DOI 10.1002/star.201300212

Starch/Stärke 2014, *66*, 58–71

REVIEW

How environmental stress affects starch composition and functionality in cereal endosperm

Diane M. Beckles and Maysaya Thitisaksakul

Department of Plant Sciences, University of California, Davis, CA, USA

Received: September 7, 2013
Revised: October 24, 2013
Accepted: October 28, 2013

Stressful environments can alter starch biosynthesis in cereal endosperm. The aim of this review is to carefully examine how starch functional properties are altered when plants encounter environmental parameters outside of the normal range. This is important because while growers and processors require grain yield stability and product uniformity this will be challenging in an era of variable weather patterns. Being able to predict the general physico-chemical nature of the starch as a result of growth status is a step towards the "precise" agriculture required for the 21st century. Variations in soil moisture and nutrient availability, ambient temperature, and atmospheric composition were all shown to affect starch functionality. Elevated temperature led to the most significant changes in both tropical and temperate cereals and amylose content was the most sensitive parameter under various environmental conditions. Genotypic variation appears to be a primary contributor for the response of cereal starches to environmental stress. Nonetheless, while a large amount of data from single controlled environmental stress experiment is currently available, comparably little is known about whether similar results would be achieved in multifactorial and large-scale settings. The challenges in terms of the need for more detailed experimental descriptions to lessen the study-to-study discrepancies of data and to enhance their interpretability were also discussed.

Keywords:
Endosperms / Environmental stress / Starch composition / Starch functionality

1 Introduction

The amount, composition, and unique molecular structure of modern-day commercial cereal starches are the result of careful agricultural management [1] combined with 1000s of years of selection for desirable germplasm [2–6]. Cereal starch now makes up 50% or more of the diet of many people [7, 8] and its role as a source of calories is well understood. The diversification of starch as a functional food [9, 10], biopolymer [11, 12], and biofuel [13]; however, is expanding rapidly. These applications often function efficiently with optimal cost-benefit ratio when starches of specific physico-chemical properties are used [10, 14]. It is well established that the environment has a large effect on both starch biosynthesis [15] and properties [16], and that in future years, environmental changes will become increasingly unpredictable [17–21]. Some growers are already faced with changes in planting seasons, higher than average night temperatures, decreased water availability, and deteriorating soil quality, which can alter starch accumulation and physical characteristics, making the grain and flour quality less desirable for some intended downstream uses [22]. In addition to sustained modifications of the climate in some cultivated areas, episodic stresses may also occur, changing product quality even in the absence of pronounced reductions in grain yields. Anticipating these changes may help each group along the supply chain to better plan and target suitable markets for these "stressed products" [23]. A comprehensive review on this topic was last published 12 years ago by Tester and Karkalas [16], since which there have been voluminous

---

Correspondence: Maysaya Thitisaksakul, Department of Plant Sciences, University of California, One Shields Avenue, Davis, CA 95616, USA
E-mail: mthitisaksakul@ucdavis.edu
Fax: +1-530-752-9659

Abbreviations: CO_2, carbon dioxide; **DPA,** days post anthesis; **N,** nitrogen; **NTAT,** night-time air temperature; **O_3,** ozone; **ppm,** parts per million; **RVA,** rapid viscosity analysis

Additional corresponding Author: Diane M. Beckles, dmbeckles@ucdavis.edu

literature on how growth environments affect starch functionality. In addition, there has been a recent and intense focus on predicting how environmental changes will affect agricultural productivity and the quality of food [23]. This review seeks to update our current knowledge in the field.

2 Starch structure and composition

Starch is the main carbon reserve in cereal endosperm, accounting for 50–90% of dry matter in the tissue [24–28]. It is deposited as discrete particles, of which the size, morphology, and relative numbers are strongly dependent on genetic, developmental, and environmental factors [25, 29, 30]. The diverse uses of storage starches are facilitated by the wide array of molecular structures that exists [31, 32]. For a more comprehensive understanding of starch molecular structure and composition, readers are referred to these reviews [27, 33], as only a brief description will be given here.

Starch consists of chains of α-1,4-linked D-glucose units of different lengths that are interconnected by α-1,6-linkage branchpoints. These chains are organized into two glucan polymers called amylose and amylopectin in a 30:70 of the dry weight of starch respectively in non-mutant cereal endosperm [27, 34]. Amylose has a MW of 10^6–10^8 Da and consists of α-1,4-linked glucoses that are branched by α-1,6-linkages every 200–10,000 glucoses [27, 35]. Amylopectin in contrast is larger, of MW 10^8–10^9 Da, and the α-1,4-linked glucan chains are branched at approximately every 20 glucoses [35]. The branching in amylopectin is defined, and leads to a recognizable pattern of glucan chains of defined lengths arrayed into alternating concentric crystalline and amorphous lamellae [33, 36, 37]. Adjacent α-1,4-linked glucan chains associate to form helical structures giving rise to crystalline lamellae, while the α-1,6-branchpoints are found in the amorphous region [33, 35]. Amylose appears to be randomly deposited amongst the amylopectin skeleton primarily in the amorphous region [33], yet, has an influence on the arrangement of amylopectin in the crystalline lamellae [31] through cross-linking of the two polysaccharides [33, 38]. The lipids content in cereal starches are comparatively high and is found complexed with amylose, although some proportion of amylose may have no associated lipids [39].

3 Relationship between starch structure and functionality

The functional behavior of starch is intricately linked to its structure and morphology. Changes in the proportion of amylose to amylopectin, glucan chain length distribution, degree of crystallinity, or granule size distribution can alter starch physico-chemical characteristics [31]. The organization of the crystalline lamellae influences the water-uptake property of starch, while the relative proportion of amylose and the structural organization of the amylopectin molecules are important for starch thermal property and gelatinization [31], as is the lipid complexed with amylose [40]. Starch is usually cooked wet or dry before consumption, which disrupts granule crystallinity [10, 31]. The ensuing solid-gel phase transitions in large part determine texture and eating quality attributes [31]. To assess starch functionality, parameters such as starch swelling power, viscosity, gelatinization, and retrogradation are used to predict potential applications and quality [10]. Although identifying an exact relationship between starch structural composition and its processing properties remains inconclusive [31], in this section, we provide a snapshot of such relationship based on these functionality parameters. For a more illustrative review on the topic, readers are referred to [31, 41, 42].

3.1 Starch swelling power

At the onset of starch gelation, water ingresses into the granules, making them “swell.” The swelling pattern occurs in two phases, first in the amorphous core of the granule, and second in the semicrystalline lamellae when most of the amylose molecules have leached out of the granules [41, 43, 44]. The presence of the amylose-lipid complex and the aggregated amylose molecules is responsible for restraining swelling events [39, 41]. Small granules were found to have higher water absorbability compared to the large granules, due potentially to the differences in the way the glucan chains are ordered [45], and the higher surface area per unit weight of the small granules [46, 47].

3.2 Starch viscosity

Viscosity occurs during gelatinization when, mainly, amylose leaches from the starch granule and forms a matrix on the exterior surface of the granule [31, 39]. This matrix holds water and along with the unwinding of amylopectin helices [48], increases the viscosity of the mixture [31, 48]. Using rapid viscosity analysis (RVA), the paste viscosity can be observed throughout the gelatinization process. Paste viscosity reaches its maximum when all granules are swollen, but still intact [31, 49], and once the granules break down and the polysaccharides become dispersed in the medium, the paste viscosity diminishes [31]. Paste viscosity rises again once the temperature lessens until it reaches the final point (aka “setback”) [31]. Starch with low amylose content will have high peak viscosity [31, 50], and low setback viscosity, reflecting the diminished amylose gel network [50]. The complexes of amylose and lipid increase the peak viscosity temperature in maize, rice, wheat, and barley starches [50]. Smaller granules have lower peak viscosity and breakdown, but higher peak viscosity temperature in comparison to the larger granules [51].

3.3 Starch Gelatinization

Gelatinization is described as the phase transition of the starch granule in the presence of heat and excess plasticizer, typically water [41]. The internal structure of the granule breaks down, leading to granule disassembly and leaching of the polysaccharides into the medium [52]. An irreversible loss of crystallinity only occurs when the temperature reaches the threshold where both the interactions among the neighboring amylopectin side-chains and between the side-chains of the double helices are lost [53]. This temperature is, however, varied according to the composition of starch [50] and the abundance of water [54, 55]. A high degree of crystallinity provides structural stability, making the granules less susceptible to gelatinization and is reflected in higher transition temperature [56]. Amylose content, in general, is negatively correlated with gelatinization temperature [31, 57]. Starches with higher proportions of long amylopectin side-chains [50], greater amount of amylose-lipid complexes [50], or smaller granules [45, 47] exhibit low gelatinization temperatures. However, a strict correlation between starch granule size and gelatinization behavior was not universally found [58].

3.4 Starch retrogradation

Retrogradation of gelatinized starch occurs when the amylose and amylopectin molecules realign and interact to create more crystalline molecules as the starch cools [59]. This negatively affects the storage [41] and freeze-thaw stability [48] of starch in industrial applications. Low amylose content [53, 60], high proportions of small side-chains amylopectin [41], low lipid content [50], and large granule size [47] prevent starch from retrograding.

