Effect of Preheating on Potato Texture

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ABSTRACT: Preheating potatoes at 50 to 80°C has a firming effect on the cooked potato tissue. This effect is particularly pronounced at a preheating temperature of 60 to 70°C followed by cooling. Several theories have been presented in the literature to explain this firming effect: retrogradation of starch, leaching of amylose, stabilization of the middle lamellae and cell walls by the activation of the pectin methylesterase (PME) enzyme, and by the release of calcium from gelatinized starch and the formation of calcium bridges between pectin molecules. Most probably, none of these theories alone can explain the phenomenon and more than one mechanism seems to be involved. Some of these mechanisms seem to be interdependent. As an example, calcium could be considered as a link all the way through release after starch gelatinization to cross-linking pectin substances in the cell wall and the middle lamellae, which has been demethylated by the PME enzyme. More research and "clear cut" experiments are needed in order to elucidate the role of each mechanism, especially which of them is the main contributor to the process of firming. Most probably, the calcium-pectin-PME mechanism plays a secondary role, that is, it only retards the collapse of the tissue structure that would otherwise occur during the final heating without preheating, and it is not the main factor of firmness.

KEY WORDS: potato, texture, pectin methylesterase, mineral ions, blanching, calcium, preheating.

I. INTRODUCTION

Heat treatment of potatoes greatly affects their texture. Preheating at 50 to 85°C has for a long time been a common practice to improve the texture of canned potatoes, French fries, potato chips, and granules and flakes for mashed potatoes. This preheating, traditionally called blanching, has a number of functions but also makes the texture after the final heating firmer and mealier than without preheating. Starch, pectic substances, minerals, and pectin methylesterase (PME) are usually considered to be the components of importance in this context. Other parameters are the specific gravity of the tuber, cell size, pH, and the composition of the cooking liquor. Of all these factors, the role played by calcium in combination with the PME enzyme activity is the subject of this study.

Preliminary experiments on the effect of preheating parameters on the diffusivities of nutritionally important components have shown that: (1) when the transport is from the tissue to the blanching solution calcium does not follow a Fickian pattern;[1,3] (2) when the transport is from a calcium-containing solution into the tissue, the behavior is Fickian (Andersson et al. submitted). Before further investigating this matter, it was natural to undertake a literature review. When considering the results of this work it is important to remember that potato composition varies both among varieties and in the same variety, depending on production year, growing location, harvest time (maturity), duration of storage, and storage temperature.

Composition varies also within the same potato tuber.[4–8]

II. POTATO STRUCTURE AND TEXTURE MEASUREMENTS

A. Anatomy of the Raw Tuber

The tuber itself is essentially an abruptly thickened underground stem closely resembling the aerial stem of the plant. Figure 1 shows the organization of the principal internal tissues of the mature potato tuber. The tuber is divided into a bud end and a stem end, the latter being situated on the stolon. The bud end of the tuber is richer in eyes than the stem end. The outer skin consists of a layer of corky periderm, approximately 10 cells deep.[9] These cork cells are dead cells; they do not contain starch or protein grains. These cells have much thicker cell walls than parenchyma cells.[9] Underlying the periderm (the skin) is the cortex, a thin layer of parenchyma tissue. The cells normally contain numerous round and oval-shaped starch grains. These cells appear to be the largest in the tuber, with dimensions up to 146 × 189 μm. Their walls are thin, regardless of their size or starch content. Vascular storage parenchyma, high in starch content, lies within the shell of cortex. Xylem and phloem are found in minute strands or bundles, most of which form a narrow, discontinuous ring (the vascular ring) somewhat within the boundary between the cortex and the vascular area. Storage parenchyma cells adjacent to vascular tissue contain starch granules that are generally small and round. Cells located only three cells away contain oval grains that are at least twice as large.[9] Forming a small central core, but radiating narrow branches to each of the eyes, is the pith, sometimes called the water core or the medulla. The cells in the pith are smaller and have a lower starch content. The internal phloem (perimedullary zone) occupies close to 75% of the total tuber volume. Fedec et al.[9] showed by microscopic observations that starch grain abundance and size correlated well with the dry matter content of the tuber. They found that the dry matter was 20.1% in the periderm plus part of the cortex, 25.5% in the external phloem region, 20.0 to 24.6% in the internal phloem, and 16.2% in the pith.

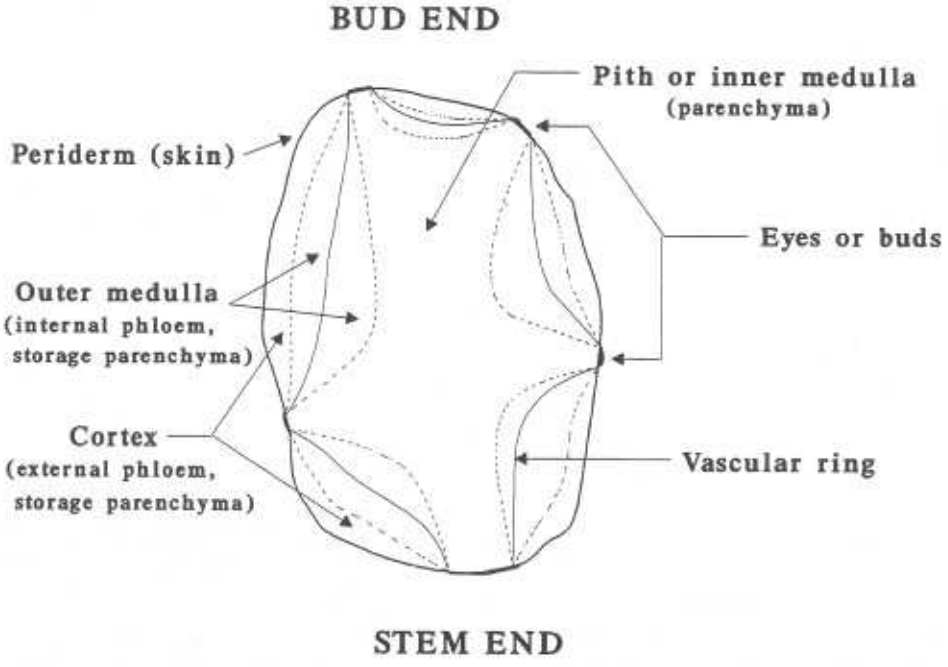


FIGURE 1. Longitudinal cross-section of the potato tuber.

Characteristic of potato cells and other plant cells is the existence of a strong cell wall that limits expansion of the cytoplasm, resulting in turgor pressure. Cell walls are composite microstructures of cellulose microfibrils embedded in a matrix of polysaccharides and some proteins.[10] The cell wall can be seen as a polymer network of polysaccharides. The middle lamella, the outer layer of the cell wall, is composed mainly of pectic material and cements cells together. The primary wall is a more organized layer consisting of a skeleton of cellulose microfibrils embedded in an amorphous matrix of pectic substances, hemicelluloses, and, possibly, proteins. Dead cells also have a secondary wall inside the primary wall in contact with the lumen and contain lignin associated with the amorphous matrix. Cellulose constitutes some 15 to 28% of the weight of the cell wall, hemicellulose 6 to 10%, and pectic substances 47 to 66%.[11] When cooked potato is subjected to compressive or shear force it fails, and examination of the mode of failure indicates that the separation of the surfaces occurs in the middle lamella of the cell wall rather than through the cells themselves. Consequently, the cell wall composition and structure are very important for the texture of the final potato product.

B. Effect of Heating on Potato Structure

During heating the starch granules within the cell absorb the cellular water and swell to form a gel (Figure 2). In general, the gelled starch remains within the cell, although some of the amylose may diffuse through the cell wall. The other major changes that occur are the loss of integrity of the cell membranes, resulting in a loss of turgor and the free diffusion of cellular contents throughout the tissue. Additionally, there is the effect of heat on the structure of the cell wall and the denaturation of protein, leading to a reduction in cell adhesion. The net result of all these changes is gelled starch and a softer tissue in which the cells are more easily separated. Figure 2 shows that the separation of cells occurs in the middle lamella rather than through the cells.

