granules with a microscope. However, this is very labor intensive, qualitative, and subjective.

4.2. Colorimetric

One colorimetric method, described by Williams (1969), enables one to measure starch damage as a routine parameter. The test is based on colour development resulting from the treatment of a sample with a solution concentrated in sodium sulphate containing 15% of formamide and 0.2% of sulphosalicylic acid. Absorption of the extract is measured and compared with a range of flours tested by an enzymatic method. The test precision is equivalent to the one of this latest technique.

Though it is simpler than enzymatic techniques, this method requires qualified staff, complicated manipulations and specific equipment (colorimeter...).

4.3. Polarimetric

This method (Chiang et al. 1973) is based on the polarimetric determination of starch in a solution of calcium chloride and the fact that damaged starch is more easily digested by α -amylases than native granules.

The flour sample is subjected to α -amylases in control conditions for 30mn. After centrifugation, the residue is washed with alcohol and dissolved in a solution of calcium chloride. Proteins are precipitated with uranyl acetate and then filtered. The optical inversion of the light filtrate is obtained with a polarimeter. Total starch is obtained by the same method without digestion by α -amylases. The difference between the two readings gives percent starch damage.

This technique is more complex than the colorimetric method and it integrates the enzymatic variability in the sample preparation.

4.4. Spectroscopic

Spectroscopy in the near infrared can sometimes be used to measure starch damage. This method has the advantage of being very quick and requiring little sample preparation. However, being an indirect or secondary method, an NIR instrument must be calibrated to some

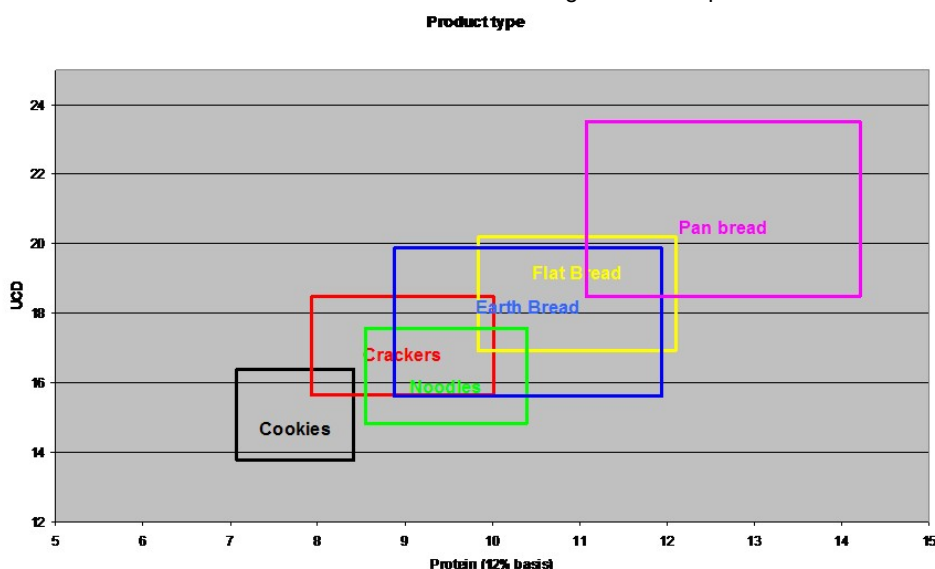


Figure 3: Relation between starch damage (UCD) and protein for different types of products.

Grant and al. (1993) have studied the effect of replacing semolina into the milling process to increase starch damage. They discovered that water absorption increases and dough firmness decreases with the increase of starch damage. For lower gluten quality samples, they noticed that the "sticky" factor correlates well with starch damage.

Just as in soft wheat, starch damage plays an important role in durum wheat and flour processing.

3.6. Tortillas

Although Mexican tortillas are often associated with corn, the North and more so in the United States prefer soft wheat tortillas.