4 Effect of the environment on starch structure and functionality

The structure and composition of starch are important indicators of the quality and palatability of food [6, 61, 62] and its healthful benefits [63], the nutritional value of cereal grains as an animal feed [64, 65], its suitability as a feedstock for biofuels (Tanadul et al, submitted for publication) and [66], and the variety of biopolymers that can be synthesized from any botanical starch source [67]. Starch functionality is in turn affected by, in addition to genotypes, growing season temperature, rainfall patterns and humidity, growth locations, and sustained or episodic environmental stresses [61]. In some instances, year-to-year variations in weather [68], shifts in planting seasons [14], or growth in various locations [69–72] may sometimes have a greater influence on starch functionality than genotypic differences. The environment alters starch by acting on sensitive starch biosynthetic enzymes, i.e., those involved in substrate production, the elongation of the α-1,4-glucan chains and their branching, and the maintenance of granule crystallinity [15]. These enzymes form interdependent complexes that cooperatively synthesize starch [73, 74]. Changes in the spectrum of enzymes in these complexes will substantially alter the structure and composition of the granules [15]. The starch biosynthetic enzymes in different genotypes are affected differently by changes in environmental conditions [15]. The readers are referred to the recent review [15] on the topic for more detailed information. Here we review the effects of a variety of stresses on starch structure, composition, and funtionality in cereals.

4.1 Temperature extremes

Temperature has long been known as a critical element determining agricultural productivity. It is almost impossible to control this factor in the field and so it is among the most pernicious [17]. Future climatic predictions all suggest that on average, higher temperatures will be the new norm [22] and as a result, the effect of elevated temperatures on crop productivity has been extensively studied [17]. An interesting but neglected corollary is that higher temperatures in some regions can be directly linked to a cooling trends in other regions [75], and crops in the latter areas may be increasingly subjected to chilling stress.

4.1.1 Heat

High air and soil temperatures are the primary stressors that reduce grain starch production and alter starch functionality [16, 76, 77]. The optimum temperatures for “normal” grain filling vary by species [22], and there may also be diurnal variations in heat sensitivity with higher night-time air temperature (NTAT) having a larger effect on rice starch quality [14, 78]. High growth temperature decreased amylose content in maize [79] and increased it in wheat [80–86], but the magnitude of these changes were neither as significant nor as consistent compared to Japonica rice where amylose may be reduced as much as 20% at temperatures above 30 °C [87–95]. Indica rice amylose, however, appears to be more stable at high temperature, with some types showing minor or no change [90, 96–99]. Naturally low-amylose Indica [96, 97, 99, 100] and Japonica [101] rices had greater reductions in amylose when compared with inherently high-amylose genotypes exposed to elevated temperatures. Nevertheless, seemingly minor changes in amylose may still be consequential for functionality, since a 1% variation in amylose effectively altered starch gelatinization and pasting properties in some flours [80, 102]. In contrast to maize, wheat, and rice, there was no substantive evidence for consistent changes in amylose content in normal barley [16, 76, 103] and sorghum [70, 104] grains exposed to high temperature. This response may be due to the intrinsic nature of these species, or point to the limited diversity of genotypes studied, given that the amylose content in naturally high-amylose barley was reduced by elevated temperatures [103]. Caution must be hence taken before making predictive generalizations of the ensuing starch properties without exhaustive analyses on a divergent set of genotypes.

The chain-length distribution of amylopectin glucan chains may also be modified in the endosperm starches experiencing heat stress. The long glucan chain fraction in most [69, 77, 87, 91, 92] but not all [93] rice varieties increased. Conversely, the trend in wheat is toward the accumulation of shorter glucan chains [82, 83], while a single report for sorghum suggests it responded similarly to rice [104]. There have been limited studies in maize, and there appears to be no propensity to synthesize either longer or shorter chains when an array of cultivars were exposed to high temperature stress [79].

High growth temperatures alter starch granule size, shape, and structure, and may also cause pitting and fissures, with the extent determined by the severity and time of stress application [81]. In wheat [80, 83, 86, 105, 106] and barley [107], the size of both A- and B- granules decreased, with the proportion of the large A-granules increasing at the expense of the small B-granules. The size of wheat A-granules was disproportionately affected when the heat stress was applied close to anthesis [81]. Heat also caused reductions in granule size in sorghum [104], rice [108], and normal maize [79], while in waxy maize granule size enlarged [109].

Rice grain appearance changes detrimentally at elevated growth temperature, whereby the translucent grain becomes chalky [92]. Besides being visually unappealing, these grains are difficult to polish, easily fractured during milling, and become stickier when cooked [92], making them less desirable in many Asian markets [93, 110, 111]. Changes in amylopectin chain-length distribution may contribute to grain opacity [92, 111, 112], but granule physical factors are also important [93, 108]. Chalky sectors of the grain have aberrantly-shaped starch granules interspersed with numerous air pockets [93, 94, 111], which allow increased water absorption and thus granule swelling power during the cooking process [113].

Starches from rice [71, 88, 89, 91, 114], wheat [82, 84], maize [115, 116], and barley [117] experiencing elevated growth temperatures generally showed higher gelatinization temperatures. Heat stress also altered starch pasting profiles in wheat [81], maize [109, 115], and rice [99].

4.1.2 Cold

Generally, there were increases in the ratio of amylose to amylopectin in the grain of rice grown in controlled low temperature environments [114], cooler field locations [69], and colder seasons [61]. Similar results were also seen in wheat [118, 119] and maize [120]. There have not been many in-depth analyses of starch functionality on cold-treated cereals, nonetheless, gelatinization and pasting temperatures generally decreased in most [69, 121] but not all [118] studies. In the field study by Dang and Copeland [61], several rice cultivars had a lower peak viscosity and greater setback of the rice flour when ambient temperatures were reduced. Even in barley where no significant changes in the amylose to amylopectin ratio were found when plants were exposed to low temperatures in controlled conditions [122], in the field in which a complex interaction of environmental factors could play a role, barley starches that developed during a cool summer had altered granule size distribution, lower lipid content, and lower peak gelatinization temperature [121]. These starches also showed greater amylolysis in vitro, indicating changes in the molecular structure of starch [121].

4.2 Soil moisture and nutrient composition

Soil physical structure, osmotic properties, and chemical composition can influence grain starch. Although modern agriculture emphasizes drip irrigation, cereal production in many regions is still rain-fed [123]. Poor agricultural management of soils and high radiation together are increasing soil salinity [124]. Increasing social, political, and economic pressures to reduce chemical inputs for agriculture suggests that growers will be more judicious in terms of the rates and amounts of fertilization applied. How these elements change grain starch properties are considered in this section.

4.2.1 Water deficit

Inducing a moderate water deficit in cereals can cut starch accumulation by up to 40%, leading to changes in starch composition, structure, and functionality [15]. In several studies in wheat [119, 125–127] and rice [128–131], amylose content was significantly lower, while barley starch appeared to be more resistant [132]. Starch granule size distribution in wheat was altered, with a higher proportion of A-type granules detected and this was commensurate with fewer B- and C-type granules [126, 127, 133–135]. However, rain-fed wheat with variable watering through development and overall lower soil moisture content compared with that of the irrigated control, had a higher proportion of B- and fewer A-granules, suggesting the timing of the stress may also be critical [125]. Starch granule size distribution in barley endosperm was more resilient with changes only evident under long-term water stress, following a similar pattern to that seen in wheat [132, 136, 137]. Inspite of that, under drastic water deficit, i.e., 4% soil moisture content for 20 days, barley starch granules were eroded due to premature degradation [137].

Restricting watering to rice and wheat was shown to alter starch functionality, especially the pasting properties. In rice, although there was some variation in the two phenotypically divergent cultivars studied, generally, water stress increased flour swelling power, peak viscosity, cohesiveness, gel hardness, and granular breakdown [128, 129]. There was also an increase in grain chalkiness and milling properties in another study [131]. In wheat, water deficit during growth reduced grain starch-lipid content and increased pasting temperature, causing higher viscosity and setback [126, 127]. Similar results were seen in field-grown wheat that underwent different seasons and plots that were irrigated vs. rain-fed [119, 125].

4.2.2 Salinity

Salinity stress effects on starch functionality have been studied in rice and triticale. Rice is highly sensitive to saline soil but the response is not influenced by the salt-sensitivity of the cultivar [138, 139]. There also appears to be great genetic variability for this trait [138, 139], and the type of salt used may have a greater effect on starch structure than the salt concentration [138]. Of the two genotypes studied by Peiris et al. [138], amylose was only altered in Pokkali and this was only observed when plants were exposed to high chloride ions, whereas there was no apparent effect found in other salts studied. Despite changes in amylose content, gelatinization temperature remained constant [138]. However, apparent amylose content in IR5929 was not affected, but gelatinization temperature was lower under all salt concentrations [138]. These experiments materially illustrate the specificity of the response, depending on the salt-type and concentration, as well as the genotypes studied.

In the only other major study, Siscar-Lee et al. grew four basmati rices in a field where the soils were saturated with 40 mM sodium chloride. Three out of four genotypes accumulated less apparent amylose, but there was no indication that starch gelatinization nor paste viscosity was affected by the treatment [139]. Grain translucency was reduced and cooking hardness increased in some cultivars [139], suggesting that saline soils may affect rice cooking and eating properties, even though the specific effects on starch molecular structure were unclear [138].