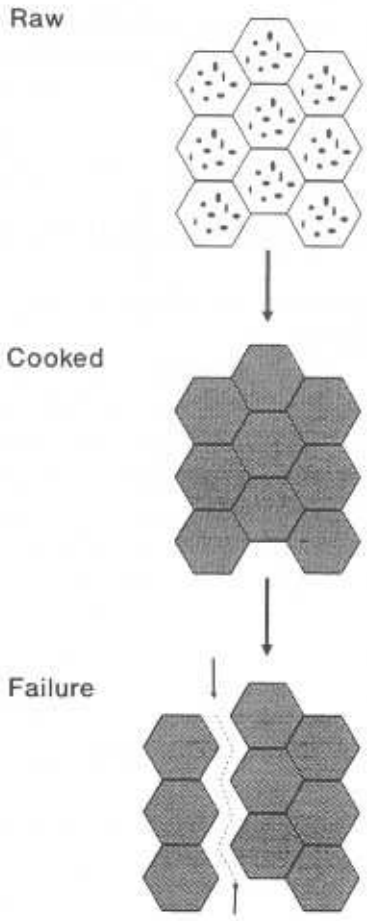


FIGURE 2. Schematic figure describing the effect of heat treatment on potato tissue.

C. Texture of Heat-Treated Potato

The texture of cooked potatoes is often described in terms of mealiness, waxiness, sloughing, and firmness. The textural characteristic, mealiness, refers to the feel of the potato in the mouth. A mealy potato, when cooked, retains its form but is easily broken down and will give a slurry consisting essentially of single cells. The opposite of a mealy potato is a waxy one. A waxy tuber exhibits no sign of being undercooked but may be cut into slices and many cells will be ruptured on mashing. Another aspect of potato texture is the sloughing or disintegration of tubers during cooking. Because this is the result of cell separation rather than cell rupture, the explanation of its mechanism must be looked for in the composition of the intercellular material.

Sloughing and firmness can be measured by objective measurements, while mealiness/waxiness have to be measured by subjective tests (sensory panel).

D. Objective Measurements of Texture

It is essential to relate the subjective assessment of textural attributes arrived at by a sensory panel to physical and chemical characteristics that can be measured only. Firmness, compressibility, shear, elasticity, adhesiveness, cohesiveness, chewiness, gumminess, or combinations of these are some of the physical characteristics that can be quantified. Objective tests can be divided into direct tests that measure real textural properties of materials and indirect tests that measure physical properties that correlate well with one or more textural properties. Instrumental analysis can be used to imitate the human masticatory process or to measure some fundamental mechanical property of the food.

Imitative devices function on the principle that the closer the texture-measuring equipment duplicates the action occurring in the mouth, the closer the results will be to those assessed by human subjects. A group at the General Foods Corporation Technical Center has been a forerunner in this area. They developed an instrument, the GF Texturometer, designed to simulate mastication by means of a mechanical chewing device. An arm, moving in an arc, forces variously designed plungers into a food sample placed on a stationary platform attached to a strain gauge. The amplified results of the strain gauge deformation are recorded. The instrument operates by partially compressing the sample twice, imitating the first two bites taken of a food. Several parameters are obtained from the resulting force vs. time plots, as can be seen in Figure 3, and these have been found to correlate highly with sensory ratings. The values of the various parameters are collectively called the instrumental texture profile.

It is much easier to measure some fundamental mechanical property of the food and obtain data in basic SI physical units. Thus, it is simple to compress a sample between two flat plates and note the Newtons of force required to reach a

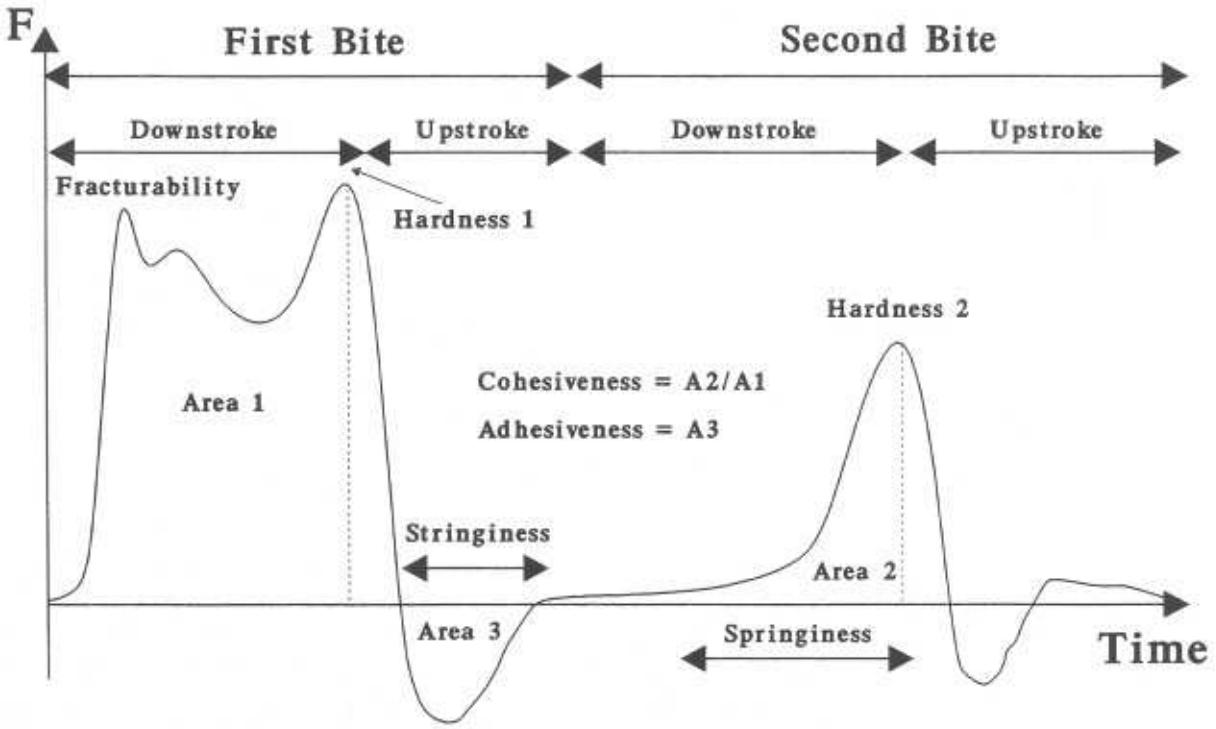


FIGURE 3. A generalized texture profile analysis curve obtained from an Instron.

yield point. Unfortunately, the drawback of this approach is that such one-point measurements of mechanical properties are rarely adequate predictors of sensory response. Usually, one of the three common types of stresses are applied: compressive, tensile or shearing (Figure 4). These instruments give results either as force vs. deformation or as stress vs. strain results. Although some instruments are still being used that give only one reading, usually the maximum force, these are either being replaced or connected to recorders to give a graph of the complete deformation process either as a function of distance or of time.

III. POTATO TEXTURE

The texture of cooked potatoes is often described in terms of mealiness, waxiness, sloughing, and firmness. Mealiness and sloughing are often related to the separation of intact cells. Firmness is often related to starch swelling and gelatinization as well as to the stability of the pectic substances in the cell wall and the middle lamellae (see Table 1). Intercellular cohesion, being important for the texture of the cooked potato, is related to the amylose content of the starch, polyuronide, calcium, and magnesium content of the tuber but not to protein or heavy metals.[12-14] (The terms adhesion and cohesion have both been used in the literature for the intercellular forces. We believe cohesion is more correct as a term in this context. [Adhesion usually means that something smaller adheres to something bigger, for example, a microorganism adheres to a surface.] Two cells adhering to each other cohere.)

Warren and Woodman[15] disagree that mealiness should be directly related to cell separation only because a positive correlation was found between mealiness and mechanical strength, the latter being negatively correlated to cell separation. Their theory is that mealiness is a subjective measure of viscosity. The viscosity depends on the starch or solid content of the potato and less on the potato cell cohesiveness. Mechanical strength or firmness is associated also with pectic substances and is correlated with the initial breakdown of the potato tissue, which depends both on cell cohesion and viscosity. It has also been suggested that sloughing depends on cell cohesion, which is inversely related to the distance between adjacent cells and directly related to the viscosity of the intercellular material. Intercellular distance in the parenchymatous tissue was increased during boiling from 2 to 3 μm in raw potatoes to 4 to 6 μm in cooked ones. This indicates the hydration of the cell-wall matrix, affecting both middle lamella thickness and its viscosity. This will reduce the force needed for cell separation to a small fraction of that required in the raw tissue.

