

Review

Starch Retrogradation: Role of Food Ingredients and Extrinsic Factors

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Received: 28 April 2023; **Revised:** 10 July 2023; **Accepted:** 24 July 2023

Abstract: Starch retrogradation is one of the significant properties of starch wherein the reassociation or recrystallization of the polysaccharides in gelatinized starch (amylose and amylopectin) occurs. Though, the process is desirable in terms of nutritional and textural properties for some starchy foods, it tends to exhibit many undesirable effects on storage and sensory qualities of starchy foods. Extensive studies have been done worldwide to understand the in-depth mechanism of retrogradation and its effect on foods. Various factors are involved in hindering/accelerating the retrogradation process thereby influencing the food product properties. This review provides a thorough insight into food constituents as well as extrinsic factors which influence the starch retrogradation in food systems. It also explains the role of amylose and amylopectin in retrogradation independently, providing a better understanding to the reader on retrogradation phenomena.

Keywords: starch retrogradation, amylose, amylopectin, food ingredients, recrystallization

1. Introduction

Cellulose, chitin and starch are the three major polysaccharides broadly distributed in nature. Starch is used as a food ingredient in a broad range of food products such as pasta, tortillas, bakery products, and snacks, where it provides digestibility characteristics, functional and physiochemical properties to them. Though they are packed densely and are water-insoluble, the plant's metabolic enzymes can still reach and act upon them. The starch granules have specific forms, surfaces (smooth or rough), and sizes depending on their botanical sources which play a vital role in functionality and digestibility [1].

The functional qualities of starch in food processing, digestion, and industrial applications are largely determined by the changes it experiences in gelatinization and retrogradation. These characteristics decide the end product's quality, nutritional value, acceptability, and shelf life [2]. Due to its significant mechanism in bread-staling and in other starchy foods, starch retrogradation is often thought to have negative consequences as it results in a reduction of storage stability and consumer acceptance. However, due to changes in structural, mechanical, and sensory qualities, starch retrogradation is acceptable in certain food preparations, such as the creation of parboiled rice, dried mashed potatoes and in some breakfast cereals. Because of the delayed enzymatic breakdown of retrograded starch and the controlled release of glucose in the bloodstream, starch retrogradation is beneficial nutritionally. Due to the disaggregation of amylose and amylopectin chains of gelatinized starch, in retrogradation; the mechanism causes an increase in turbidity

and viscosity of pastes, water exudation and gel formation [3].

There are two phases in the starch retrogradation pathway (Figure 1). Nucleation is the initial process, during which with the decrease in temperature below glass transition temperature (T_g) the rate of nucleation increases. The second step is propagation (growth) which increases with increasing the temperature up to crystal melting temperature (T_m) [140 °F/60 °C] approximately.

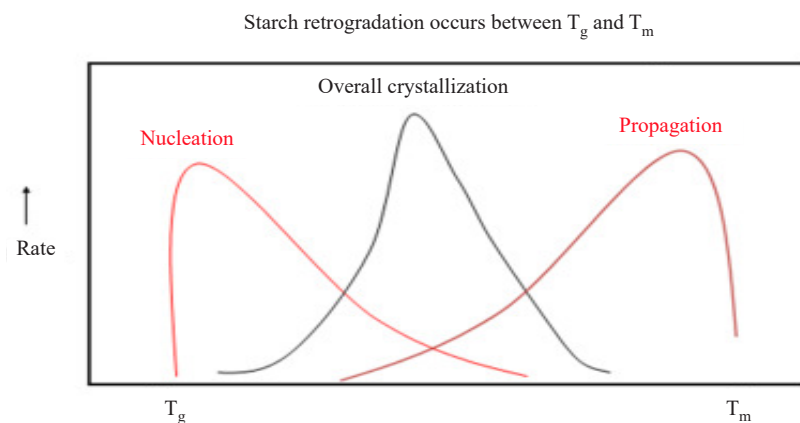


Figure 1. Starch retrogradation kinetics-nucleation rate faster near T_g while propagation rate faster near T_m [4]

During retrogradation, both amylose and amylopectin have the ability to form A-type helices in the presence of limited water, typically trapping around nine water molecules. In contrast, in the presence of abundant water, both amylose and amylopectin can form B-type helices, which can trap approximately thirty-six water molecules [5].