Triticale starch exposed to 50, 100, and 200 mM sodium chloride at grain initiation had a higher proportion of larger A-granules, higher amylose and lower gelatinization temperatures, namely lower peak and conclusion temperatures [140]. At 100 and 200 mM sodium choride the granules surface was studded with indentations [140].

4.2.3 Nitrogen deficiency

Variation in soil nitrogen (N) usually has direct consequences for the starch-to-protein ratio in grain, which would suggest ramifications for starch functionality [141], although several studies demonstrated that the effect on starch is unpredictable [142]. In general, when soil N-levels are decreased, amylose content increased, and this was documented in rice [143–147], wheat [148, 149], and triticale [150]; however, other studies failed to show an effect (rice [151, 152], triticale [142], and wheat [153]). While genotypic differences may explain some of these divergent responses [145], Champagne et al. [143] suggested that the general nutrient composition of the soil could be an important factor and other works also support this idea [148, 149]. Wang et al. [148] found that lower N increased amylose in wheat but this effect could be reversed, i.e., amylose *increased*, if the wheat was also irrigated at a higher frequency. Li et al. [149] found that low N decreased amylose in wheat but only when Sulphur status was simultaneously altered, otherwise there was no effect.

The percentage of B-granules increased in wheat [149] and tritcale [150] due to lower soil N. The same was found in a field study comparing the effects of organic N on wheat grain quality [153]. There is not much data on rice, but scanning electron micrograph suggested that applying a smaller amount of N may have ostensibly led to smaller starch granules in the regions of the rice grain that were chalky [154].

Sub-optimal N fertilization can also alter some aspects of starch functionality. Lower pasting temperatures [145, 146], increased starch gel hardness [145], and decreased gel cohesiveness [145] and consistency [144] were all found in rice. Gelatinization parameters are not greatly impacted in some studies [144, 145], but in another study, both transition temperatures and enthalpy of gelatinization were reduced [146]. In wheat [148] and triticale [150], there were changes in pasting properties when N was altered. While these changes were measurable, genotypes and other interacting environmental factors reduced the severity of the impact of nitrogen deficiency [149, 150, 155].

4.3 Atmospheric composition

The relative proportion of CO_2, O_3, and other pollutants in the atmosphere continues to increase and this is anticipated to have repercussions for grain productivity [156, 157]. The cultivar used, the concentration of CO_2 and O_3, mode of delivery, duration of exposure, crop developmental stage, as well as general environmental conditions may, in concert, lead to a wide range of alterations in starch properties [15]. Elevated CO_2 and O_3 are predicted to have opposing effects, with the former improving yield and the latter decreasing it [158, 159]. Such alterations would presumably, by extension, affect starch composition and functionality.

4.3.1 Elevated CO_2

How higher than normal CO_2 affects cereal starch shows little commonality even within species [15]. For example, wheat grown at 700 ppm of CO_2 accumulated higher amylose [84], while in other studies, lower (550 ppm) [160] or higher

(900 ppm) [161] concentrations of CO_2 did not change grain amylose content. These variable results were also seen in considerably large number of studies in rice [162]. In the various published works reviewed by Wang et al. [162], five cultivars showed no change in amylose, four cultivars had elevated amylose, while one cultivar had decreased values at elevated CO_2 [163–170]. This disparity could be explained in part by differences in experimental design, but genotype may still have an outsize effect. Madan et al. [96] exposed three distinct rice cultvars to the same concentration of CO_2 and found that only one of the three cultivars had changes in amylose content [96], supporting the genetic background as a major contributory factor.

The influence of CO_2 on starch granule size has been best studied in wheat, but there was again, no accordance in the results obtained from different studies. At 550 ppm CO_2, a higher proportion of the large A-granules accumulated in Hartog [160], whereas in a separate study at 900 ppm CO_2, there was a *decrease* in the proportion of A-granules in this cultivar [161]. This suggests that CO_2 concentration was the primary determinant of the differential effect in Hartog, though this may be an oversimplification. When Hartog was compared with another cultivar Rosella at 900 ppm CO_2 [161], the latter did not change in granule distribution, again indicating that genotype is playing a major role in the variable results shown in wheat.

Notably, very few studies have been done in other cereals besides rice; however, changes in starch functionality to high CO_2 in this species showed little consistency [162]. There were changes in the proportion of chalky grains, the area of chalkiness in the grain, and the degree of chalkiness in some studies, but not in all [162]. There was also great variation in gelatinization temperatures and viscosity in high CO_2 rice starches, so no exact pattern could be ascribed [162]. Rice starch gel consistency was the only parameter that gave similar results in all studies, and it remained unaffected by elevated CO_2 [96, 162]. These data underscore the difficulty in painting a comprehensive picture of how starch is affected in plants grown under high CO_2.

4.3.2 Elevated O_3

There are very limited accounts of how higher O_3 affects grain starch. Of the three published studies available, there was no change in the amount of starch accumulated in the wheat grain in one study [171], while it decreased in the other studies in wheat and rice [159, 172]. Nevertheless, O_3 reduced grain yield in several studies [158, 159, 173–178], which would imply that starch content and functionality could also be altered.

The most extensive study on how O_3 affects starch functionality was done in rice [179]. Plants were exposed to 5% v/v O_3, which is 25% higher than ambient level, using free-air gas concentration enrichment in two consecutive years [179]. Amylose was only reduced in 1 year, while gel consistency remained unchanged [179]. Chalky grain percentage, gelatinization temperature, and setback values increased in response to O_3 [179], suggesting that elevated O_3 could cause substantive changes to rice cooking and sensory properties through alterations in starch.

5 Challenges in understanding the effect of environments on starch functionality

There have been great discrepancies in the data reported from different studies, and their interpretation should be done with caution because they may be due to extraneous factors, independent of the applied environmental stress [16]. Comparing a wide array of cereal genotypes at divergent developmental stages would be expected to generate significant differences among the data observed. In addition, variations in treatment concentration, period (long-term vs. short-term stress), time of application, as well as treatment stability are crucial for determining grain starch composition and functionality. These factors hence require careful consideration when designing stress experiments on cereal starch quality. Since reproducing similar experimental conditions in individual laboratories, greenhouses, or chambers is likely to be impossible, recording and reporting the environmental variables that the plants were exposed to would be important for data interpretation and comprehensibility. In this section, we wish to emphasize some interactors that could have profound effects on starch functionality, and could come into question when interpreting the environmental stress experimental data.

5.1 Crop genetic variations

Although the growth environment is consequential for starch synthesis, most of the work we have reviewed here showed that genotypic background is a critical contributory factor for starch functionality parameters [103, 123, 150, 180]. Some genotypes may vary in their inherent resistance to abiotic stress. For example, there may be differences in the spectrum of starch biosynthetic enzymes tolerant of poor conditions. Studying how the starch in cultivars with contrasting compositional and structural features (e.g., waxy vs. non-waxy starches) changes when grown under stress may offer novel insight into starch chemistry and biology [103]. Studying how a broad spectrum of cereal genotypes from highly tolerant to highly sensitive types responds to stress may also inform on the mechanisms for maintaining granule stability.

5.2 Grain developmental stages

The effect of extreme environments is generally greatest during grain initiation and early grain filling due to the interference of sensitive cell physiological and biochemical processes required for organ establishment and starch biosynthetic activity [15]. Measurable changes were pronounced at late grain filling, and could be the accumulated effect from the earlier stages [127, 181, 182]. Time-course treatment regimes would help to pinpoint the interaction of the treatment and plant developmental stages [109]. In order to do so, an unambiguous way of universally reporting developmental stages is needed. For rice, a precise growth and developmental staging system was invented to improving communication between researchers, growers, and educators [183].

5.3 Extraneous factors

The circumstances faced by plants during their growth often affects physiological and biochemical processes, and may either maximize or lessen the observed changes in starch composition and functionality due to the treatment effect. This could be problematic when the array of phenotypes, which could be potentially observed, is masked by variation in growing environments.

5.3.1 Light

Both the source and intensity of light can influence starch deposition. In barley, mercury lamps gave lower light intensity compared with sodium lamps, and this led to unexpected differences in starch such as, the abolition of diurnal growth rings in the granule, modulations in amylose, and granule numbers and size [117]. Low light intensity also changed granule size distribution in wheat [184], and decreased viscosity parameters in waxy maize starch [185].

5.3.2 Diurnal temperature

Both elevated day-time temperature alone [98–100] and elevated day- and night-time temperatures [93, 95, 186] at grain filling have been long shown to affect rice starch composition and cooking properties. However, elevated NTAT alone was recently proved to significantly affect rice grain qualities both in the field [182] and in controlled environmental growth conditions [187]. The importance of elevated NTAT on rice grain quality was insightfully emphasized in a recent review [14].

5.3.3 Soil temperature

Guedira et al. showed that high temperature applied to root caused alterations in grain starch quality, distinct from the degree and compositional aspects recorded when high temperature was applied to the shoot [188]. This points to the notion that the soil temperature measurement should be taken into account when designing temperature stress experiments.