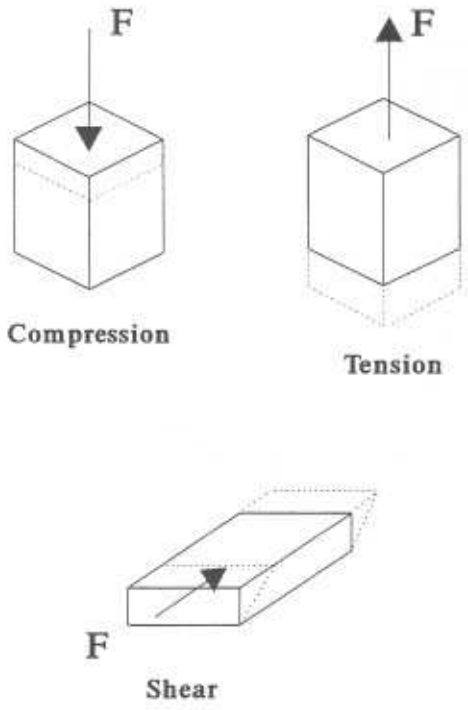


FIGURE 4. Action of forces on solids.

TABLE 1
Parameters Describing Cooked Potato Texture: Associated Phenomena At Cell Level

Parameter	Phenomena at cell level
Mealiness/waxiness (mouthfeel)	Separation of intact cells
Sloughing (disintegration)	Separation of intact cells
Firmness (cellular cohesion)	Starch swelling, gelatinization
Firmness (cellular cohesion)	Stability of pectic substances in cell wall and the middle lamella

Both tensile strength (measured according to Personius and Sharp[16]) and shear strength were, on the other hand, found to be unrelated to potato texture (organoleptic, mealiness). In the mechanical tests, there was a separation of intact cells. As microscopic studies showed, there was a considerable cell separation in the cooked samples of mealy potato varieties, whereas no or little separation existed in the waxy (or soggy) ones. Cell separation was found to be the principal physical attribute of a mealy potato; the degree of cell separation is a measure of the degree of mealiness. It was concluded that the starch content is the main determining factor in potato texture. Pectic materials have an effect opposite to that of the starch on texture. Starch tends to cause rounding of cells and separation, whereas pectic material tends to prevent cell separation by a cohesiveness force. Calcium ions, by linking together adjacent pectin molecules, counteract the swelling tendency of the middle lamellae in hot water that would otherwise give a greater cell separation.[17]

Woodman and Warren[18] found that the subjective parameter *mouthfeel* (mealiness-waxiness) was independent of the breakdown of the tissue (sloughing), and that mouthfeel could be measured objectively by extruding the sample through a grid-extrusion cell of the Kramer Shear Press and measuring the force required. The TS (total solids) of the tuber was the primary factor controlling mouthfeel. The breakdown could be objectively measured through the volume of the sediment formed by the disintegrated tissue from a known weight of sample.

Sloughing or breakdown of potato tissue during cooking could be measured as the cooked potato weight, CPW. A high negative correlation was found between cooked potato weight and scores given by the test panel for the texture test and also with specific gravity.[19]

Harada and Paulus[20] recognize the role of many factors for the texture: specific gravity, total solids, starch content, cell size and surface area, soluble amylose, pectin, and polyvalent cation content. Amylose, starch retrogradation, PME activity, and the degree of methylation of the pectin were not found to be of interest for the texture of directly cooked potato. The picture might, however, be different for cooked potatoes that have been previously preheated. Then the PME has enough time to influence the texture before it becomes inactivated by heat.

More recently, in the frame of COST (European Cooperation in Scientific and Technical Research) one study was devoted to potato texture.[21] The parameter of interest was tissue firmness and the measured property was the maximum shear force as tested on mechanical instruments such as Instron and Zwick. Raw as well as heat-treated Bintje and Saskia potatoes were used in the study. A marked decrease of tissue firmness was observed after treatment in water at temperatures over 70°C. This distinct reduction in firmness has been explained as being due to the splitting of pectin in the middle lamella. The authors also found that the decrease in tissue firmness could be delayed by increasing the Ca^{2+} content in the water bath.

Any disagreement among authors could, at least to a certain extent, be due to the different methods used. Nevertheless, concerning texture measured instrumentally and the structural, compositional, and seasonal complexities of the foods, it is advantageous, and perhaps essential, to evaluate the mechanical properties of the foods by more than one experimental technique. By comparing the results of different testing models problems in methodology may be discovered. Such a comparison, however, necessitates collaboration in order to develop calibration methods in the spirit of the European COST program.[2,94] The reader will find an interesting discussion about subjective and objective texture measurement in the recent book of Aguilera and Stanley.[102]

A. Blanching or Preheating

Hot water blanching is one of the most important unit operations in food processing. In the commercial production of French fries and other frozen potato products, blanching makes it possible to control the color, texture, and, to some extent, the flavor of the final product. The main objectives of blanching in potato processing are the inactivation of enzymes and the regulation of the content of reducing sugars in the superficial layers of the tissue that play a predominant role in

TABLE 2
Recommended Optimal (T,t) Blanching Conditions

Conditions (first step)	Conditions (second step or posttreatment)	Remarks
(80°C, 15 min)	(95°C, 1 min)	Second step to inactivate peroxidase[22]
(60°C, 10 min)	(97°C, 2 min)	Improved texture[24]
Microwave blanching	(97°C, 1 min)	Improved texture and minimal ascorbic acid loss[28]
Whole unpeeled potato tubers, (50–60°C, 3–24 h)	None	Firmer texture, resistance to physical breakdown during further processing; the longer time the firmer[59]
(50–55°C, 2–30 min)	(100°C, 10–90 s) 65°C at thermal center	Preserves organoleptic quality of young potatoes (d <4 cm) after freezing[60]
(65–77°C, 0.5–3 min)	Cooling to under 26°C, then frying	Removes sugars 50–90%[61]
(82–100°C, 5–15 min) 2–5% NaCl or KCl	Washing with cool water, then air drying to 15% weight loss, parfrying 171–185°C, 1–3 min, freezing	Complete gelatinization of starch, improves texture (soft mealy interior/crisp exterior of French fries)[62]
As above but no salts (blanching in water only)	Infusion in brine solution (4–27°C), washing, cooling in water, air drying, parfrying, freezing	As above[62]

color development during frying. Other reasons for blanching, especially for French fries and potato chips, are to reduce fat uptake for health reasons and sugar content for the sake of the color after frying. Recently, the nutritional aspects of blanching have also been underlined and studied.[3]

The needs for the various purposes mentioned above, in terms of operational conditions in blanching, are often contradictory. Thus, leaching of sugar requires time, and a low temperature is desirable to avoid overcooking. By contrast, a relatively high temperature and short time are the requirements of enzyme inactivation.

All the above make the blanching step a unit operation typically amenable to optimization. Recommended optimal blanching conditions have been reported by various authors and are summarized in Table 2. The optimal conditions vary according to the author. This is not surprising because different main goals for the blanching were being arrived at. In most cases, it seems that the common aspect of the treatment is a combination between a first LTLT step (low temperature, long time) followed by a HTST step (high temperature, short time). The first step is to adjust the color of the final product and to improve its texture, while the purpose of the second step is to inactivate enzymes that cause the deterioration of the quality. Others prefer a different kind of posttreatment (instead of a second preheating step) such as cooling and/or the use of brine solution at low temperatures. Microwave heating as the first step has also been reported.

Brown and Morales[22] found the temperature and time conditions at which a reduction of shear resistance of 50% was observed (100% is the resistance of uncooked potato), as follows: 75°C in 60 min; 85°C in 15 min; 95°C in 5 min. The optimal conditions of the heat pretreatment were 80°C and 15 min. These conditions were the optimum with respect to texture and color of the fried product. Because some peroxidase activity

still remained, a second step (95°C, 1 min) was necessary to complete enzyme inactivation.

Ludwig[23] found that blanching of potato strips at temperatures under 70°C had only a minor effect on the texture after treatment when compared with the texture of the raw potato. Preheating at 55 to 70°C, followed by parfrying, increased the firmness of the final product. The firmness appeared to increase with the immersion time in the preheating bath (up to 60 min).

Canet et al.[24,25] compared HTST (97°C, 2 min) blanching of potato slices (D = 25.4 mm, h = 5 mm) with both one-step blanching (80°C, 6 min) and stepwise blanching at 50, 60, 70°C, for 10 min each, followed by cooling and reheating at (97°C, 2 min). The stepwise blanching at 60 and 70°C improved the texture after blanching and also after freezing and cooking.