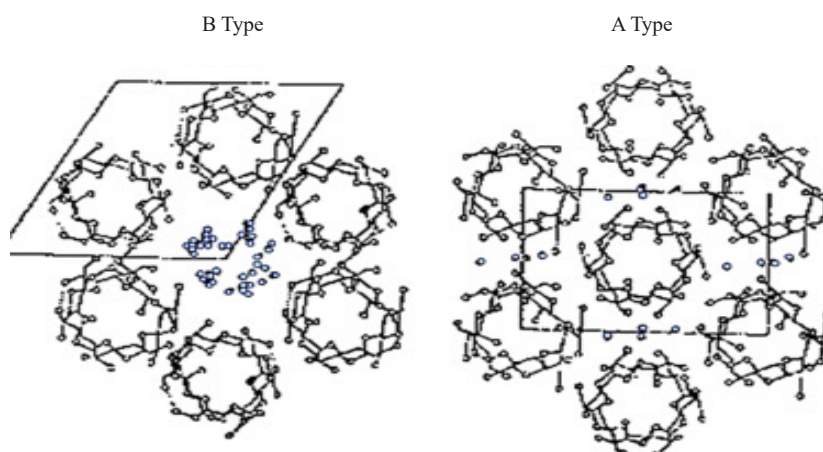


Figure 2. Molecular arrangements of A- and B-type helical unit cells of crystalline amylose [5]

Retrogradation is a continuous process that begins with the quick recrystallization of amylose molecules and progresses to sluggish recrystallization of amylopectin molecules. This phenomenon is dependent on various factors which interfere with it. The role of these factors in the retrogradation of starch is elaborated further.

2. Role of food components and ingredients in starch retrogradation

2.1 Polysaccharides

2.1.1 Amylose

Amylose is an essential carbohydrate with a linear structure that consists of alpha (1 → 4) glycosidic linkage. It is a water-soluble component accounting for 20-25% of starch. Amylose retrogradation was discovered to be a relatively quick process when compared to that of amylopectin. Soluble amyloses were observed to rapidly fall due to retrogradation during the first 24 hours of baking, and then exhibit no change later. Similar results were observed by Van Soest et al. [6] who studied the potato starch-water (10% w/w) system retrogradation. They discovered two stage retrogradation processes, an initial process being the production of helices and the quick formation of crystalline amylose areas while the retrogradation of amylopectin was a significantly slow process. Miles et al. [7] studied diluted amylose solutions (10% starch w/w) using a various methods such as turbidity, viscometer, and X-ray diffraction, and discovered that if polymer-polymer entanglements take place at C^* concentration, precipitation occurs at C^* , wherein a gel forms at $> C^*$. The formation of gel was connected to the phase-separated system in which the crystallinity of the polymer-rich phase evolved steadily.

Gidley [8] reported, using Nuclear Magnetic Resonance (NMR) studies that gelation could occur from 'dilute non-entangled' amylose solutions without the necessity for phase separation, implying a special interaction of molecules occurred during gelation. In extremely low concentration amylose gels (10% w/v), precipitation along with detection of crystalline B-type packing was observed. Furthermore, in amylose gels with higher concentration, mobile amorphous gels and B-type double helices were seen.

Goodfellow and Wilson [9] created an amylose gel with concentration 10% w/v and used Fourier Transform Infrared Spectroscopy (FTIR) to monitor its retrogradation. The amylose undergoes reordering quickly leading to formation of double helices which contribute in formation of gel network and this happens concurrently or prior to phase separation. The helices formed can potentially create crystalline formations when they clump together. However, there was no prominent change in bond energy ranges, that could be detected by FTIR in amylose gels. As there was presence of disordered amorphous regions which connected to aggregated regions and delayed crystallization.