5.3.4 Irrigation regime

A water-saving irrigation regime altered several grain quality parameters in comparison to the conventional irrigation in China [131]. The same was found in wheat in studies where there were differences in the periodicity of watering [119, 125]. Therefore, the way plants are irrigated influences grain starch functionality experiment.

5.3.5 Nutrient supplementation

Applying various amounts of nutrients at varying rates and in different combinations may contribute to differences in starch structure and functionality. For example, varying the dose and rate of N and sulfur fertilization in wheat had a pronounced effect on both pasting and thermal properties of starch [149]. High phosphorus fertilization was also found to alter starch functionality in wheat [189].

5.3.6 Wind

The effect of wind on grain starch quality is not widely studied; however, applying a dry-wind treatment at the grain filling stage led to an increase in chalky rings in rice kernel, thus reducing its quality [190].

5.4 Combinatorial stresses

Most studies examining the environmental effects on cereal starch functionality have focused on a single type of stress, while in the field, the plants are likely to be concurrently exposed to several types of stresses, which may pose more confounding effects on grain biosynthetic processes [191]. It is often difficult to predict the effect of combinatorial stress based on the effects seen when each stress is individually applied. Combining drought and high temperature stresses in spring wheat [192], and water and heat stresses after anthesis in winter wheat [133], caused a greater effect on starch yield and quality than that of either stress alone. Wild and cultivated barley grain subjected to drought and salt stresses also caused irregular granule packing characteristics when compared to starch that had undergone either drought or salt stress alone [137]. Nonetheless, in another combinatorial study, wheat starch content and thermal property were strongly affected by elevated temperature, with very little effect when CO_2 concentration was increased in concert [84]. Elevated CO_2 alone had a positive impact on rice cooking quality; however, with N supplementation, no significant changes in starch properties were found [168]. These examples therefore suggest a possible interaction between treatments when two or more stresses are present. This should encourage more investigation of the impact from various stress combinations on starch functionality in all major cultivated cereals in spite of the associated expenses.

5.5 Field studies

Stress studies conducted in controlled-environment greenhouses or chambers may or may not yield the same degree of alterations in kernel starch composition and functionality if conducted in a field experiment. A study of 27 rices cultivars grown in the cold and hot regions in the US yielded the same findings in terms of starch composition and thermal properties when compared to the non-field studies conducted by other researchers [69]. Nevertheless, triticale grain starch was not significantly influenced by locations, rather, cultivars and growing year made a remarkable impact [142]. Extrapolating data from non-field studies to large-scale and long-term cereal cultivation in the fields may not be accurate and more of the field-type stress studies are required to ensure the applicability of the stress research data to commercial settings.

6 Conclusions

Starch structure is directly related to its physico-chemical property, which largely determines its quality in downstream applications. This could be heavily modulated when plants encounter harsh environment during the growing seasons. If the growing environment alters the compositional parameters of starch, the downstream processing of these starches for specific application may need to be adjusted to maintain product quality [16], which could result in lower efficiency and higher cost. While there is a need of comprehensive understanding of how starch functionality is affected by certain environmental extremes, there are discrepancies in the current knowledge due to variations from study to study. This coud be explained by the variations in several experimental factors mentioned above. It is essential to expand the repertoire of genotypes studied to identify those resistant to stress and which could be implemented into breeding program. The combinatorial nature of environmental extremes plants are confronted with in the fields also adds to the need for both multiple stresses treatment and field studies. Acquiring a more comprehensive understanding of how the environment affects starch quality could help both local and international growers, and industrial sectors to come to terms with how "stressed starch" could be utilized and marketed in this era of variable climatic patterns.

Work on cereal starch biosynthesis in DMB's lab is supported by California Hatch Project CA-D-PLS-7198-H. MT acknowledges support from the Royal Thai Government and the Henry A. Jastro Graduate Research Award.*

The authors have declared no conflict of interest.

7 References

[1] Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R., Polasky, S., Agricultural sustainability and intensive production practices. *Nature* 2002, *418*, 671–677.

[2] Uhlmann, N. K., Beckles, D. M., Storage products and transcriptional analysis of the endosperm of cultivated wheat and two wild wheat species. *J. Appl. Genet.* 2010, *51*, 431–447.

[3] Whitt, S. R., Wilson, L. M., Tenaillon, M. I., Gaut, B. S., Buckler, E. S., Genetic diversity and selection in the maize starch pathway. *Proc. Natl. Acad. Sci. USA* 2002, *99*, 12959–12962.

[4] Wilson, L. M., Whitt, S. R., Ibanez, A. M., Rocheford, T. R., et al., Dissection of maize kernel composition and starch production by candidate gene association. *Plant Cell* 2004, *16*, 2719–2733.

[5] Olsen, K. M., Caicedo, A. L., Polato, N., McClung, A., et al., Selection under domestication: Evidence for a sweep in the rice waxy genomic region. *Genetics* 2006, *173*, 975–983.

[6] Tian, Z. X., Qian, Q., Liu, Q. Q., Yan, M. X., et al., Allelic diversities in rice starch biosynthesis lead to a diverse array of rice eating and cooking qualities. *Proc. Natl. Acad. Sci. USA* 2009, *106*, 21760–21765.

[7] FAOSTAT, Production of cereals and their share in the world 2004. *FAO Statistics Yearbook* 2009, 1.

[8] Rahman, S., Bird, A., Regina, A., Li, Z., et al., Resistant starch in cereals: Exploiting genetic engineering and genetic variation. *J. Cereal Sci.* 2007, *46*, 251–260.

[9] Lynch, D. R., Liu, Q., Tarn, T. R., Bizimungu, B., et al., Glycemic index – A review and implications for the potato industry. *Am. J. Potato Res.* 2007, *84*, 179–190.

[10] Liu, Q., *Understanding Starches and Their Role in Foods*, CRC Press, Taylor & Francis Group, Boca Raton, FL 2005.

[11] Simkovic, I., What could be greener than composites made from polysaccharides? *Carbohydr. Polym.* 2008, *74*, 759–762.

[12] Shewmaker, C. K., Stalker, D. M., Modifying starch biosynthesis with transgenes in potatoes. *Plant Physiol.* 1992, *100*, 1083–1086.

[13] Smith, A. M., Prospects for increasing starch and sucrose yields for bioethanol production. *Plant J.* 2008, *54*, 546–558.

[14] Siebenmorgen, T. J., Grigg, B. C., Lanning, S. B., Impacts of preharvest factors during kernel development on rice quality and functionality. *Annu. Rev. Food Sci. Technol.* 2013, *4*, 101–115.

[15] Thitisaksakul, M., Jimenez, R. C., Arias, M. C., Beckles, D. M., Effects of environmental factors on cereal starch biosynthesis and composition. *J. Cereal Sci.* 2012, *56*, 67–80.

[16] Tester, R. F., Karkalas, J., The effects of environmental conditions on the structural features and physico-chemical properties of starches. *Starch/Stärke* 2001, *53*, 513–519.

[17] Battisti, D. S., Naylor, R. L., Historical warnings of future food insecurity with unprecedented seasonal heat. *Science* 2009, *323*, 240–244.

[18] Fitzgerald, M. A., Resurreccion, A. P., Maintaining the yield of edible rice in a warming world. *Funct. Plant Biol.* 2009, *36*, 1037–1045.

[19] Saini, H. S., Westgate, M. E., Reproductive development in grain crops during drought. *Adv. Agron.* 2000, *68*, 59–96.

[20] YinPeng, L., Wei, Y., Meng, W., XiaoDong, Y., Climate change and drought: A risk assessment of crop-yield impacts. *Climate Res.* 2009, *39*, 31–46.

[21] Lobell, D. B., Gourdji, S. M., The influence of climate change on global crop productivity. *Plant Physiol.* 2012, *160*, 1686–1697.

[22] Hatfield, J. L., Boote, K. J., Kimball, B. A., Ziska, L. H., et al., Climate impacts on agriculture: Implications for crop production. *Agron. J.* 2011, *103*, 351–370.

[23] Wang, Y., Frei, M., Stressed food – The impact of abiotic environmental stresses on crop quality. *Agric. Ecosyst. Environ.* 2011, *141*, 271–286.

[24] Smith, A. M., Denyer, K., Martin, C., The synthesis of the starch granule. *Ann. Rev. Plant Physiol. Plant Mol. Biol.* 1997, *48*, 65–87.

[25] Evers, A. D., Blakeney, A. B., O'Brien, L., Cereal structure and composition. *Aust. J. Agric. Res.* 1999, *50*, 629–650.

[26] Myers, A. M., Morell, M. K., James, M. G., Ball, S. G., Recent progress toward understanding biosynthesis of the amylopectin crystal. *Plant Physiol.* 2000, *122*, 989–997.

[27] Tester, R. F., Karkalas, J., Qi, X., Starch – Composition, fine structure and architecture. *J. Cereal Sci.* 2004, *39*, 151–165.

[28] Keeling, P. L., Myers, A., Biochemistry and genetics of starch synthesis. *Annu. Rev. Food Sci. Technol.* 2010, *1*, 271–303.

[29] Jane, J. L., Kasemsuwan, T., Leas, S., Zobel, H., Robyt, J. F., Anthology of starch granule morphology by scanning electron-microscopy. *Starch/Stärke* 1994, *46*, 121–129.