During heat treatment of potatoes in water, there is a loss of material from the tuber as well as an uptake of water and solutes from the liquor to the tuber. Eipson and Paulus[26] found that during canning the dry matter content was reduced to approximately 80 to 90% of the original, and the amount of starch was also reduced by the same amount. Davis et al.[27] found considerable losses of minerals and nitrogen during the soaking of potatoes in distilled water prior to cooking. Thus, blanching and cooling of potatoes will cause a deterioration of the nutritional value due to the loss of minerals, as well as of both water-soluble and heat-sensitive vitamins.

To overcome this disadvantage, the possibility of using microwave blanching has been investigated.[28] Conventional blanching (97°C, 2 min), stepwise blanching (70°C, 10 min), followed by cooling and an HTST step (97°C, 2 min), and microwave blanching (30 to 60 s) with or without cooling, combined with an HTST step (97°C, 1 min) were compared with respect to firmness (measured with an Instron) and ascorbic acid loss. The conventional blanching method gave the poorest firmness. The third combination, namely, microwave blanching (60 s) with an HTST step (97°C, 1 min), gave the best results in terms of both texture and ascorbic acid retention considered together.

According to Taguchi et al.,[29] preheating at (75°C, 30 min) gave maximum texture retention expressed in terms of fracturability (the g. force at the first breaking point) after boiling. The duration of pretreatment had no effect on the samples that have been microwave-treated instead of boiled.

A mathematical model has been developed recently for the effect of blanching conditions (T, t) on the hinderance factor, K, defined as $K = D_o/D_{eff}$, where D_{eff} is the effective diffusivity in the tissue and D_o the diffusivity in the solution of six components, glucose, fructose, citric acid, potassium, magnesium, and calcium. T and t were varied in the interval 50 to 90°C and 2 to 20 min, respectively. The solutes diffuse in the occluded solution in the potato and are obstructed by the potato matrix. This obstruction effect (hinderance factor) decreases dramatically when the cell membranes are denaturated (>50°C). The diffusivity of the minerals was hindered by the potato matrix much more than the diffusivity of the molecular species was.

In conclusion, Table 2 and the results above show that a two-step blanching gives a final product with firmer texture.[22–24,28,59–61] The first step has to be in the temperature range 50 to 70°C, and the firmness appears to increase with immersion time. The blanching conditions that increased firmness also increased the proportion of pectic acid portion while decreasing the water-soluble portion.[69] Firming treatments decreased the degree of methylation of the pectic substances.[69] These results indicate that the enzyme pectin methylesterase is involved. PME is very active in the temperature range 50 to 70°C, but it is rapidly inactivated at temperatures above 70°C.[76]

B. Specific Gravity

The specific gravity of potato was found to be directly related to starch content and total solids.[30] Bettelheim and Sterling[31] studied the correlation of the specific gravity of 10 varieties of potato (5 mealy, 5 waxy) assessing texture subjectively by test panels. They found 68% of the variation in the scores could be explained by variations in the specific gravity. The correlation between total starch of both the raw and the cooked tuber with the test scores was 78%. The composition of the

starch, however, did not seem to have any influence on texture because neither amylose nor amylopectin content gave any significant correlation with the test panel scores. Barrios et al.,[32] in contrast, did not find any correlation between specific gravity and mealiness of four cultivars studied. Within two restricted tuber populations, Keijbets et al.[33] found a negative relationship between specific gravity and intercellular cohesion measured objectively.

McComber et al.[34] found no correlation between specific gravity with shear strength nor could it be used to predict sensory mealiness scores of four different cultivars, of which two had typically high specific gravity (mealy) and two typically low specific gravity (waxy). Lujan and Smith[35] state that within each variety the mealiness of the cooked tubers is highly correlated with their specific gravity; the specific gravity of the raw tuber is the best gauge of mealiness within the same variety, but different varieties of identical specific gravity may differ in mealiness. This indicates that specific gravity alone cannot be used to predict mealiness.

In conclusion, there have been many attempts to correlate specific gravity, starch content, and total solids with the texture of heat-treated potato. The results are somewhat confusing and sometimes contradictory, probably because of a number of reasons, such as (1) the fact that the above factors are interrelated; (2) cultivar or seasonal differences; (3) different methods of measurement (objective/subjective); and (4) different aspects of texture being the main target of each study.

C. Starch and Amylose

Especially in older Literature, starch swelling, occurring before gelatinization takes place,[21] is thought of as giving a "swelling pressure" that tends to make the cells take on a more rounded shape, thus reducing the cohesion forces between the cells and enhancing cell separation. However, nobody seems to have measured this pressure experimentally.[36]

Starch gelatinization takes place over a range of temperature. This range differs, however, according to cultivar, year, and whether gelatinization takes place in water or in the juice of the tuber.[34] Briant et al.[37] studied starch in polarized light during heating of diluted suspensions from room temperature up to 85°C. The first sign of loss of anisotropy came at approximately 58°C and all anisotropy was lost at approximately 70°C. Most of the starch granules lost their anisotropy within 2 to 3°C. There was some variation. The first sign of loss of anisotropy varied over the range 53.9 to 63.5°C, and the final disappearance of anisotropy ranged over the interval 63.4 to 72.3°C.

In cooked potato tubers, a weak positive correlation has been found between starch content and intercellular cohesion ($R = 0.48$) and a relatively stronger positive correlation between amylose content and intercellular cohesion ($R = 0.76$).[13] It has been suggested that the relationship found between starch and intercellular cohesion was because of the relationship between amylose and intercellular cohesion. In fact, it may not be a relationship between amylose content and intercellular cohesion either, the relationships found may simply reflect biochemical changes producing changes in the cell wall and in the middle lamellae during the growth of the tuber. In a model experiment[14] with free potato tuber cells, the effect of mixing the cells with solutions of 10% (w/v) amylose and amylopectin on their compressive strength was studied. It was found that amylose increased the compressive strength by 45% compared with water, while amylopectin had almost no effect. Therefore, it seems that amylose strengthens the cell wall. Other authors, however, did not find any correlation between breakdown and the amylose content of the tuber.[40] Briant et al.[37] investigated starch granule size in nine potato varieties and found the proportion of starch granules less than 0.02 mm in diameter was negatively correlated with mealiness. This is an indication that the smaller the starch granules, the less mealy the potato.

According to a theory,[41] texture in terms of firmness in potatoes that are preheated then cooled and finally cooked is due to starch retrogradation. The term retrogradation implies that the crystallinity lost during gelatinization is (at

least partly) regained during the cooling step. This crystalline structure will prevent swelling of the starch during the cooking step. The phenomenon seems to be of a complex nature as quite a few structural changes with different kinetics have been observed (Table 3).[41] It has been shown that potato starch starts to retrograde slowly at 50°C, the phenomenon being accelerated at temperatures as low as 25°C.[42] The degree of retrogradation depends on moisture and starch content. A water content in the range 20 to 58% seemed to favor retrogradation, whereas a starch content of less than 20% had the opposite effect.[42] It has also been observed that starch may retrograde at the preheating temperatures of 60 to 75°C.[43]

The microstructure of potato starch pastes and gels in the concentration range 5 to 10 (% w/w) was studied by Svegmark and Hermansson,[44] as a function of shear and heat treatment, using light microscopy. Heating induced extensive swelling of potato starch granules, and the swollen granules filled the whole volume of the starch pastes that were subjected to minimum shear. The granules with the lowest gelatinization temperatures swelled quickly without restrictions, so that less water was available for the leakage of amylose and for the swelling of granules with higher gelatinization temperatures. The swelling and the contents of amylose and amylopectin differed between granules of different gelatinization temperature. Shearing during heating altered the structure completely. The granules were broken down into fragments, and an extensive solubilization of the granules took place.