2.1.2 Amylopectin

Amylopectin is a highly branched component of starch composed of alpha (1 → 4)-linked glucose linear chains and alpha (1 → 6)-linked branch points. It constitutes up to 80% of starch and is water-soluble in nature. Many investigations have demonstrated that amylopectin retrogrades longer than amylose which is likely due to amylose's linear structure as compared to amylopectin's branched structure [10]. Ring et al. [11] reported that the outer amylopectin branched chains solidified upon retrogradation, just as they did in the native starch granule in contrast to amylose crystallization. The branched structure of amylopectin crystallization monitored using FTIR revealed that, if helices are being formed once, they are still being connected through alpha (1 → 6) branch points to main polymer chain, and that as the helices aggregated to form crystals, the bond energies range as well as branching point segments reduces [9]. Amylopectin retrogradation was thought to have two different stages, like amylose retrogradation. The key difference between the two polymers' retrogradation is because of its highly branching structure, the double helices that are formed in amylopectin are all attached to same backbone of the polymer with closer proximity. As a result, unlike amylose, they aggregate together to form crystals even in concentrated systems, as discussed above. The alpha (1 → 6) branch point might help in retaining the two amylopectin chains in proximity and forms double helix by aligning them together [12]. Miles et al. [7] reported that amylopectin crystallinity was reversible in dilute gels at temperatures below 100 °C, but not at temperatures over 100 °C. They proposed that shorter amylopectin chains were linked to the larger chains as clusters; however, unlike amylose, the inter-chain association can occur only across DP-15 (degree of polymerization) chains before being disrupted by a branch point. Due to linear chains present in amylose, it forms more durable and longer inter-chains connections. It was further verified by of Ring et al. [11] study, who felt that in amylopectin, DP-15 chain segments were involved in inter-chain association, whereas these segments were prominently longer with DP-50 in amylose [13].

2.1.3 Other polysaccharides

Many researchers are currently working on carbohydrates to limit the rate of starch retrogradation. Several conflicting conclusions have been reached about the polysaccharides effect on retrogradation of starch in the literature [14-16].

In a study guar gum added interfered with the interactions between amylose and amylopectin in polysaccharides. The higher the molecular weight (MW) of the guar gum, the easier it is for the guar gum to interact with amylopectin, which makes sense given the conformational complex structure of amylopectin. Above the molecular weight of 10,105 g/mol, the interactions were independent between amylose and guar gum. This can be explained due to the fixed length of chains of amylose which interacted with guar gum. Thus, suggesting the interactions between starch components (amylose) and polysaccharide [17]. Starch retrogradation was also demonstrated to be influenced by smaller sugar molecules and monosaccharides. They discovered that fructose and isomaltose caused more recrystallization of amylopectin than other sugars, while sugar alcohols caused slightly more recrystallization than their sugar counterparts. The following was the order of their impacts on amylopectin chain association: rhamnose > sucrose > maltose > glucose > fructose [18]. Non-starch hydrocolloids such as xanthan gum, pentosans, carrageenan, pectin, carboxy methyl cellulose appear to enhance short-term retrogradation while inhibiting long-term retrogradation, probably by affecting on amylose-amylose and amylopectin-amylopectin interactions. They suppress starch retrogradation in a concentration-dependent manner [19].

2.2 Lipids

Cereals and starchy foods contain moderately small quantities of lipids, usually ranging between 2 to 6%, but these lipids, nevertheless, have a major role in regulating the characteristics of starch. Lipids are known to form complexes with starch by entrapping in the amylose helical cavity [20]. These complexes increase the functionality of starch in foods through inducing hydrolysis of starch and protecting bioactive, volatile and other food-sensitive components in addition to increasing their bioavailability and deliver in the system. Many interpretations are established about lipids inducing retrogradation of starch. By incorporating lipids in starch-water systems, the water penetration; granular swelling and amylose leaching during heating can be hampered. This results in constraining the mobility of amylose molecules which causes slowing of amylose retrogradation [13]. The crystallization of amylopectin can also be hindered by the presence of amylose-lipid complexes. Studies also propose lipids form complexes with amylopectin through outer branches and have an anti-retrogradation effect in food systems [21]. These lipids-starch complexes are dependent on fatty acids chain length, amylose chain length, saturation degree, substrate concentration and ratio, reaction temperature, heating time, water content, and pH [22].