Some studies point out the importance of starch damage on tortillas characteristics. Mao and Flores (2001) have demonstrated that starch damage positively influences

therefore relevant to ask - why is this characteristic often overlooked? By reviewing methods past and present, the answer will be clear.

4. Existing methods to measure starch damage

To date, most methods used to measure starch damage have suffered from several flaws; they are labor intensive, subject to operator error, dependent upon enzymes that change over time, and generally provide poor repeatability.

4.1. Microscopic

A very simple technique, using highly diluted colouring (iodine in iodo-iodide

³ Very important quality criteria for customers.

sort of reference method. Thus, the problem is to have a reference method that provides repeatable and reproducible results. Unlike water or protein which have specific absorption bands in the NIR, damaged starch can not be distinguished (by chemical means) from native starch.

4.5. Enzymatic

Among all methods presented, enzymatic methods are the most commonly used by institutes, universities, and research centres. That is the reason why the bibliography is so rich in articles about this matter. The most recognized methods are Audider (1966), Farrand (1964) and AACC.

The enzymatic methods often consist of five steps :

- 1) Bring flour into contact with an enzyme (often α -amylases). Conditions such as time, temperature, PH and enzymatic activity must be rigidly controlled.
- 2) The reaction is typically stopped by enzyme denaturation.
- 3) Filtration or centrifugation of the solution is used to recover the aqueous phase.
- 4) Determination of the concentration in reducing sugar of the filtrate by titration or spectrometric analysis.
- 5) Transformation of concentration into % of damaged starch.

Enzymatic methods are very complicated; they need highly-qualified staff and often a not inconsiderable material investment. The activity of the enzyme used can also change over time leading to erroneous results. They are not adapted to daily needs of millers, particularly those without large quality control laboratories.

4.6. Amperometric

The amperometric method was described by Medcalf and Gilles in 1965 and is based on the work of Coton (1955). The principal uses the amperometric determination of the kinetics of iodine absorption by a diluted slurry of flour.

Basically, I_3^- ions are created in a solution. These ions generate an electric current (measured in μA) in direct relation to their

concentration in the solution. Iodine is absorbed (fixed) by starch – the more so when the starch is damaged. Thus, the method consists in creating a certain quantity of I_3^- ions and allowing them to come in contact with the flour during a constant period of time. The current in μA is measured at the end of the test. The lower the current the more absorbed/fixed I_3^- ions thus indicating high starch damage.

The first uses of this method were difficult as it was necessary to make create an expensive glassware assembly. In 1986, Mr. Berger tested the prototype of an automated device using the amperometric method previously described. He concluded that this prototype, "simple to use should enable to realise at low cost, an analysis that up to now is made by only few laboratories". The concept was sold to Chopin in the early 90' and Chopin created several devices on this principal including the SD4 and then the Rapid F.T. (**Figure 4**).

Many authors have compared the amperometric and enzymatic methods. The study of Rogers et al (1994) shows that the electric value measured can actually be used as an indicator to measure starch damage. The author improves the correlation by separating the high values obtained on hardest wheat from the values obtained on soft wheat.

This remark corroborates the observations made by Medcalf and Gilles who noticed that on mechanically damaged flour, the response of enzymatic methods was not linear. More enzyme or less flour was required when starch damage was high. However, the amperometric method shows a very good linearity across the entire range.

5. Description of a new amperometric method

With greater than 10 years experience with using amperometric principle to

measure starch damage, Chopin completely overhauled its design to create an instrument that is much easier to use and much more precise. This project was done in cooperation with researchers from CNAM⁴. Objectives were the following:

- Simplify the device (the Rapid F.T.) and make it more user friendly.
- Remove liquid solution dependence by adding granular chemicals
- Simplify flour weighing and precision requirement
- Reduce use of external accessories (double boiler, glassware...)
- Completely control test conditions (the amperometric method is sensitive to temperature change).
- Create and measure the quantity of I_3^- ions **prior to** introduction of flour to know the exact quantity of iodine that fixes to the flour sample.

Figure 5: The SDmatic.