In conclusion, the most abundant chemical constituent present in the potato is starch. Therefore, it is not surprising that in the past correlations between starch content and the texture of cooked potato was studied. Both positive and negative correlations were established, depending on whether the measurement of texture was subjective or objective.[13,14,18,40] Interpretation is even more complicated because of the assumed identity between mealiness and intercellular cohesion. The relationship between starch content and intercellular cohesion is not consistent and is probably indirect. But it is evident that mealiness depends on flow properties in the potato, which, in turn, are related to the total solids content or starch.[15,18]

D. Cell Properties

1. Cell Size

Cell size is also thought to correlate with potato texture. Changes in cell size during cooking was found to occur by some authors but not by others. The discrepancy may be due to the fact that different techniques were used. Linehan et al.[46] found a direct positive relationship between cell size, expressed as total surface area of the cells per unit volume of the potato tuber, and intercellular cohesion. The correlation factor R was 0.63, implying that cell size accounts for only a part of the cohesion between cells. Polyuronides (uronides are the building elements of the pectic substances), calcium, and amylose level were also of importance. Seasonal differences have been observed as well.[47] In the 1969 growing season, there was a clear correlation between breakdown and cell volume, but this was not repeated the

TABLE 3
Phenomena Associated with Starch Retrogradation

Phenomena	Detection method
Phase separation into polymer-rich and polymer-deficient regions	Turbidity measurements[63]
Formation of a crystal nucleus in the polymer-rich zone	Light scattering[64]
Aggregation of amylopectin	Turbidity measurements[65]
Starch crystallization	X-ray diffraction, DSC[65,66]
Aggregation of amylose and amylopectin and mixtures	Pulsed-NMR, X-ray diffraction[67]

next following year, nor was any relationship found when the two seasons were pooled.[47]

The larger the cells, the smaller the contact surface between cells, giving lower values of cell cohesion. The swelling of the starch during heat treatment and the "swelling pressure" should give both rounding and cell swelling. Bretzloff[48] cooked potato tissue in water on a microscope slide and took photographs during warming, at the cooking temperature, during cooling, and also after freezing, thawing, and reheating. No changes in cell size were found, and consequently, no support for the theory that starch gelatinization causes distention of the cell walls during cooking. Harada and Paulus,[20] on the other hand, found an increase in cell size during cooking of approximately 18%, and Barrios[32] found that the cells in cooked potatoes of four different varieties were 40 to 62% larger than in the raw potato, depending on the variety. Cell size was highly positively correlated (R = 0.998) with total starch content as cell size with mealiness (R = 0.939).

Warren et al.[49] found only a weak correlation between cell surface area and breakdown. Total solids gave the highest correlation (R = 0.51) with breakdown among 19 factors investigated. The polyuronide (pectic substance) amount per unit cell wall area also correlated well (R = 0.45) with breakdown for two varieties, two specific gravity groups and two harvest dates. No evidence was found for the swelling pressure theory. No single parameter could account for more than 25% of the variation in breakdown.

The size of the cells, as measured by SEM, was as follows:[50]

parenchyma (inner part of the cortex)	146 × 189 μm
parenchyma (inner phloem)	89 × 134 to 176 × 195 μm
pith	70 × 132 to 96 × 158 μm

2. Cell Separation and Rupture

Breakdown on cooking is usually because of cell separation and not cell rupture.[49] The cell wall and the middle lamella constituents are important for both cell separation and cell wall rupture. The cell walls of starch-containing cells were found to contain pectinaceous, proteinaceous, and cellulose substances. The middle lamellae are composed of calcium pectate, the primary cell wall possibly contains some protein, but the secondary cell wall is composed mainly of cellulose and pectinaceous substances.[51] When potato tissue was heated in water, the pectins in the middle lamellae were altered at 60 ± 10°C. In the meantime, the pectins in the primary and secondary walls changed, causing the separation of the compact lamellae into microfibrils and a local decrease in the amount of pectin, the result being that cell walls became easily fractured.[51]

Fedec et al.[50] studied the potato cell in raw, precooked, steamed, and granulated tissue using electron microscopy. In parenchyma cells, only one primary wall was found, consisting of a cellulose network in a pectin matrix. The thickness of the cell wall was 0.24 μm, whereas the thickness of the middle lamella was 0.08 μm (comparable to the plasmalemma's 0.09 μm). Precooking at 65 to 80°C for 10 to 20 min caused partial cell separation due to the partial hydrolysis of the constituents of the middle lamella. No cell rupture was found, the cell size being the same as in raw potato. After cooling to room temperature for 20 min, followed by steam cooking for 20 min, further dissolution of the middle lamellae and further cell separation occurred. Some material, probably amylose, was found, having leached out of the cells. After cooking in water, instead of steam, more cell rupture due to cell wall distention was observed and the cells were to some extent enlarged. The cells were still angular in shape, but swollen. There were great local variations (in different parts of the potato tuber) in cell size, cell wall thickness, and in the size and shape of starch granules.

Personius and Sharp[16] measured the tensile strength (minimum longitudinal stress required to pull a section of potato tuber tissue apart) of both raw and heat-treated potato tissue. No relationship was evident between the texture and variety in the case of the raw potatoes. The temperature effect on tissue tensile strength was studied without water or salt exchange between water bath and tissue. No reduction in tensile strength was found at T ≤50°C. At T >50°C the rate of tensile strength reduction increased with increased temperature. The tensile strength decreased to a constant value, which was lower for higher temperatures. Because the weakening of cell

cohesiveness started at temperatures below those at which starch gelatinization starts, these authors concluded that cell separation and starch gelatinization were independent of each other. Furthermore, no difference was found between soggy and mealy potatoes as far as cell cohesion was concerned in both raw and cooked tissues.

Further evidence for the independence of the two mechanisms, that is, starch gelatinization and cell separation, was supplied by experiments done by Reeve.[38] In these the tissue was preheated on a microscope slide at 75 and 90°C and then boiled (100°C). It was shown that starch gelation did not cause cell wall distention until the tissues were boiled. Starch swelling was not pronounced until the temperature had reached boiling point and the cell shape remained angular, although the middle lamellae appeared to be weakened. The tissue heated at 75 and 90°C showed a rapid gelatinization of the starch with no or little distention of the cell wall. In the same study, the sloughing of boiled and steamed potato slices was also considered. The sloughed tissue was composed of separated cells distended by their content of swollen starch. Some of the walls of the separated cells were ruptured and the gelled starch had extruded from the cells. The boiled potato slices showed more cell rupture than the steamed ones. There were also some varietational differences (more cell rupture in a waxy then in a mealy type) as well as dependence on the maturity of the tuber. Slices soaked in water at 75°C and cooled to room temperature before cooking or steaming did not slough. Soaking in cold water for 30 to 60 min before heating resulted in an abnormally high tissue turgor. These cells showed a greater degree of rupturing when boiled or steamed. Cell rupture was thought to be caused by starch swelling. Escape of gelled starch from ruptured cells in cooked tissue caused a sticky or gummy texture. In potatoes of the waxy type, however, the swelling was not sufficient to cause sloughing, and in the mealy type the cell was separated after cooking but did not swell enough to cause intense cell rupturing and leakage of gelled starch.

The same subject, revisited by the same author 23 years later,[52] led to results that have in a sense modified the previous conclusions. Thus, the new conclusion was that the initial slight swelling and the cell wall distension due to the swelling pressure of the gelatinized starch might aid in cell separation because the pectic substances and other polyuronides of the cell walls and middle lamellae were broken down by cooking. The stickiness and gumminess due to gelled starch having escaped from the ruptured cells was reconfirmed in this study.[52] Cell rounding was observed also in a baked, mealy potato. Cell rupture was first observed after boiling for 10 min, but the percentage of ruptured cells remained at a low 1% after 19 min and did not exceed 2 to 3% after 30 min (1.27-mm-thick slices of the Russet Burbank variety).

Conversely, Nonaka[53] did not find any evidence of cellular distortion (cells being angular and without exuded starch gel) during the cooking of potato slabs 16 mm thick for 8 and 18 min, respectively. Cell separation occurred without rupturing. The differences between the results of Nonaka[53] and Reeve[52] might be due to the fact that they used samples of different thickness. Because Nonaka's samples were thicker, the heat treatment at the center was not as intense as at the center of Reeve's samples. This explanation is enhanced by the fact that Nonaka also found the susceptibility to cell rupture to be increased with cooking time. A consideration of the Fourier dimensionless number should be applicable here.[2] Sterling[54] did not either find broken cell walls due to the cooking of potato, carrot, and apple, but apples in particular showed an extensive separation of intact cells. On the other hand, the intensity of cell rupture and its dependence on total solids and cooking time were found to be related to variety.[55]

The electrical permeability of potato tuber tissue, of both the mealy and the soggy type, was investigated by measuring the electrical resistance.[56] It was found that the resistance of tuber tissue decreased slowly at $T < 60°C$ and $T > 75°C$, whereas it rapidly decreased (from approximately 2000 W to approximately 200 W) in the intermediate temperature interval 60 to 75°C, that is, the same interval in which most of the starch swelling takes place. This coincidence gave the authors the impulse to study the resistance of starch (16%) suspensions in potato juice as a function of temperature. Whereas the slight decrease in

resistance outside the said interval was again observed, the big difference was that a slight increase occurred within the temperature interval. The conclusion drawn was that the marked decrease in resistance occurring in the case of the potato tissue was because of the increase in the electrical permeability. This increase of tissue permeability was found to be independent of the decrease of cell cohesion.[56]

In conclusion, a consistent relationship exists between cell size and disintegration of potato tissue. Immature tubers seldom disintegrate and normally cook to a firm, waxy texture, as do those tubers with small cells. The larger the cells, the smaller the contact surface between cells, giving lower values of cell cohesion.[48] Changes in cell size during cooking were observed by some authors but not by others.[20,32,48] Breakdown on cooking is usually due to cell separation and not to cell rupture.[49] Starch gelatinization does not seem to be related to cell separation or cell cohesiveness.[16,38,50,52] Because the weakening of cell cohesiveness starts at temperatures below those at which starch gelatinization starts, it can be concluded that cell separation and starch gelatinization are independent of each other.