[30] Shapter, F. M., Henry, R. J., Lee, L. S., Endosperm and starch granule morphology in wild cereal relatives. *Plant Genet. Resour.* 2008, *6*, 85–97.

[31] Copeland, L., Blazek, J., Salman, H., Tang, M. C. M., Form and functionality of starch. *Food Hydrocolloid.* 2009, *23*, 1527–1534.

[32] Chaudhary, D., Adhikari, B., Effect of temperature and plasticizer molecular size on moisture diffusion of plasticized-starch biopolymer. *Starch/Stärke* 2010, *62*, 364–372.

[33] Perez, S., Bertoft, E., The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review. *Starch/Stärke* 2010, *62*, 389–420.

[34] Morell, M. K., Li, Z., Regina, A., Rahman, S., et al., *Control of Starch Biosynthesis in Vascular Plants and Algae*, Blackwell Publishing Ltd, Oxford, UK 2006.

[35] Tetlow, I. J., Starch biosynthesis in developing seeds. *Seed Sci. Res.* 2011, *21*, 5–32.

[36] Hizukuri, S., Polymodal distribution of the chain lengths of amylopectin, and its significance. *Carbohydr. Res.* 1986, *147*, 342–347.

[37] Jenkins, J. P. J., Cameron, R. E., Donald, A. M., A universal feature in the structure of starch granules from different botanical sources. *Starch/Stärke* 1993, *45*, 417–420.

[38] Kasemsuwan, T., Jane, J., Location of amylose in normal starch granules. 2. Locations of phosphodiester cross-linking revealed by P-31 nuclear-magnetic-resonance. *Cereal Chem.* 1994, *71*, 282–287.

[39] Tester, R. F., Morrison, W. R., Swelling and gelatinization of cereal starches. 1. Effects of amylopectin, amylose, and lipids. *Cereal Chem.* 1990, *67*, 551–557.

[40] Morrison, W. R., Lipids in cereal starches – A review. *J. Cereal Sci.* 1988, *8*, 1–15.

[41] Hermansson, A. M., Svegmark, K., Developments in the understanding of starch functionality. *Trends Food Sci. Technol.* 1996, *7*, 345–353.

[42] Parker, R., Ring, S. G., Aspects of the physical chemistry of starch. *J. Cereal Sci.* 2001, *34*, 1–17.

[43] Bowler, P., Williams, M. R., Angold, R. E., A hypothesis for the morphological changes which occur on heating lenticular wheat starch in water. *Starch/Stärke* 1980, *32*, 186–189.

[44] Jenkins, P. J., Donald, A. M., Breakdown of crystal structure in potato starch during gelatinization. *J. Appl. Polym. Sci.* 1997, *66*, 225–232.

[45] Chiotelli, E., Le Meste, M., Effect of small and large wheat starch granules on thermomechanical behavior of starch. *Cereal Chem.* 2002, *79*, 286–293.

[46] Vasanthan, T., Bhatty, R. S., Physicochemical properties of small- and large-granule starches of waxy, regular, and high-amylose barleys. *Cereal Chem.* 1996, *73*, 199–207.

[47] Tang, H., Watanabe, K., Mitsunaga, T., Structure and functionality of large, medium and small granule starches in normal and waxy barley endosperms. *Carbohydr. Polym.* 2002, *49*, 217–224.

[48] Jobling, S., Improving starch for food and industrial applications. *Curr. Opin. Plant Biol.* 2004, *7*, 210–218.

[49] Singh, N., Singh, J., Kaur, L., Singh Sodhi, N., Singh Gill, B., Morphological, thermal and rheological properties of starches from different botanical sources. *Food Chem.* 2003, *81*, 219–231.

[50] Jane, J., Chen, Y. Y., Lee, L. F., McPherson, A. E., et al., Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch1. *Cereal Chem. J.* 1999, *76*, 629–637.

[51] Noda, T., Takigawa, S., Matsuura-Endo, C., Kim, S. J., et al., Physicochemical properties and amylopectin structures of large, small, and extremely small potato starch granules. *Carbohydr. Polym.* 2005, *60*, 245–251.

[52] Donald, A. M., Plasticization and self assembly in the starch granule. *Cereal Chem.* 2001, *78*, 307–314.

[53] Donald, A. M., Kato, K. L., Perry, P. A., Weigh, T. A., Scattering studies of the internal structure of starch granules. *Starch/Stärke* 2001, *53*, 504–512.

[54] Zeleznak, K. J., Hoseney, R. C., The glass-transition in starch. *Cereal Chem.* 1987, *64*, 121–124.

[55] Biliaderis, C. G., Page, C. M., Maurice, T. J., Juliano, B. O., Thermal characterization of rice starches – A polymeric approach to phase-transitions of antigranulocytes starch. *J. Agric. Food Chem.* 1986, *34*, 6–14.

[56] Barichello, V., Yada, R. Y., Coffin, R. H., Stanley, D. W., Low-temperature sweetening in susceptible and resistant potatoes – Starch structure and composition. *J. Food Sci.* 1990, *55*, 1054–1059.

[57] Sasaki, T., Yasui, T., Matsuki, J. Effect of amylose content on gelatinization, retrogradation, and pasting properties of starches from waxy and nonwaxy wheat and their F1 seeds. *Cereal Chem.* 2000, *77*, 58–63.

[58] Li, J. Y., Yeh, A. I., Relationships between thermal, rheological characteristics and swelling power for various starches. *J. Food Eng.* 2001, *50*, 141–148.

[59] Hoover, R., Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydr. Polym.* 2001, *45*, 253–267.

[60] Tang, M. C., Copeland, L., Investigation of starch retrogradation using atomic force microscopy. *Carbohydr. Polym.* 2007, *70*, 1–7.

[61] Dang, J. M. C., Copeland, L., Genotype and environmental influences on pasting properties of rice flour. *Cereal Chem.* 2004, *81*, 486–489.

[62] Sun, M. M., Abdula, S. E., Lee, H. J., Cho, Y. C., et al., Molecular aspect of good eating quality formation in Japonica rice. *PLos One* 2011, *6*, e18385.

[63] Hazard, B., Zhang, X. Q., Colasuonno, P., Uauy, C., et al., Induced mutations in the starch branching enzyme II (SBEII) genes increase amylose and resistant starch content in durum wheat. *Crop Sci.* 2012, *52*, 1754–1766.

[64] Moritz, J. S., Parsons, A. S., Buchanan, N. P., Calvalcanti, W. B., et al., Effect of gelatinizing dietary starch through feed processing on zero- to three-week broiler performance and metabolism. *J. Appl. Poult. Res.* 2005, *14*, 47–54.

[65] Svihus, B., Uhlen, A. K., Harstad, O. M., Effect of starch granule structure, associated components and processing on nutritive value of cereal starch: A review. *Anim. Feed Sci. Technol.* 2005, *122*, 303–320.

[66] Wu, X. R., Maier, A., Wu, T. T., Li, N. B., et al., Evaluation of Nebraska waxy sorghum hybrids for ethanol production. *Cereal Chem.* 2013, *90*, 198–203.

[67] Lu, D. R., Xiao, C. M., Xu, S. J., Starch-based completely biodegradable polymer materials. *Express Polym. Lett.* 2009, *3*, 366–375.

[68] Rosicka-Kaczmarek, J., Kwasniewska-Karolak, I., Nebesny, E., Miskiewicz, K., Influence of variety and year of wheat cultivation on the chemical composition of starch and properties of glucose hydrolysates. *J. Cereal Sci.* 2013, *57*, 98–106.

[69] Aboubacar, A., Moldenhauer, K. A. K., McClung, A. M., Beighley, D. H., Hamaker, B. R., Effect of growth location in the United States on amylose content, amylopectin fine structure, and thermal properties of starches of long grain rice cultivars. *Cereal Chem.* 2006, *83*, 93–98.

[70] Beta, T., Corke, H., Genetic and environmental variation in sorghum starch properties. *J. Cereal Sci.* 2001, *34*, 261–268.

[71] Cameron, D. K., Wang, Y. J., Moldenhauer, K. A., Comparison of physical and chemical properties of medium-grain rice cultivars grown in California and Arkansas. *J. Food Sci.* 2008, *73*, C72–C78.

[72] Campbell, L. D., Boila, R. J., Stothers, S. C., Variation in the chemical-composition and test weight of barley and wheat-grain grown at selected locations throughout Manitoba. *Can. J. Anim. Sci.* 1995, *75*, 239–246.

[73] Tetlow, I. J., Morell, M. K., Emes, M. J., Recent developments in understanding the regulation of starch metabolism in higher plants. *J. Exp. Bot.* 2004, *55*, 2131–2145.

[74] Tetlow, I. J., Wait, R., Lu, Z. X., Akkasaeng, R., et al., Protein phosphorylation in amyloplasts regulates starch branching enzyme activity and protein-protein interactions. *Plant Cell* 2004, *16*, 694–708.

[75] Cohen, J. L., Furtado, J. C., Barlow, M. A., Alexeev, V. A., Cherry, J. E., Arctic warming, increasing snow cover and widespread boreal winter cooling. *Environ. Res. Lett.* 2012, *7*, 014007.

[76] Tester, R. F., Influence of growth conditions on barley starch properties. *Int. J. Biol. Macromol.* 1997, *21*, 37–45.