The project ended in the creation of a new device, the SDmatic (**Figure 5**). The SDmatic procedure is as follows:

- The operator prepares a solution with 120ml of distilled water and 3g (+/- 1g) of boric acid and potassium iodide.
- The solution is placed inside the device and the measuring head is lowered into position.
- A heater brings the solution to 35°C - a thermometer controls the temperature in real time.
- 1g of flour (+/- 0,1g) is placed inside the device onto a vibrating system
- When the solution reaches 35°C, a pair of electrodes generates an electric current in the solution that creates free iodine for a specific time determined by the quantity of sample (**Figure 6**).
- A second pair of electrodes measure the electric current generated: I_m (thus the quantity of iodine).
- The flour is then automatically introduced in the reaction bowl.
- The test continues for 180 seconds during which time the free iodine is bound to the damaged starch

Figure 4 : The Rapid F.T.



⁴ Mr Nicolas, Potus, Deruelle and Mr. Catonné (industrial biochemistry and electrochemistry). We thank them very much.

- The device then measures the intensity of the residual current I_R .
- Iodine absorption is calculated: $A_I = 1 - (I_R/I_M)$ which is proportional to the quantity of damaged starch.

The results are obtained in less than 10 minutes and can be converted to UCD, Audier, Farrand or AACC units on the basis of known reference flours.

6. Conclusions

Starch damage is a logical and inevitable consequence of all wheat milling processes. The importance of this damage is real and concerns nearly all baked around the world.

The lack of an accurate, reproducible, user-friendly test has led this very important parameter to be under utilized.

Laboratories of the cereal industrial are fully equipped with efficient means to

control the quantity and quality of proteins. Rare are those who are concerned with starch damage. To emphasize its importance, recognize that starch represents 80% of flour produced or used. The lack of a simple, rapid analysis method can explain this situation in part.

Very few millers in the world would measure the protein content of their flour if it was still necessary to use the Kjeldahl method. The complexity, requirement of high-qualified staff, and safety issues limited its use considerably. The creation of automatic devices for protein determination (Kjeltec) gave all cereal laboratories access to protein measurement.

In a similar manner, the SDmatic will now allow the measurement of starch damage to become a routinely analyzed parameter. Starch damage measurement will enable all laboratories of the cereal industry to measure this parameter that influences so many aspects of dough including: dough hydration, handling (stickiness...), fermentation and the final product characteristics (volume, colour, stability....).

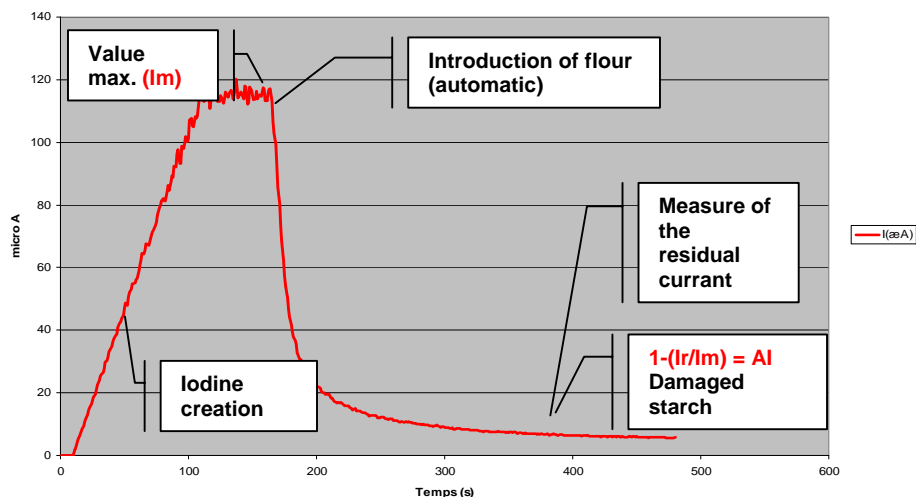


Figure 6: Measurement cycle of starch damage with amperometric method.

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