E. Pectic Substances

The pectic substances (PS) seem to be of great importance in the cell separation and cell rupture occurring during heat treatment. They are located in the middle lamellae and in the primary cell walls. They are α 1-4 linked galacturonic acid and its methyl ester. The monomeric unit of the pectic substances is shown in Figure 5. For the nomenclature associated with pectic substances, being the subject of confusion in the literature, we refer to the classic book of Kertesz,[57] where *Revised Nomenclature of the Pectic Substances*, adopted by the American Chemical Society in 1944, is discussed and commented on in detail. In Table 4 we show the terminology used for the purpose of this literature review, which conforms with the suggestions made by Kertesz.[57] To summarize, protopectin stands for water-insoluble PS, pectic acid for the polygalacturonic acid with a low methoxyl content, pectinic acid for poly-

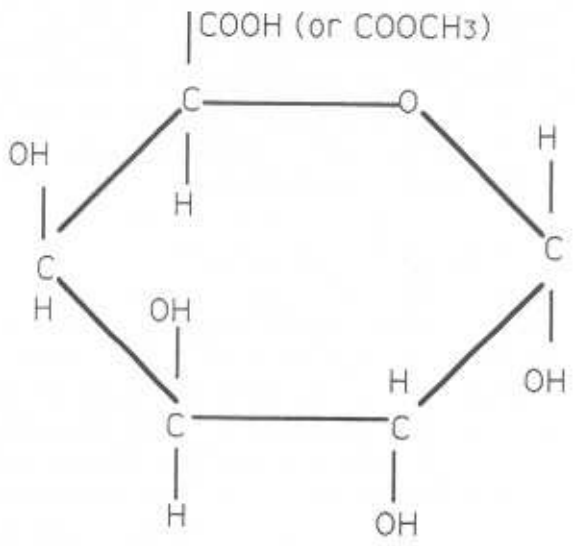
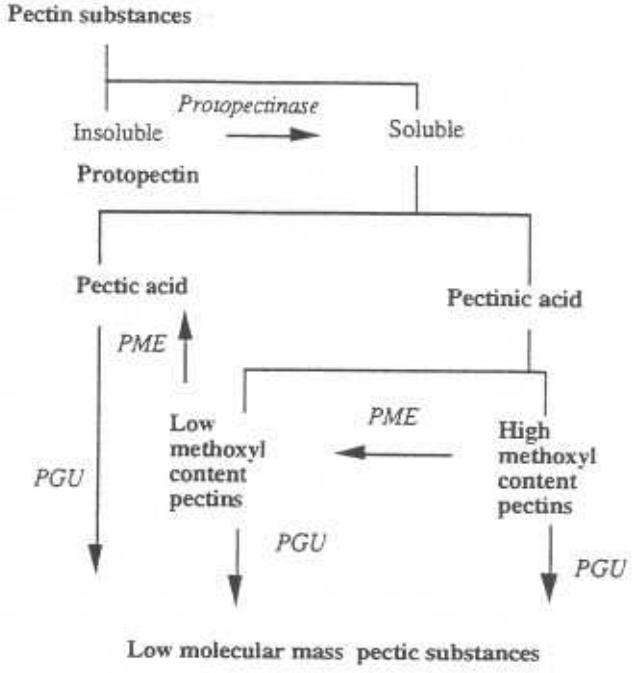


FIGURE 5. The monomer unit of pectic substances: galacturonide. Pectic substances are sugar acids belonging to the group of polyuronides.

TABLE 4
A Classification Scheme of the Pectic Substances Showing the Enzymatic Reactions Between the Various Types[a]



[a] PME, pectin methyl esterase; PGU, poly galacturonase; Protopectinase, its existence is only speculative.

galacturonic acid with a high methoxyl content, pectin for water-soluble pectinic acids of varying methylester content and degree of neutralization, and finally, polyuronides is a wider term, including PS. In some cases, however, the term pectins is used instead of pectic substances.

The degree of esterification differs among fruits and vegetables. Sometimes neutral carbohydrates such as L-arabinose, L-rhamnose, and D-galactose are contained in the pectic substances. PS are stable at a pH 3–4.[58,68] The degree of methylation of potato pectin was found to vary between 34 and 64% during the growing season, but no clear trend was found for variation with maturity. No difference was found between the two varieties tested (Maris Peer and King Edward). In October, the value was approximately 55% for both varieties.[57]

Firming treatment decreased the degree of methylation of the PS. The greater the firmness the less the pectic methyoxylation.[69] The pectin content of the potato decreased by cooking to an extent depending on variety, fertilizer dose, maturity, and the duration of storage. The degree of pectin esterification depended on fertilizing with Ca and Mg.[70] Linehan and Hughes[13] found no correlation between the amount of polyuronide and intercellular cohesion in cooked potatoes. Potatoes cooking "hard" were characterized by a far higher content of insoluble pectins and hemicellulose, than those "cooking soft".[71] The cellulose content was about the same in all tubers. Considerable material loss may occur during heat processing.[26] During heating for 12 min at 120°C, up to 37 to 43% of the cell wall material was lost. Pectic substances were reduced to about 8%, the amount of polyuronide to 5 to 6%, and calcium content to 6 to 7% of the respective values in the fresh tuber.

After extraction of PS from potato tissue with water, Calgon (sodium hexametaphosphate, a Ca sequestering agent) and hot acid, the water-soluble fraction was only a small proportion of the total with high methoxyl content (47 to 66% esterification degree), while the hot acid extract contained the major part of the pectic material and had a low methoxyl content (16 to 39%).[72] The Calgon-soluble fraction had also a low methoxyl content, approximately the same as the hot acid-soluble fraction. The water-soluble fraction, further, had low calcium content and a high intrinsic viscosity or weight-averaged molecular mass. Upon cooking, the water-soluble fraction was increased due to the solubilization of the pectic material, while the calcium content and intrinsic viscosity decreased. No direct relationship between PS characteristics and potato texture was seen, however.

Jaswal[73] states that the middle lamellae consist mainly of calcium and some magnesium protopectin salts, as do the primary and secondary cell walls. Potatoes of high and low specific gravity did not differ in protopectin, degree of esterification, water-soluble pectins, or divalent cations. The low specific gravity potato, however, gave a higher degree of deesterification, more pronounced protopectin breakdown, and higher levels of free calcium than those of high specific gravity. Low specific gravity potato was not suitable for French fries because it gave a poor texture. The reason is presumably that there are fewer and/or weaker cross-linkages in the protopectin of the low specific gravity potato.

Isolated potato cell walls were studied and found to contain 16.3% anhydrogalacturonic acid with a degree of esterification (d.e.) of 56%, and 25% of the total PME of the tuber.[76] Cell wall precooking in a model system resulted in a degree of esterification of 53%. There was a noticeable decrease in the value of d.e., commencing with 50°C and persisting at precooking temperatures up to 70°C. Precooking the walls at 75 or 100°C resulted in a value of d.e. coinciding with that of a native cell wall. This suggested that PME activity observed at 25°C is enhanced between 50 to 70°C, but is inactivated at or above 75°C. The solubilization degree (%) of the pectin was influenced by temperature. Interestingly, there was a minimum in the region of 50 to 75°C. This temperature range coincides with the optimum PME-activity temperatures *in vivo*. The temperature effect on the PME activity could thus be followed as reflecting the degree of esterification (d.e.).