[77] Jiang, H. W., Dian, W. M., Wu, P., Effect of high temperature on fine structure of amylopectin in rice endosperm by reducing the activity of the starch branching enzyme. *Phytochemistry* 2003, *63*, 53–59.

[78] Peng, S. B., Huang, J. L., Sheehy, J. E., Laza, R. C., et al., Rice yields decline with higher night temperature from global warming. *Proc. Natl. Acad. Sci. USA* 2004, *101*, 9971–9975.

[79] Lu, T. J., Jane, J. L., Keeling, P. L., Singletary, G. W., Maize starch fine structures affected by ear developmental temperature. *Carbohydr. Res.* 1996, *282*, 157–170.

[80] Hurkman, W. J., McCue, K. F., Altenbach, S. B., Korn, A., et al., Effect of temperature on expression of genes encoding enzymes for starch biosynthesis in developing wheat endosperm. *Plant Sci.* 2003, *164*, 873–881.

[81] Liu, P., Guo, W., Jiang, Z., Pu, H., et al., Effects of high temperature after anthesis on starch granules in grains of wheat (*Triticum aestivum* L.). *J. Agric. Sci.* 2011, *149*, 159–169.

[82] Matsuki, J., Yasui, T., Kohyama, K., Sasaki, T., Effects of environmental temperature on structure and gelatinization properties of wheat starch. *Cereal Chem.* 2003, *80*, 476–480.

[83] Shi, Y. C., Seib, P. A., Bernardin, J. E., Effects of temperature during grain-filling on starches from 6 wheat cultivars. *Cereal Chem.* 1994, *71*, 369–383.

[84] Tester, R. F., Morrison, W. R., Ellis, R. H., Piggott, J. R., et al., Effects of elevated growth temperature and carbon-dioxide levels on some physicochemical properties of wheat-starch. *J Cereal Sci.* 1995, *22*, 63–71.

[85] Stone, P. J., Nicolas, M. E., A survey of the effects of high-temperature during grain filling on yield and quality of 75 wheat cultivars. *Aust. J. Agric. Res.* 1995, *46*, 475–492.

[86] Panozzo, J. F., Eagles, H. A., Cultivar and environmental effects on quality characters in wheat. I. Starch. *Aust. J. Agric. Res.* 1998, *49*, 757–766.

[87] Asaoka, M., Okuno, K., Sugimoto, Y., Fuwa, H., Developmental-changes in the structure of endosperm starch of rice (*Oryza-sativa*-L). *Agric. Biol. Chem.* 1985, *49*, 1973–1978.

[88] He, G. C., Kogure, K., Suzuki, H., Development of endosperm and synthesis of starch in rice grain.3. Starch property as affected by the temperature during grain development. *Jpn. J. Crop Sci.* 1990, *59*, 340–345.

[89] Lanning, S. B., Siebenmorgen, T. J., Ambardekar, A. A., Counce, P. A., Bryant, R. J., Effects of nighttime air temperature during kernel development of field-grown rice on physicochemical and functional properties. *Cereal Chem.* 2012, *89*, 168–175.

[90] Liu, Q. H., Wu, X., Ma, J. Q., Li, T., et al., Effects of high air temperature on rice grain quality and yield under field condition. *Agron. J.* 2013, *105*, 446–454.

[91] Suzuki, Y., Sano, Y., Ishikawa, T., Sasaki, T., et al., Differences in starch characteristics of rice strains having different sensitivities to maturation temperatures. *J. Agron. Crop Sci.* 2004, *190*, 218–221.

[92] Yamakawa, H., Hirose, T., Kuroda, M., Yamaguchi, T., Comprehensive expression profiling of rice grain filling-related genes under high temperature using DNA microarray. *Plant Physiol.* 2007, *144*, 258–277.

[93] Lisle, A. J., Martin, M., Fitzgerald, M. A., Chalky and translucent rice grains differ in starch composition and structure and cooking properties. *Cereal Chem.* 2000, *77*, 627–632.

[94] Inukai, T., Hirayama, Y., Comparison of starch levels reduced by high temperature during ripening in Japonica rice lines near-isogenic for the Wx locus. *J. Agron. Crop Sci.* 2010, *196*, 296–301.

[95] Lin, C. J., Li, C. Y., Lin, S. K., Yang, F. H., et al., Influence of high temperature during grain filling on the accumulation of storage proteins and grain quality in rice (*Oryza sativa* L.). *J. Agric. Food Chem.* 2010, *58*, 10545–10552.

[96] Madan, P., Jagadish, S. V. K., Craufurd, P. Q., Fitzgerald, M., et al., Effect of elevated CO2 and high temperature on seed-set and grain quality of rice. *J. Exp. Bot.* 2012, *63*, 3843–3852.

[97] Paule, C. M., Variability in amylose content of rice. *MS thesis*, University of the Philippines, Los Baños, Philippines 1977.

[98] Resurreccion, A. P., Hara, T., Juliano, B. O., Yoshida, S., Effect of temperature during ripening on grain quality of rice. *Soil Sci. Plant Nutr.* 1977, *23*, 109–112.

[99] Zhong, L. J., Cheng, F. M., Wen, X., Sun, Z. X., Zhang, G. P., The deterioration of eating and cooking quality caused by high temperature during grain filling in early-season indica rice cultivars. *J. Agron. Crop Sci.* 2005, *191*, 218–225.

[100] Cheng, F. M., Zhong, L. J., Zhao, N. C., Liu, Y., Zhang, G. P., Temperature induced changes in the starch components and biosynthetic enzymes of two rice varieties. *Plant Growth Regul.* 2005, *46*, 87–95.

[101] Umemoto, T., Terashima, K., Activity of granule-bound starch synthase is an important determinant of amylose content in rice endosperm. *Funct. Plant Biol.* 2002, *29*, 1121–1124.

[102] Zeng, M., Morris, C. F., Batey, I. L., Wrigley, C. W., Sources of variation for starch gelatinization, pasting, and gelation properties in wheat. *Cereal Chem.* 1997, *74*, 63–71.

[103] Kiseleva, V. I., Tester, R. F., Wasserman, L. A., Krivandin, A. V., et al., Influence of growth temperature on the structure and thermodynamic parameters of barley starches. *Carbohydr. Polym.* 2003, *51*, 407–415.

[104] Li, E. P., Hasjim, J., Singh, V., Tizzotti, M., et al., Insights into sorghum starch biosynthesis from structure changes induced by different growth temperatures. *Cereal Chem.* 2013, *90*, 223–230.

[105] Bhullar, S. S., Jenner, C. F., Differential responses to high temperatures of starch and nitrogen accumulation in the grain of four cultivars of wheat. *Aust. J. Plant Physiol.* 1985, *12*, 363–375.

[106] Blumenthal, C., Bekes, F., Gras, P. W., Barlow, E. W. R., Wrigley, C. W., Identification of wheat genotypes tolerant to the effects of heat stress on grain quality. *Cereal Chem.* 1995, *72*, 539–544.

[107] Wallwork, M. A. B., Jenner, C. F., Logue, S. J., Sedgley, M., Effect of high temperature during grain-filling on the structure of developing and malted barley grains. *Ann. Bot.* 1998, *82*, 587–599.

[108] Mitsui, T., Shiraya, T., Kaneko, K., Wada, K., Proteomics of rice grain under high temperature stress. *Front. Plant Sci.* 2013, *4*, 36.

[109] Lu, D. L., Sun, X., Yan, F., Wang, X., et al., Effects of high temperature during grain filling under control conditions on the physicochemical properties of waxy maize flour. *Carbohydr. Polym.* 2013, *98*, 302–310.

[110] Cheng, F. M., Zhong, L. J., Wang, F., Zhang, G. P., Differences in cooking and eating properties between chalky and translucent parts in rice grains. *Food Chem.* 2005, *90*, 39–46.

[111] Yamakawa, H., Omics-based approach for cereal starch biosynthesis: Towards a determination of key factors for quality of rice grain affected by high temperature. *J. Appl. Glycosci.* 2011, *58*, 35–38.

[112] Tashiro, T., Wardlaw, I. F., The effect of high-temperature on kernel dimensions and the type and occurrence of kernel damage in rice. *Aust. J. Agric. Res.* 1991, *42*, 485–496.

[113] Lin, J. H., Pan, C. L., Singh, H., Chang, Y. H., Influence of molecular structural characteristics on pasting and thermal properties of acid-methanol-treated rice starches. *Food Hydrocolloid* 2012, *26*, 441–447.

[114] Asaoka, M., Okuno, K., Sugimoto, Y., Kawakami, J., Fuwa, H., Effect of environmental temperature during development of rice plants on some properties of endosperm starch. *Starch/Stärke* 1984, *36*, 189–193.

[115] Lu, D. L., Lu, W. P., Effects of heat stress during grain filling on the functional properties of flour from fresh waxy maize. *Cereal Chem.* 2013, *90*, 65–69.

[116] Lenihan, E., Pollak, L., White, P., Thermal properties of starch from exotic-by-adapted corn (*Zea mays* L.) lines grown in four environments. *Cereal Chem.* 2005, *82*, 683–689.

[117] Tester, R. F., South, J. B., Morrison, W. R., Ellis, R. P., The effects of ambient temperature during the grain-filling period on the composition and properties of starch from four barley genotypes. *J. Cereal Sci.* 1991, *13*, 113–127.