Molecular modelling, X-ray diffraction (XRD), Raman, and nuclear magnetic resonance (NMR) spectroscopy studies of starch-lipid complexes show that the aliphatic chain of the lipid is inserted into the internal cavity of the amylose helix, while the carboxyl group of the fatty acid (FA) or the glyceride moiety of a monoacylglycerol remains exposed on the outside of the helix due to steric hindrance and electrostatic repulsions. The helices that contain lipids can stack form crystalline lamellae when they are perpendicular to the plane of the stacks. However, there is still disagreement over how these lamellar structures progress into V-type crystallinity [23-24]. Different explanations for the reduction in retrogradation created on by lipids during storage have been put forth. These include steric hindrance caused on by starch-lipid complexes that prevent amylose molecules from cross-linking to one another [25]. Thus, addition and presence of lipids in food system could lead to reduction in retrogradation of starch.

2.3 Proteins

Proteins along with starch can produce various gels in food systems. The mechanisms involved between starch and protein complex are based on water solubility, hydrogen bonding, electrostatic interactions and covalent bonding [26].

The capacity of proteins to bind water in the starch matrix is one of the more basic processes of protein-starch interactions having a bearing on retrogradation. The release of water from the starch matrix is a result of starch retrogradation. High water-binding protein fractions can sequester this released water, lowering the amount of free water in the system and molecular mobility. According to low-field NMR spin-spin relaxation time data, Zhang et al. [27]

found that the addition of up to 10% rice protein to rice starch decreased the free water fraction and increased the lightly and tightly bound water fractions, and that the higher the protein addition, the smaller the change in percent crystallinity over a 21-day time period.

There is some proof that proteins and starch can form hydrogen bonds, which could prevent starch from retrograding. The reduction of short- and long-term starch retrogradation by grass carp proteins was demonstrated by Xiao et al. [28] using confocal microscopy, atomic force microscopy, differential scanning calorimetry, and X-ray diffraction data. Hydrogen bonding was determined to be the most likely mechanism. Microscopy results revealed an equal distribution of proteins throughout the starch matrix, and thermal and crystallinity data demonstrated that retrogradation was reduced in starch samples with protein addition. The authors consequently hypothesized that proteins in the continuous phase prevented hydrogen bonds between starch polymers, either directly through starch-protein complexation or indirectly through lower mobility [28].

Wheat starch retrogradation is a major concern in baking industry due to which baked goods undergo staling resulting in loss of their textural pliability. Studies indicate that wheat proteins such as albumins, gliadins, glutenins and globulins tend to exhibit a varied effect of wheat starch retrogradation. Upon addition of isolated protein fractions into wheat starch, only glutenin had antiretrogradation property while the rest three promoted it. According to differential scanning calorimetry (DSC) studies the onset temperature (T_o), conclusion temperature (T_c), peak temperature (T_p), of the endothermic peak, and the endothermic enthalpy of retrograded wheat starch moved to lower field with addition of wheat proteins except for glutenins and gliadins T_p . The melting peak temperatures of wheat starch blended with different proteins were 128.46, 132.03, 126.14, 121.65, and 134.84 °C for the control with no protein, glutenins, albumins, globulins, gliadins groups, respectively. This might be due to formation of less hydrogen bonds due to presence of proteins in retrograded starch. Higher T_p of gliadins and glutenins were because of their higher molecule weights with long chains which consist of more hydrogen bonds [29].

Addition of protein concentrates and protein hydrolysates has also been reported to influence the retrogradation of starch. Addition of soybean 11S globulin to the corn starch gel slowed retrogradation and reduced retrogradation enthalpy. Adding soybean 7S globulin, on the other hand, improved starch retrogradation and raised the retrogradation enthalpy [30]. In another study, whey protein hydrolysate (WPH) was added to rice starch. It resulted in enhanced shelf life along with gel stability by retarding hydrogen bonding within starch chains thus ultimately retarding the starch retrogradation in the storage period [31]. Rice protein hydrolysate (PRPH) was added to wheat starch where it lowered the peak viscosity, setback and breakdown value of starch. Dynamic viscoelastic measurements showed the presence of PRPH-2 indicated a decrease in the storage modulus (G') and an increase in the loss tangent ($\tan \delta$) thus having an inhibitory effect on retrogradation.