Moledina et al.[77] studied the effect of precooking for potato granule production in a freeze-thaw process. Preheating (70°C, 20 min) followed by cooling (18°C, 10 min) of cylinders 1.85 mm thick made the tissue firmer than without pretreatment prior to steaming. When the pretreated

potato was mashed it became doughy and gluey. Cells ruptured in the mashing stage, rather than separating into single cells. In the precooked tubers, the PS were solubilized to a lesser extent than without precooking. After the complete treatment (preheating and steam cooking) the cell walls were closely bound together, but some solubilization of the cell binding material occurred; after steam cooking without precooking the cells were well separated, indicating a higher d.s. (degree of solubilization) in the middle lamellae. The results showed the importance of the middle lamella pectic substances as well as that preheating was necessary to make pectic substances less degradable. Thickness of the middle lamella was 0.13 ± 0.06 μm; that of the adjacent cell walls was 0.56 ± 0.18 μm.[77]

Depolymerization by a β-elimination reaction could solubilize esterified pectin at pH above 4.5 and was enhanced by heating. The phenomenon was more pronounced during boiling of potato cell walls, in the pH region 6.1 to 6.5.[78] With whole potatoes the same phenomenon (β-elimination) was found to be of minor importance compared with protopectin thermal degradation of another kind.[79]

Hughes et al.[80] found that the loss of comprehensive strength of potato during cooking was related to PS released into the cooking liquor, whereas the release of starch was not related so well. The presence of Ca in the liquor hindered PS release, leaving starch release unaffected. The monovalent K reduced the compressive strength but without having any definite effect on PS and starch release. The effect of Ca is not clear because its addition as $CaCl_2$ also affects the pH of the cooking solution. After cooking, the pH was reduced from initially 6 to approximately 4.5, making it difficult to distinguish between the effect of Ca and the effect of pH.

The interaction between K, Ca and the –COOH group of pectin (i.e., the stability constant of calcium pectinate) was found to depend on the ionic strength of the solution as well as on the degree of esterification and the mean distance of the free carboxyl groups in the pectin molecule.[83] The stability constant in a potassium and calcium chloride solution decreased with increased ionic strength (0.01 to 0.15) at pH 7.5. The lower the degree of esterification and higher the divalent cation content and the firmer the cell walls.

In conclusion, because sloughing or disintegration of tubers during cooking is the result of cell separation rather than cell rupture, the explanation of its mechanism must be looked for in the composition of the intercellular material. The middle lamella is rich in pectins, and pH and metal ions play a crucial role in the strength of the gel of the pectic substances formed between the cells during cooking. Firming treatment decreases the degree of the methylation of the PS. The greater the firmness, the less the pectic methoxylation.[69,76] The effect on the pectin polymer is to decrease its solubility, particularly in the presence of calcium salts. It has been definitely shown that removal of pectic materials from potato tissue reduces intercellular cohesion.[80]

F. Calcium and Other Minerals

The distribution of minerals, especially of calcium, is not uniform in the tuber. Magnesium, on the other hand, is more uniformly distributed than calcium.[8] Cunningham et al.[85] found marked local differences of sloughing, that is, the outer tissue sloughed more than the inner tissue, probably because of local differences in the concentration of K, P, and organic acids in the tuber. Warren[86] found that the concentration of both calcium and pectin was highest in the outer part of the potato tuber. Because sloughing is more pronounced in this section, it seemed to be a contradiction as far as the importance of calcium and pectin for firmness was concerned. The paradox could be solved by considering the variation of another factor, namely, cell size. The periderm cells are much smaller (1/4 in diameter) than the storage parenchyma cells, implying a fourfold increase of the cell wall area per unit weight of fresh tissue. Thus, the amount of calcium and pectin per unit cell wall area should be considered, and this was found approximately to be the same in all parts of the tuber.

On baking, a migration of minerals from the cortex to the pith was observed, but this was not significant for calcium and magnesium.[89] Frying

reduced the mineral content, especially in the cortex tissue. Marked variations in the mineral content was also observed.[89]

If calcium is present in the cooking water or if the tuber is soaked during the precooking procedure in the presence of calcium, the potato tissue becomes firmer, sloughing is reduced, and mealiness is reduced. This information is supplied by many studies (see Table 5) and the mechanism given as an explanation is the formation of calcium bridges (crosslinking) between carboxyl groups in the pectin molecules.

Indirect evidence is provided by the fact that the addition of organic acids, notably citrate, increases sloughing, because they form complex compounds with calcium, thereby reducing the amount of calcium available to interact with the cell wall and middle lamella.[36] Immersion of potato slices in different salt solutions at 65°C showed that chemicals capable of removing calcium, such as ammonium oxalate, sodium citrate, and sodium fluoride, were all very effective in reducing potato cell cohesion. By contrast, divalent ions such as calcium (especially), barium, strontium, and magnesium were able to increase or at least prevent or retard the decrease of the cohesion forces between adjacent cells on preheating at 65°C. Using a $CaCl_2$ solution, cell cohesion that had been reduced because of the addition of NH_4-oxalate could be recovered.[90]

Blanching in water containing $CaCl_2$, $MgCl_2$, and Ca-citrate improved the texture (in terms of firmness, chewiness, and brittleness) of French fries made of potatoes of low specific gravity. $CaCl_2$ was most effective. Best conditions: T = 70°C, 15 min, pH = 6, $[CaCl_2] = 0.5\%$.[74] Based on the results of Zaehringer and Cunningham,[91] agents causing sloughing can be classified as follows, in order of increased action:

distilled H_2O < malate, oxalate, Cl < citrate < Na, K

By contrast, soaking potato slices in $CaCl_2$ decreased sloughing.[93] Soaking in distilled water also decreased sloughing during boiling. When monovalent cations (K, Na, NH_4, as chlorides of these) or potassium salts of malate, oxalate, phytate, and citrate were added to the soaking

TABLE 5
Experimental Evidence of the Role of Calcium in Enhancing the Texture and in Retarding or Preventing the Decrease in Tissue Firmness in Potatoes

Effect	Evidence	Ref.
Decrease of sloughing, prevention of cell separation	Indirect; organic acids have opposite effect as forming complexes with Ca	36
Improvement of cell cohesion	Decrease caused by ammonium oxalate could be reversed by $CaCl_2$	90
Overall improvement in the texture of French fries	Addition of $CaCl_2$, calcium citrate, $MgCl_2$ in blanching water improved the texture; best combination: 70°C, 0.5%(w/w) $CaCl_2$, pH 6	74
Hindrance of sloughing, enhancement of firmness	Addition of Ca while cooking decreased sloughing and increased firmness	92
Decrease of sloughing	Soaking of potato slices in water with $CaCl_2$ before cooking decreased the sloughing	93
Enhancement of firmness after cooking	Precooking in water with Ca (200 µg/l) at 65–75°C enhanced the firmness of the final product (but not cooking alone in the presence of Ca)	76
Decrease of firmness delayed during thermal treatment	Shear strength change kinetics	21

water, the effect was reversed and sloughing was increased. Further addition of calcium again decreased the degree of sloughing, whereas magnesium did not seem to have any effect.[93] The degree of sloughing of 1.3-mm-thick slices was decreased by soaking for 6 h in distilled water prior to cooking. The soaking treatment caused substantial losses of cell material, notably of K (71%) and P (69%), while the loss of Ca was 35%, which may have been responsible for the decrease in sloughing (in particular K losses).[27]

During boiling, however, leachates from the potatoes increased sloughing; the reason was assumed to be the weakening of the intercellular cement rather than starch swelling.[91] An early loss of PS to the cooking liquor was observed when the potato tissue was cooked in NaCl in the presence of 2% Na-hexameta-phosphate, and, further, the compressive strength decreased earlier than when the tissue was cooked in water only.[81]

Moledina et al.[76] found that starch is a source of calcium that, after gelatinization, can stabilize pectic galacturonan, making pectin less soluble at 60°C and more pronouncedly at 70°C. The same was not valid for magnesium found in starch. The uptake of calcium by the cell wall was ten times higher when precooking was followed by cooling than without cooling. Cooling, however, did not influence the degree of solubilization of pectin. The experiments were done with isolated cell wall tissue. Precooking (65 to 75°C) and cooling in deionized water did not improve firmness of 6.4-mm-thick potato slices. If the water contained 200 mg calcium, the tissue became considerably firmer after cooking, the effect being more pronounced at the higher temperature. But cooking alone in the presence of calcium did not make the tissue firmer. Because salt levels in the tissue were found to permit no more than 11.3% pectin demethylation, it was concluded that the benefit of precooking was not primarily the activation of PME, but rather the supply of calcium from the starch and the stabilization of the Ca bridges during the cooling step.[76]

Other results have provided evidence that the presence of calcium ions (but not Mg or K ions) kept the PS in the cell wall insoluble despite β-elimination. The opposite effect (solubilization of PS) of citrate, phytate, and malate has also been confirmed. The explanation is that citrate and malate are calcium chelating agents, whereas phytate precipitates calcium at pH >5.4. All the ions mentioned above were found to stimulate the β-elimination reaction of pectic galacturonan.[33] The ratio $[Ca^{2+}]/[COO^{-}]$ was of importance for both β-elimination and pectin stability. At a ratio of between 1 to 2 pectin had its optimal stability, whereas at higher ratios the β-elimination reaction was favored.