[118] Labuschagne, M. T., Elago, O., Koen, E., The influence of temperature extremes on some quality and starch characteristics in bread, biscuit and durum wheat. *J. Cereal Sci.* 2009, *49*, 184–189.

[119] Singh, S., Gupta, A. K., Gupta, S. K., Kaur, N., Effect of sowing time on protein quality and starch pasting characteristics in wheat (*Triticum aestivum* L.) genotypes grown under irrigated and rain-fed conditions. *Food Chem.* 2010, *122*, 559–565.

[120] Fergason, V. L., Zuber, M. S., Influence of environment on amylose content of maize endosperm. *Crop Sci.* 1962, 209–211.

[121] Myllarinen, P., Schulman, A. H., Salovaara, H., Poutanen, K., The effect of growth temperature on gelatinization properties of barley starch. *Acta Agric. Scand. Sect. B-Soil and Plant Sci.* 1998, *48*, 85–90.

[122] Anker-Nilssen, K., Færgestad, E. M., Sahlstrøm, S., Uhlen, A. K., Interaction between barley cultivars and growth temperature on starch degradation properties measured in vitro. *Anim. Feed Sci. Technol.* 2006, *130*, 3–22.

[123] Brennan, C. S., Samaan, J., El-Khayat, G. H., The effect of genotype and environmental conditions on grain physiochemical properties of Syrian durum wheat cultivars. *Int. J. Food Sci. Technol.* 2012, *47*, 2627–2635.

[124] Mittler, R., Blumwald, E., Genetic engineering for modern agriculture: Challenges and perspectives. *Annu. Rev. Plant Biol.* 2010, *61*, 443–462.

[125] Dai, Z., Yin, Y., Wang, Z., Starch granule size distribution from seven wheat cultivars under different water regimes. *Cereal Chem.* 2009, *86*, 82–87.

[126] Fabian, A., Jager, K., Rakszegi, M., Barnabas, B., Embryo and endosperm development in wheat (Triticum aestivum L.) kernels subjected to drought stress. *Plant Cell Rep.* 2011, *30*, 551–563.

[127] Singh, S., Singh, G., Singh, P., Singh, N., Effect of water stress at different stages of grain development on the characteristics of starch and protein of different wheat varieties. *Food Chem.* 2008, *108*, 130–139.

[128] Gunaratne, A., Ratnayaka, U. K., Sirisena, N., Ratnayaka, J., et al., Effect of soil moisture stress from flowering to grain maturity on functional properties of Sri Lankan rice flour. *Starch/Stärke* 2011, *63*, 283–290.

[129] Gunaratne, A., Ratnayaka, U. K., Sirisena, N., Ratnayaka, J., et al., Erratum: Effect of soil moisture stress from flowering to grain maturity on functional properties of Sri Lankan rice flour. *Starch/Stärke* 2011, *63*, 392.

[130] Liu, D. H., Zhang, J. L., Cao, J. H., Wang, Z. H., et al., The reduction of amylose content in rice grain and decrease of Wx gene expression during endosperm development in response to drought stress. *J. Food Agric. Environ.* 2010, *8*, 873–878.

[131] Cheng, W., Zhang, G., Zhao, G., Yao, H., Xu, H., Variation in rice quality of different cultivars and grain positions as affected by water management. *Field Crops Res.* 2003, *80*, 245–252.

[132] Brooks, A., Jenner, C. F., Aspinall, D., Effects of water deficit on endosperm starch granules and on grain physiology of wheat and barley. *Aust. J. Plant Physiol.* 1982, *9*, 423–436.

[133] Balla, K., Rakszegi, M., Li, Z. G., Bekes, F., et al., Quality of winter wheat in relation to heat and drought shock after anthesis. *Czech J. Food Sci.* 2011, *29*, 117–128.

[134] Nicolas, M. E., Gleadow, R. M., Dalling, M. J., Effect of post-anthesis drought on cell-division and starch accumulation in developing wheat grains. *Ann. Bot.* 1985, *55*, 433–444.

[135] Zhang, T., Wang, Z., Yin, Y., Cai, R., et al., Starch content and granule size distribution in grains of wheat in relation to post-anthesis water deficits. *J. Agron. Crop Sci.* 2010, *196*, 1–8.

[136] Savin, R., Nicolas, M. E., Effects of short periods of drought and high temperature on grain growth and starch accumulation of two malting barley cultivars. *Aust. J. Plant Physiol.* 1996, *23*, 201–210.

[137] Ahmed, I. M., Cao, F., Han, Y., Nadira, U. A., et al., Differential changes in grain ultrastructure, amylase, protein and amino acid profiles between Tibetan wild and cultivated barleys under drought and salinity alone and combined stress. *Food Chem.* 2013, *141*, 2743–2750.

[138] Peiris, B. D., Siegel, S. M., Senadhira, D., Chemical Characteristics of grains of rice (*Oryza-Sativa*-L) cultivated in saline media of varying ionic composition. *J. Exp. Bot.* 1988, *39*, 623–631.

[139] Siscar-Lee, J. J. H., Juliano, B. O., Qureshi, R. H., Akbar, M., Effect of saline soil on grain quality of rices differing in salinity tolerance. *Plant Foods Hum. Nutr.* 1990, *40*, 31–36.

[140] He, J.-F., Goyal, R., Laroche, A., Zhao, M.-L., Lu, Z.-X., Effects of salinity stress on starch morphology, composition and thermal properties during grain development in triticale. *Can. J. Plant Sci.* 2013, *93*, 765–771.

[141] Beckles, D. M., Tananuwong, K., Shoemaker, C. F., Starch characteristics of transgenic wheat (*Triticum aestivum* L.) overexpressing the Dx5 high molecular weight glutenin subunit are substantially equivalent to those in nonmodified wheat. *J. Food Sci.* 2012, *77*, C437–C442.

[142] Buresova, I., Sedlackova, I., Famera, O., Lipavsky, J., Effect of growing conditions on starch and protein content in triticale grain and amylose content in starch. *Plant Soil Environ.* 2010, *56*, 99–104.

[143] Champagne, E. T., Bett-Garber, K. L., Thomson, J. L., Fitzgerald, M. A., Unraveling the impact of nitrogen nutrition on cooked rice flavor and texture. *Cereal Chem.* 2009, *86*, 274–280.

[144] Dong, M. H., Sang, D. Z., Wang, P., Wang, X. M., Yang, J. C., Changes in cooking and nutrition qualities of grains at different positions in a rice panicle under different nitrogen levels. *Rice Sci.* 2007, *14*, 141–148.

[145] Gunaratne, A., Sirisena, N., Ratnayaka, U. K., Ratnayaka, J., et al., Effect of fertiliser on functional properties of flour from four rice varieties grown in Sri Lanka. *J. Sci. Food Agric.* 2011, *91*, 1271–1276.

[146] Singh, N., Pal, N., Mahajan, G., Singh, S., Shevkani, K., Rice grain and starch properties: Effects of nitrogen fertilizer application. *Carbohydr. Polym.* 2011, *86*, 219–225.

[147] Wang, Q., Huang, J. L., He, F., Cui, K. H., et al., Head rice yield of "super" hybrid rice Liangyoupeijiu grown under different nitrogen rates. *Field Crops Res.* 2012, *134*, 71–79.

[148] Wang, X., He, M., Li, F., Liu, Y., et al., Coupling effects of irrigation and nitrogen fertilization on grain protein and starch quality of strong-gluten winter wheat. *Front. Agric. China* 2008, *2*, 274–280.

[149] Li, W. H., Shan, Y. L., Xiao, X. L., Zheng, J. M., et al., Effect of nitrogen and sulfur fertilization on accumulation characteristics and physicochemical properties of A- and B-wheat starch. *J. Agric. Food Chem.* 2013, *61*, 2418–2425.

[150] Nowotnaa, A., Gambus, H., Kratsch, G., Krawontka, J., et al., Effect of nitrogen fertilization on the physico-chemical properties of starch isolated from german triticale varieties. *Starch/Stärke* 2007, *59*, 397–399.

[151] Ahmad, M., Chughtai, M. I. D., Relationship between various physicochemical characters in rice kernels. *Pakistan J. Sci. Res.* 1982, *34*, 157–163.

[152] Tamaki, M., Ebata, M., Tashiro, T., Ishikawa, M., Physicoecological studies on quality formation of rice kernel. I. Effects of nitrogen top-dressed at full heading time and air temperature during ripening period on quality of rice kernel. *Jpn. J. Crop Sci.* 1989, *58*, 653–658.

[153] Fredriksson, H., Salomonsson, L., Andersson, R., Salomonsson, A.-C., Effects of protein and starch characteristics on the baking properties of wheat cultivated by different strategies with organic fertilizers and urea. *Acta Agric. Scand., Sect. B Soil Plant Sci.* 1998, *48*, 49–57.

[154] Qiao, J. F., Liu, Z. H., Deng, S. Y., Ning, H. F., et al., Occurrence of perfect and imperfect grains of six japonica rice cultivars as affected by nitrogen fertilization. *Plant Soil* 2011, *349*, 191–202.