Soft gels were formed by adding soy protein isolate (SPI) in starch, as evaluated by texture profile analysis. During initial storage time, starch-SPI gel and starch-only gel had same firmness; as addition increased the retrogradation of gel delayed in storage time, suggesting that proteins can easily interact with amylose and amylopectin's branches that are exposed via noncovalent bonding which are hydrogen bonds [32]. Free amino acids, as well as soy and pea protein hydrolysates, have also been demonstrated to delay starch retrogradation in maize. The alkaline amino acid arginine reduced potato starch syneresis, whereas addition of acidic amino acids such as glutamate and aspartate increased it [33]. However, the specific effects can vary depending on the type of amino acids or protein hydrolysates used and the specific starch system being studied.

2.4 Salts

Food scientists are fascinated by salts because they have an impact on the acceptability, shelf life and overall quality of starch-based meals. The retrogradation, thermal, gelatinization, rheological and thermal characteristics of starch have shown to be affected by the type of valency and concentration of salts [34]. Salt addition was demonstrated to have a significant influence on promoting the development of rice-starch gel using differential scanning calorimetry (DSC), pulsed NMR and dynamic viscoelastic testing. A charge screening effect was achieved by a considerable deduction of the amount of leached amylose out of starch granules and salt, which reduced segmental repulsion [35]. Salt in the form of sodium chloride (NaCl) is usually added in dough formulations of cereal-based foods up to 2% (flour basis) concentrations to induce improvement of its physical, microstructure and sensory characteristics. During processing and storage, salt addition can modify the quantity of retrogradation and gelatinization. Starch gels with salt

when held at 4 or 25 °C, the retrogradation levels were often reduced [36].

Beck et al. [37] studied the effect of several chloride salts on starch retrogradation. They suggested that the various cations could have a substantial impact alter the rate of starch recrystallization. Further, bivalent cations such as Ca^{2+} , Mg^{2+} reduced the starch re-crystallization rate (k) than univalent cations (Li^+ , NH_4^+ , Na^+ , and K^+) based on the postulation that cations with higher charge densities exhibit more hydration with lower a_w values than cations with lower charge densities. Salt is a powerful substance in water, an electrolyte can be ionized to form cations and anions. These ions have an effect on the hydrogen bonds between water and starch systems, as well as starch molecule interactions.

2.5 Food additives

As one of the most common food additives, emulsifiers have been useful in delaying and inhibiting retrogradation through interference with starch molecule reassociation. The antistaling effect of emulsifiers is dependent on their specific characteristics and its interaction within starch molecules [38]. Amylose and amylopectin can bind to emulsifiers in various ways. Amylose is commonly known to have a linear molecular structure, although this linearity is disrupted in gelatinized amylose. Emulsifiers can interact with the helical inclusion complexes formed by amylose through physical entrapment, complex formation, or starch modification, potentially leading to retrogradation [39].

Amylopectin, with its branched structure, has a tendency to form fewer complexes with emulsifiers compared to amylose. However, emulsifiers can still interact with the surface of amylopectin starch, leading to changes in the distribution of water within the starch molecules. Consequently, these interactions can alter the hydrogen bonding and interactions of the branched chains in amylopectin. The specific mechanism by which emulsifiers affect the interaction and water distribution within amylopectin starch is complex. Furthermore, the effects of emulsifiers can vary depending on the specific type of emulsifier employed in different food systems [40].

Studies on addition of various emulsifiers in food system showed an impact on retrogradation of starch. Increasing the amount of sodium lauryl sulphate (SLS) in a cake lowered the dough's, surface tension, specific gravity and consistency coefficient. Increased sodium lauryl sulphate levels also reduced crumb hardness and cohesiveness, according to a texture profile examination of cake crumbs [41]. Though addition of SLS gave antistaling effect in cakes further investigation of impact of SLS on retrogradation in other products is needed.

Rice cakes retrogradation kinetics and characteristics were studied with the addition of glycerol (GLY) and sucrose fatty acid ester (SE). Both rice cakes containing glycerol (RGLY) and rice cakes containing sucrose fatty acid ester (RSE) had less early stiffening than the control for up to 5 days. RSE's X-ray diffraction (XRD) pattern revealed a B+V-type pattern, and analysis of the relative crystallinity revealed that GLY and SE inhibited the initial and end stages of rice cake crystallization. The differential scanning calorimeter's (DSC) retrogradation enthalpy, glass transition temperature, and ice melting enthalpy were all impacted by GLY and SE. But independent of additives, rice cake's ^1H NMR relaxation time (T_2) reduced [42].