Calcium content also correlated with fat absorption and color. Ng et al. found that high calcium content resulted in a light color and low fat uptake.[95]

In conclusion, minerals in the tuber or in the blanching liquor may have a great influence on the texture of the final potato product. Divalent cations such as Ca, and perhaps also Mg, form bridges between the pectin molecules, thus making the pectin less soluble. This leads to a firmer potato texture after cooking. Monovalent cations, such as Na and K, tend instead to solubilize the pectin and make the texture softer.[12,69,84] Increasing the concentration of NaCl and KCl salts implied decreased compressive strength.[82]

G. Effect of pH

The pH of the heating medium (preheating or final heating) is an important factor for firmness of fruits and vegetables, including potatoes. In general, increasing the pH (>3) means a loss of firmness. The effectiveness of added acids is attributed to their inhibitory action on the pectic enzymes.

Furthermore, pH and calcium have been found to be interrelated factors during cooking, because when calcium cross-links the pectin HCl is produced, lowering the pH and giving a firmer tissue. One must be careful to distinguish between the firming effect of calcium and the firming effect of pH.[82]

H. Pectin Methylesterase, PME

Sources of the enzyme pectin methylesterase (sometimes referred to as pectin esterase) are fungi, bacteria, and higher plants. The physiological role

of the enzyme is not quite clear; nevertheless, it is thought that it makes the fruit softer during ripening (and storage) by deesterifying pectin and thereby making it more prone to degradation by polygalacturonase. Table 4 provides a scheme of the pectic substances in which the action of the enzymes is shown. As with enzymes in general, a series of actors such as pH, temperature, salt, and substrate concentration affect the enzyme activity. Fungal PMEs are in general less influenced by salts and their pH optimum is lower than that of enzymes from higher plants.[58,68]

PME is a highly specific enzyme removing methoxyl groups by hydrolyzing $-COOCH_3$ groups and leaving –COOH groups in place (Figure 6). The result is a decrease of pectin solubility, more pronounced in the presence of calcium salts. Salts in general were found to enhance PME activity.[69] As Figure 6 shows, PME is supposed to hydrolyze only a methylester group if it is next to a free carboxyl group, thus proceeding linearly along the polyuronide chain.[88] Total demethylation is then impossible, stopping usually at a methoxyl content of 5%.[57]

In potato, the enzyme activity was found to depend on the location in the tuber. The highest activity was measured in the bud end (not surprisingly as this is the place of highest metabolic activity), whereas in the inner phloem (the perimedullary zone) the activity of the enzyme was the lowest. Twenty-five percent of the total activity was found in the cell wall fraction.[76] The dependence on maturity was unclear but variations were found, as, for example, the Maris Peer had a more active enzyme than the King Edward variety.[47] Seasonal differences have also been traced so that a tendency observed in one season was not necessarily repeated in the next season.[88]

PME is sometimes found in different isozyme forms. At least three isozymes were found in banana pulp[96] and two isozymes of different thermostability in potato.[87,97] Five isozymes were separated by electrophoresis and were the same for all the four potato varieties examined.[98] Puri et al.[99] determined the molecular mass (MM) of potato PME by extraction on Sephadex G-100. They found only one enzyme of MM 25 kDa. If more than one isoenzyme are present, their MM should be close to the value above.

Under varying preheating conditions, the retention of potato PME activity varied as shown in Table 6.[76,101] Other conditions were pH 7.5 and 1.6% NaCl. The optimum temperature was 60°C.[76] Two enzyme fractions in potato with different thermostability were reported.[87,97] The most thermostable fraction, which accounted for approximately 17% of the total PME, was inactivated at T >75°C, whereas the thermolabile fraction became inactive at 70°C, the thermal denaturation properties of the two isozymes. The potato (variety Russet Burbank) PME was studied by Puri et al.[99] They found an optimum temperature of 55°C. Above 55°C a rapid inactivation of the enzyme occurred. The inactivation temperature of PME of four different varieties was found to be 60°C.[98]

According to Bartholome and Hoff,[101] during preheating in the temperature interval of 60 to 70°C:

1. The amount of Ca and Mg in the cell wall increased to some extent.
2. A slight decrease in methoxyl content occurred.
3. A minor portion of the cell wall was solubilized, and this fraction contained pectin.
4. The native PME adsorbed on the cell wall was activated, probably because of desorption initiated by a solute concentration of 0.15 *M*.

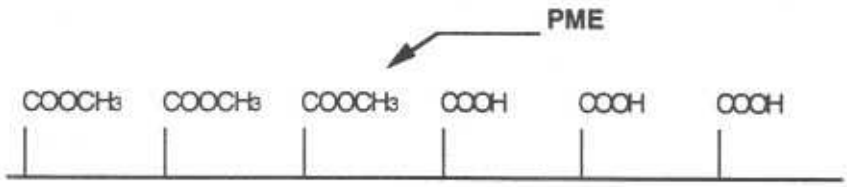


FIGURE 6. Schematic representation of the kind of action of the PME enzyme. The $COOCH_3$ groups are attacked successively, one by one, indicating a zero-order reaction.

TABLE 6
PME Enzyme Activity Retention during Preheating

Temperature (°C)	Time (min)	Activity retention (%)
60[a]	30	83
60	52	50
65	10	79
65	30	45
68	10	50
70	10	24
70	20	0
71.5	10	20
75	10	0
60[b]	60	50
70	60	0

[a] According to Moledina et al.[76] (pH 7.5, 1.6% [w/w]).
[b] According to Bartholome and Hoff.[101]

The theory put forward by the authors was that at T >50°C:

1. Intracellular solutes diffuse from the interior to the intercellular spaces, activating the enzyme.
2. PME then attacks the methylester groups of the polyuronide chains to produce free carboxyl groups.
3. In turn, divalent cations such as Ca, Mg crosslink the chains, thereby preventing further degradation.

In conclusion, it is quite clear that PME is a highly specific enzyme that removes methoxyl groups from pectin molecules by hydrolyzing $-COOCH_3$ groups, leaving –COOH groups in place.[57,69,88] The result is a decrease of pectin solubility, which is more pronounced in the presence of calcium salts. This will decrease the intercellular cohesion forces between adjacent cells.[76,77,80] PME activity observed at 25°C is enhanced between 50 to 70°C, but PME is rapidly inactivated at or above 70°C.[76,87,97,101]

IV. SUMMARY AND CONCLUSIONS

Preheating potatoes at 50 to 80°C has a firming effect on the cooked potato tissue. This effect is particularly pronounced at a preheating temperature of 60 to 70°C followed by cooling. Several theories have been presented in the literature to explain this firming effect: retrogradation of starch, leaching of amylose, stabilization of the middle lamellae and cell walls by the activation of the pectin methylesterase (PME) enzyme and by the release of calcium from gelatinized starch, and the formation of calcium bridges between pectin molecules. Most probably, none of these theories alone can explain the phenomenon and more than one mechanism seems to be involved. Some of these mechanisms seem to be interdependent. As an example, calcium could be considered as a link all the way through release on starch gelatinization to cross-linking pectin substances in the cell wall and the middle lamellae, which has been demethylated by the PME enzyme.

More research and "clear cut" experiments are needed in order to elucidate the role of each mechanism, especially which of them is the main contributor to the process of firming. Most probably, the calcium-pectin-PME mechanism plays a secondary role, that is, it only retards the collapse of the tissue structure that would otherwise occur during the final heating without preheating, and it is not the main factor of firmness.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from Nordreco AB, Bjuv, Sweden and

the Swedish Financial Organization for Technical Research and Development: NUTEK.

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