[155] Wang, Z. H., Li, S. X., Malhi, S., Effects of fertilization and other agronomic measures on nutritional quality of crops. *J. Sci. Food Agric.* 2008, *88*, 7–23.

[156] Ainsworth, E. A., Yendrek, C. R., Sitch, S., Collins, W. J., Emberson, L. D., The effects of tropospheric ozone on net primary productivity and implications for climate change. *Annu. Rev. Plant Biol.* 2012, *63*, 637–661.

[157] Wang, Y. X., Frei, M., Stressed food – The impact of abiotic environmental stresses on crop quality. *Agric. Ecosyst. Environ.* 2011, *141*, 271–286.

[158] Mishra, A. K., Rai, R., Agrawal, S. B., Differential response of dwarf and tall tropical wheat cultivars to elevated ozone with and without carbon dioxide enrichment: Growth, yield and grain quality. *Field Crops Res.* 2013, *145*, 21–32.

[159] Piikki, K., De Temmerman, L., Ojanpera, K., Danielsson, H., Pleijel, H., The grain quality of spring wheat (Triticum aestivum L.) in relation to elevated ozone uptake and carbon dioxide exposure. *Eur. J. Agron.* 2008, *28*, 245–254.

[160] Blumenthal, C., Rawson, H. M., McKenzie, E., Gras, P. W., et al., Changes in wheat grain quality due to doubling the level of atmospheric CO2. *Cereal Chem.* 1996, *73*, 762–766.

[161] Rogers, G. S., Gras, P. W., Batey, I. L., Milham, P. J., et al., The influence of atmospheric CO2 concentration on the protein, starch and mixing properties of wheat flour. *Aust. J. Plant Physiol.* 1998, *25*, 387–393.

[162] Wang, Y., Frei, M., Song, Q., Yang, L., The impact of atmospheric CO2 concentration enrichment on rice quality – A research review. *Acta Ecol. Sin.* 2011, *31*, 277–282.

[163] Conroy, J. P., Seneweera, S., Basra, A. S., Rogers, G., Nissenwooller, B., Influence of rising atmospheric CO2 concentrations and temperature on growth, yield and grain quality of cereal crops. *Aust. J. Plant Physiol.* 1994, *21*, 741–758.

[164] Dong, G. C., Wang, Y. L., Yang, H. J., Huang, J. Y., et al., Effect of free-air CO2 enrichment (FACE) on nitrogen accumulation and utilization efficiency in rice (*Oryza sativa*). *Chin. J. Appl. Ecol.* 2002, *13*, 1219–1222.

[165] Seneweera, S., Blakeney, A., Milham, P., Basra, A. S., et al., Influence of rising atmospheric CO2 and phosphorus nutrition on the grain yield and quality of rice (Oryza sativa cv Jarrah). *Cereal Chem.* 1996, *73*, 239–243.

[166] Terao, T., Miura, S., Yanagihara, T., Hirose, T., et al., Influence of free-air CO2 enrichment (FACE) on the eating quality of rice. *J. Sci. Food Agric.* 2005, *85*, 1861–1868.

[167] Xu, C. L., Li, J. Y., Xie, H., Zhu, J. G., et al., Effect of free air CO2 enrichment to rice quality of rice. *Chin. Agric. Sci. Bull.* 2008, *24*, 391–397.

[168] Yang, L. X., Wang, Y. L., Dong, G. C., Gu, H., et al., The impact of free-air CO2 enrichment (FACE) and nitrogen supply on grain quality of rice. *Field Crops Res.* 2007, *102*, 128–140.

[169] Zhang, X., Liu, Y. Z., Kong, Q. N., Huang, N. R., et al., Growth, grain yield and kernel quality of high-yield rice variety Te-San-Ai 2 growing in a simulated CO2-enriched habitat. *Chin. J. Appl. Environ. Biol.* 1998, *4*, 238–242.

[170] Ziska, L. H., Namuco, O., Moya, T., Quilang, J., Growth and yield response of field-grown tropical rice to increasing carbon dioxide and air temperature. *Agron. J.* 1997, *89*, 45–53.

[171] Scotti, I. A., Silva, S., Botteschi, G., Effects of ozone on grain quality of wheat grown in open-top chambers – 3 years of experimentation. *Environ. Pollut.* 1994, *86*, 31–35.

[172] Frei, M., Kohno, Y., Tietze, S., Jekle, M., et al., The response of rice grain quality to ozone exposure during growth depends on ozone level and genotype. *Environm. Pollut.* 2012, *163*, 199–206.

[173] Fuhrer, J., Grimm, A. G., Tschannen, W., Shariatmadari, H., The response of spring wheat (*Triticum-Aestivum* L) to ozone at higher elevations. 2. Changes in yield, yield components and grain quality in response to ozone flux. *New Phytol.* 1992, *121*, 211–219.

[174] Gonzalez-Fernandez, I., Kaminska, A., Dodmani, M., Goumenaki, E., et al., Establishing ozone flux-response relationships for winter wheat: Analysis of uncertainties based on data for UK and Polish genotypes. *Atmos. Environ.* 2010, *44*, 621–630.

[175] Wahid, A., Influence of atmospheric pollutants on agriculture in developing countries: A case study with three new wheat varieties in Pakistan. *Sci. Total Environ.* 2006, *371*, 304–313.

[176] Zhu, X. K., Feng, Z. Z., Sun, T. F., Liu, X. C., et al., Effects of elevated ozone concentration on yield of four Chinese cultivars of winter wheat under fully open-air field conditions. *Glob Change Biol.* 2011, *17*, 2697–2706.

[177] Wang, X. K., Zhang, Q. Q., Zheng, F. X., Zheng, Q. W., et al., Effects of elevated O-3 concentration on winter wheat and rice yields in the Yangtze River Delta, China. *Environ. Pollut.* 2012, *171*, 118–125.

[178] Ainsworth, E. A., Rice production in a changing climate: A meta-analysis of responses to elevated carbon dioxide and elevated ozone concentration. *Glob. Change Biol.* 2008, *14*, 1642–1650.

[179] Wang, Y. X., Yang, L. X., Han, Y., Zhu, J. G., et al., The impact of elevated tropospheric ozone on grain quality of hybrid rice: A free-air gas concentration enrichment (FACE) experiment. *Field Crops Res.* 2012, *129*, 81–89.

[180] Bao, J. S., Kong, X. L., Xie, J. K., Xu, L. J., Analysis of genotypic and environmental effects on rice starch. 1. Apparent amylose content, pasting viscosity, and gel texture. *J. Agric. Food Chem.* 2004, *52*, 6010–6016.

[181] Ambardekar, A. A., Siebenmorgen, T. J., Counce, P. A., Lanning, S. B., Mauromoustakos, A., Impact of field-scale nighttime air temperatures during kernel development on rice milling quality. *Field Crops Res.* 2011, *122*, 179–185.

[182] Cooper, N. T. W., Siebenmorgen, T. J., Counce, P. A., Meullenet, J. F., Explaining rice milling quality variation using historical weather data analysis. *Cereal Chem.* 2006, *83*, 447–450.

[183] Counce, P. A., Keisling, T. C., Mitchell, A. J., A uniform, objective, and adaptive system for expressing rice development. *Crop Sci.* 2000, *40*, 436–443.

[184] Li, W., Yan, S., Yin, Y., Wang, Z., Starch granule size distribution in wheat grain in relation to shading after anthesis. *J. Agric. Sci.* 2010, *148*, 183–189.

[185] Lu, D., Sun, X., Wang, X., Yan, F., Lu, W., Effect of Shading During Grain Filling on the Physicochemical Properties of Fresh Waxy Maize. *J. Integrative Agriculture* 2013, *12*, 1560–1567.

[186] Tanaka, K., Onishi, R., Miyazaki, M., Ishibashi, Y., et al., Changes in NMR relaxation of rice grains, kernel quality and physicochemical properties in response to a high temperature after flowering in heat-tolerant and heat-sensitive rice cultivars. *Plant Prod. Sci.* 2009, *12*, 185–192.

[187] Cooper, N. T. W., Siebenmorgen, T. J., Counce, P. A., Effects of nighttime temperature during kernel development on rice physicochemical properties. *Cereal Chem.* 2008, *85*, 276–282.

[188] Guedira, M., McCluskey, P. J., MacRitchie, F., Paulsen, G. M., Composition and quality of wheat grown under different shoot and root temperatures during maturation. *Cereal Chem.* 2002, *79*, 397–403.

[189] Ni, Y., Wang, Z., Yin, Y., Li, W., et al., Starch granule size distribution in wheat grain in relation to phosphorus fertilization. *J. Agr. Sci.* 2012, *150*, 45–52.

[190] Wada, H., Nonami, H., Yabuoshi, Y., Maruyama, A., et al., Increased ring-shaped chalkiness and osmotic adjustment when growing rice grains under foehn-induced dry wind condition. *Crop Sci.* 2011, *51*, 1703–1715.

[191] Mittler, R., Abiotic stress, the field environment and stress combination. *Trends Plant Sci.* 2006, *11*, 15–19.

[192] Altenbach, S. B., DuPont, F. M., Kothari, K. M., Chan, R., et al., Temperature, water and fertilizer influence the timing of key events during grain development in a US spring wheat. *J. Cereal Sci.* 2003, *37*, 9–20.