In another study addition of surfactant that is glycerol monostearate (GMS) to see its effect on staling of chapati was observed. The soluble starch and soluble amylose percentage reduction was less in GMS treated chapati compared to control chapatti. This might be due to formation of complexes between the hydrophilic and hydrophobic moieties in molecular structure of surfactant and starch molecules within the system [43].

Acids mainly citric acid, for example, is used for seasoning and to modify pH levels. When citric acid was introduced to a starch-plasticizer mixture, the starch underwent partial esterification and had low molecular weight. These attributes are intended to avoid retrogradation, promote polyester compatibility, improve processing ability, and accelerate starch degradation [44]. However, the impact of citric acid varies with the concentration, specific plasticizers used as well as temperature of the product.

Amylase is currently being employed in the food sector to improve dough processing qualities, quality of bread and extend starchy foods storage period. Alpha-amylases are added in bread are derived from various sources such as fungal, bacterial and cereal alpha-amylases; with each source having varying degrees of anti-retrogradation efficiency due to variability in process of extraction, pH optima and temperature stability. Despite the efforts of numerous researchers, there is still disagreement over the effect of alpha-amylases on stale bread. Many investigations on starch gels and bread have concluded that a growing number of low-molecular-weight fragments are responsible for the decreased rates of retrogradation. Other research has found that the antifirming impact of alpha-amylases is due to the reduced capacity

of the degraded starch to retrograde rather than the presence of low molecular weight dextrins [45]. In another study β -amylase was added at different hydrolysis time in wheat starch which showed short-term and long-term inhibition effect on wheat starch ageing [46].

Apart from amylases, addition of cyclomaltodextrinase also improves starch characteristics. Treating rice starch with cyclomaltodextrinase, amylose content significantly reduces whereas amylopectin tends to remain same, with no noticeable change inside chain's length distribution. At the same time, the rate of retrogradation was substantially slower than in control sample. The anti-staling effect was linked to the residual amylose and amylopectin populations altered (re) crystallization behaviour; the produced dextrins slows down the starch retrogradation by interfering with reassociation of residual starch fraction [47].

In the study rice starch was treated with transglucosidase (TG) for 4-20 hour time interval and investigated for long-term retrogradation properties. According to the findings, the TG treatment can somewhat delay the retrogradation behavior of rice starch. The ^1H NMR data show that the TG treatment duration controls the increase in the degree of branching in rice starch from 12.26 to 15.16% with increasing TG treatment time except for 20 hours which might be due to slow down of enzymatic hydrolysis upon treatment. With an increasing degree of branching (DB), the relative crystalline of the retrograded TG-treated starches fell from 26.44 to 21.57%.

As a result of the formation of a much more uniform crystal structure, the crystalline peak intensity narrowed and sharpened, which decreased the mobility of water. Additionally, as DB increased, the spin-spin relaxation period (T_2) shrank. The Avrami kinetics showed that the reduction in rate constant k following TG treatment was what caused the retrogradation rate of rice starch to be slowed down. The findings may offer a viable theoretical foundation for delaying rice starch retrogradation in order to enhance the quality and lengthen the shelf life of rice-based staple foods [48].

Polyphenols and polyalcohols have the potential to prevent starch retrogradation and generate stable gel matrices. Polyalcohols and polyphenols include many free hydroxyls that would create hydrogen bonds with starch molecules to prevent starch chain recrystallization. Polyols have been reported to inhibit starch retrogradation, which may be due to the formation of water structure impact of polyols [49].

The reduction of recrystallization in granular potato starch was proportional to the number of hydroxyl groups in the polyalcohol. Polyphenols are polyhydroxy chemicals that are found in plants. Starch retrogradation may be slowed by the creation of hydrogen bonds between polyphenols and starch. The retrogradation of starch is affected by the number of hydroxyls in polyphenols and their reactivity [50]. It is undeniable that adding polyphenols to starch or starchy food processing might not only prevent the retrogradation of starch but also improve food's nutritional value.

3. Role of extrinsic factors starch retrogradation

3.1 Temperature and storage conditions

The degree of starch retrogradation is mostly determined by temperature and storage time. Because of its impacts on the nucleation and growth phases, the starch retrogradation rate is impacted by the temperature. Retrogradation is usually quick at first and subsequently slows down. At constant temperature, the enthalpy changes and onset temperature increase with storage duration whereas the conclusion temperature doesn't show that effect [51]. These findings suggest that storing starch for longer periods of time enhances the production of more flawless starch crystallites. In another study, at constant temperature there was increase in springiness and hardness of retrograded starch gels initially; but with longer storage the change observed was marginal whereas gels held at cycled temperature of 4/30 °C resulted in hardness and springiness emerged and maintained relatively constant through longer storage period [52].

The retrogradation of starch is most frequently studied between 4 and 25 °C (or 30 °C) temperature cycling or at 4, 25, or 30 °C isothermal storage. Generally, storing at 4 °C, in starch gels the amylopectin crystallization occurs faster than storing them at 25 or 30 °C. When compared to isothermal storage at 4 °C, temperature cycling (4/30 °C) resulted in higher onset melting temperature, lower melting enthalpy of retrogradation products and lower melting temperature range, this indicates that with temperature cycling the crystallites formation is inhibited while the stability and homogeneity is improved [53].

Colwell et al. [54] held wheat starch gels at temperature range from 1°C to 43 °C to evaluate its aging using differential thermal analysis. These researchers discovered the crystallization mechanism of starch (immediate

nucleation followed by rod-like crystal growth) is similar over the whole temperature range (-1 to 43 °C). And at greater storage temperature the crystalline structure is developed more symmetrically.

In another study, rice paste was gelatinized at different temperatures (4 °C, 15 °C, 30 °C, -18/30 °C, and 4/30 °C) and with different moisture contents (30-42%). The crystalline form of rice starch converted from A-type to B-V type during retrogradation, when studied using x-ray diffraction. Under 30 °C, retrograded rice starch had the highest B-type crystallinity among the five temperature settings, and B-type crystallinity increased with increasing moisture content. Rice starch retrogradation is characterized by the recrystallization of amylopectin and amylose and is primarily attributed to amylopectin, according to DSC data. Amylopectin recrystallization was aided by a higher moisture level, whereas amylose recrystallization was unaffected. The best temperatures for recrystallization were 4 °C and 15 °C for amylose and amylopectin, respectively. The recrystallization enthalpy of amylopectin in rice starch stored at 4/30 °C varied between 4 °C and 30 °C, but it tends to be always higher than that of rice starch stored at -18/30 °C. The total retrogradation enthalpy was highest in rice starch (8.44 J/g) after being cooked at 42 percent moisture content and kept at 4 °C. However, with temperature increases to just below the crystallites' melting point (T_m), the rate of propagation grows exponentially. At a point halfway between T_g percent and T_m , the total rate of crystallization occurs. Crystals grown at 4 °C were less symmetrical and had a lower T_m than those grown at room temperature [55]. Quick freezing -20 °C, -40 °C and -80 °C for 90 min was applied to steamed oat roll prior to frozen storage and its effect on starch retrogradation and ice crystals properties was studied. Freezing at -40 °C and -80 °C inhibited the increase in peak gelatinization temperature, enthalpy and the ordered degree of oat roll starch, therefore postponing starch retrogradation. Texture analysis reported that hardness increased during frozen storage, quick freezing at -80 °C had the best texture properties. Therefore, declining the quick-freezing temperature could obtain a higher quality of frozen steamed oat roll, by means of delaying the starch retrogradation and minimising the size of ice crystals [56].

3.2 Modification and processing of starch

Modifications are any alterations in the structure of the starch molecule caused by numerous environmental, operational, and processing conditions. The structure and functioning of starch molecules may be changed either favourably or adversely as a result of these alterations. The modifications may be physical, chemical, and mechanical alterations to starches in order to improve their quality characteristics and produce diverse formulations. Hoover et al. [57] evaluated the effect of heat-moisture treatment (100 °C, 30% moisture, 16 h) and defatting (hot n-propanol-water 3:1 w/v) and on the level of retrogradation of potato, oats, lentil and wheat starch gels (40%) held at ambient temperature (using DSC and gel texture measurements). The results showed that heat-moisture treatment and defatting had no effect on the commencement of the retrogradation endotherm in wheat, potato, or lentil starches. Heat-moisture treated and defatted oat starches, on the other hand, showed a retrogradation endotherm that occurred earlier than native starch. The changes in the retrogradation endotherm transition temperatures of native and treated starches were minor, and they remained virtually unaltered throughout the retrogradation process. Defatted starches had a higher enthalpy of retrogradation (ΔH_r) than their native counterparts. This rise in defatted lentil, oat, wheat, and potato starches was 1.7, 3.6, 4.7, and 2.2 J/g after 20 days of storage, respectively. The ΔH_r increase for heat-moisture treated oat, wheat, and lentil starches were 1.6, 2.6, and 3.8 J/g, respectively. In heat-moisture treated potato starch, however, ΔH_r decreased by 1.5 J/g in oat and wheat starches, the strength of gels rose more after defatting than after heat-moisture treatment, whereas in lentil and potato starches, the rise was more prominent after heat-moisture treatment than after defatting. Another study on maize starch reported the effect of pasting, extrusion cooking and drum drying on recrystallization mechanism by X-ray diffraction, mild acid hydrolysis DSC and gel-permeation chromatography. The amylose was seen independently crystallize from amylopectin through forming complex and retro-gradating after drum drying and pasting. It was associated to amylose leaching, crystallization and phase separation within the amylose volume fraction following heat treatment. The amylose crystallites (chains with DP 35-40) were seen to be acid-resistant and showed high fusion temperature (above 100 °C) [58].

High Hydrostatic Process (HHP) is another mechanism that uses pressure in the range of 10-1,200 MPa to change the physicochemical properties of starch. This process results in partial or full gelatinization of starch. This depends on the starch's type, pressure amplitude, concentration, treatment and temperature duration. According to a study, when mung bean starch was processed using HHP treatment, followed by aging; there was enhancement of starch crystallinity, retrogradation enthalpy and transition temperature. However, there was no endothermic gelatinization peak in the

heat-gelatinized mung bean starch, indicating that no crystallized structure had formed. In the case of quinoa, wheat, amaranth starches, HHP treatment induced an increase in amylose-amylose and amylopectin-amylose chains association through the leached amylopectin and amylose during storage [59].

In another report, the effect of different freezing temperatures and storage temperatures on cooked rice starch retrogradation and textural qualities was studied. The rice cooked was frozen at various rates and stored at -18 °C for up to 7 months or 4 °C for 14 days. A texture analyzer was used to evaluate the texture of rice and a differential scanning calorimeter was used to evaluate the starch retrogradation enthalpy (ΔH_r). The results revealed a negative link between ΔH_r , freezing rates and hardness values, whereas a positive correlation was observed freezing rates and adhesiveness. On the other hand, the benefits of rapid freezing (higher adhesiveness, reduced hardness and starch retrogradation) of cooked rice were quickly lost in the first three days of storage at 4 °C. To conclude with rapid freezing and -18 °C frozen storage can successfully delay starch retrogradation and keep cooked rice's textural features for at least 7 months. As a result, by combining quick freezing with frozen storage, cooked rice of high-quality aspects can be formed [60].

4. Conclusion

Gelatinization and retrogradation are the most significant functional properties of starch that influence the quality of starchy foods. Several approaches have been applied to study starch retrogradation and elucidate the mechanism and effect of different factors at the comprehensive and molecular levels. Water content, storage time, storage temperature, and additives are all factors that influence starch retrogradation. Studies conducted have shown the impact of additives such as emulsifiers, hydrocolloids, and acids that alter retrogradation of starch by the mechanisms such as combating for water with starch or hindering reassociation of starch chains. Further research on mechanism involved in the antistaling effect of additives in food system and use of natural food ingredients in inducing retrogradation in foods need to be undertaken. Great opportunities are available in developing new products with controlled retrogradation and improved physicochemical attributes and shelf stability by using thermal and hydrothermal processing methods.

5. Acknowledgments

We would like to acknowledge Dr. Anil Dutt Semwal, Director, Defence Food Research Laboratory (DFRL), DRDO, for providing constant guidance and technical support that greatly assisted in writing this paper.

Conflict of interest

The authors declare no competing financial interest.

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