A COMPREHENSIVE REVIEW ON SCOPE, CHARACTERISTICS AND APPLICATIONS OF INSTANT STARCHES IN FOOD PRODUCTS

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Abstract
Importance of starches for diversified industries can never be neglected. This biopolymer plays a vital role in food, non-food and pharmaceutical industries. However, native starches require modification (both physical and chemical) to improve its functional traits. Physical modifications are nowadays preferable as these starches could be labelled as “Natural or Clean”. Unmodified starches require heating to solubilize at room temperature. Whereas pregel starches overcome this limitation by dissolving at room temperature. Pregelatinized/ cold water soluble/ instant starches refer to the class of physically modified starches that hydrate, without heating providing instant viscosity and smooth texture when dissolved in cold water. Physical and chemical attributes could be achieved without affecting nutritional and organoleptic attributes. Different techniques like alcoholic-alkaline method, drum drying, extrusion and autoclaving are used for preparing pregels. Among all techniques, alcoholic-alkaline method has a higher edge over remaining methods adopted for preparing pregels due to superior thermal tolerance and enhanced viscosity. Instant starches/ pregels impart unique functional characteristics that are desirable for various food products. These starches also preclude the heating step and could be dissolved at room temperature giving instant viscosity. These physically modified pregelatinized starches could be utilized in different food products as fat replacers, gluten substitute, coating agents, thickeners and as texture modifiers. This mini-review aims to give a brief overview of different methods used for preparation of pregels along with its properties and applications in food products.

Key words: Instant starches; Pregels; Physiochemical properties; applications

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1. DEFINITION
Granular cold water soluble (GCWS) / pregelatinized (PG)/ instant starches refers to the class of physically modified starches that hydrate without heating and provides instant viscosity and smooth texture when dissolved in cold water (Chen and Jane, 1994). Starch due to its versatile nature is used worldwide in food as well as non-food applications. Native starches have some limitations including inability to dissolve at room temperature and require heating which subsequently increases energy cost and necessitates the need of heating assembly. Instant starches have overcome this problem as it solubilizes under cold conditions (Dhital et al., 2012).

2. SCOPE OF PREGELATINIZED STARCHES IN FOOD PRODUCTS
Instant starches impart various applications with versatile functionality. Oil/fat uptake could be reduced by incorporating instant starches in frying batters. Frying batters made from hot water swelling starches demonstrated more oil absorption during frying process, also sensory characteristics improved due to lower oil uptake during frying process when PG starches were used. During frying, moisture from inside of food is lost in form of steam and creates voids on its surface from where the oil enters into the food increasing oil percentage in food. However coating with instant starches acts as a barrier or it allows minimum percentage of oil to enter into food surface hence, it acts as an improved oil barrier, and reduces oil absorption due to increased water retention in product (Stauffer, 1996; Shih and Daigle, 2001). Pregelatinized starch/flour has been used for many years in baked goods, pastry flour, instant puddings etc. It provides instant dispersibility, minimum agitation without lumping in cold water.
Dough water absorption and bread yield also increased when pregelatinized starches were incorporated into bread formulations (Miller et al., 2008). Cake quality had shown significant improvement on addition of 10% pregelatinized starches including increased cake volume, more softness and shelf life extension of cake. As the temperature during baking increased, viscosity also increased resulting in firmed gel structure. Increased cake volume was due to high viscosity that increased gas trapping and ultimately increased cake volume (Karaoğlu et al., 2001).

Main thing to be focused while applying any food/functional coatings is to retain the organoleptic properties of the food product while improving the physical characteristics. Both functional and physical benefits could be achieved without affecting flavor of food by applying versatile methods of coating PG starches on a pre-moistened food surface. Coating provides a glossy, sheen effect and a dry, non-greasy touch when coated over fatty foods. This invention could be practiced on variety of foods. Besides many advantages/applications; protection from oxidative deterioration is also achieved through use of instant starch coatings/films (Louis, 1970).

3. METHODS TO PREPARE INSTANT / PREGELATINIZED STARCHES

Various methods have been reported to prepare instant starches. However, physical methods are preferred being chemical free and easy to use as compared to other methods. Methods used to prepare instant/ pregel starches are as follows.

1. Alcoholic-alkaline method
2. Drum drying
3. Extrusion
4. Spray drying
5. Autoclaving

The instant starches obtained after drum drying, extrusion and autoclaving lose their granular structure due to the thermal treatment along with loss of birefringence. However, the unique feature of instant starches prepared by alcoholic alkaline method is that their granular structure is retained, however birefringence is lost. Therefore, these starches are called granular cold water soluble starches (GCWS).

3.1. Alcoholic-alkaline method

The GCWS starches are prepared by alcoholic alkaline method. It involves the treatment of native starches with different concentrations of ethyl alcohol and NaOH. Varying concentration of starch to solvents (1:0:7:3.2) and (2:4.2:2.8:5) at 25°C and 35°C were used for its preparation. Concentration of ethanol (lesser), NaOH (higher concentration) and temperature (higher) affects the efficiency of process with better CWS starches (Chen and Jane, 1994). Poly-ethylene glycol could also be used for surface modification to prepare CWS (Wang et al., 2011). Granular swelling can be controlled through use of rotary evaporation of ethanol (boiling point 82°C), eliminating use of NaOH (being harsh chemical). As swelling is directly correlated with amount of water added, hence high water content will eventually break the granular structure. Keeping this in account use of high ethanol will restrict swelling so much so that it completely avoids gelatinization (Zhang et al., 2012). Effect of varying concentration of NaOH and constant amount of ethanol was found to have a profound effect on physiochemical properties of sago starch (Kaur et al., 2011).

Water binding capacity, swelling power, solubility, apparent viscosity, freeze thaw stability of GCWS increases significantly as compared to its native counterpart. Amount of water drained during storage of GCWS starch gels was less compared to hot water swelling starch gels reflecting its higher freeze thaw stability (Paredes-López, 2000).

3.2. Drum drying

Drum drying is an economical and widely used method in industries to produce pregels. Single as well as double drum dryers are used on industrial scale. Pharmaceutical industries also take benefit of pregels as an excipient for controlled release tablet (Anvvar et al., 2006). Steam pressure (6-8 bars), drum speed (2-7rpm), drum dryer gap (0.9mm), feed
concentration (10% w/w) are the variables taken into account during practical implementation. Residence time for drying inside gelatinization pool affects the moisture uptake of sheets. More over rheology of pastes is also affected by moisture uptake and presented overwhelming results. Thermal field inside the gelatinization pool is an important variable while transferring slurry between double drum dryer (Anastasiades et al., 2002; Gavrielidou et al., 2002). Drum temperature has a profound effect on various characteristics of starches. Cold peak viscosity could be decreased by increasing drum temperature. Cross-linked PG starch is preferred for thickening application (Nakorn et al., 2009). Twin drum dryers are given preference over single drum dryer due to less mechanical shear as well as higher viscosity profiles and thinner film production by twin drum dryer in comparison to single one (Mercier, 1987). In double drum drier/twin drum drier, the gelatinization of starch takes place between drums through conductive mode of heat transfer. When slurry is poured on hot surface of drum; starch gelatinizes forming thin film followed by drying and eventually the dried film is scraped off (Gavrielidou et al., 2002). Pregelatinized starch produced by drum driers had higher viscosity at 25˚C, high swelling power, lower degree of crystallinity and highly porous structure as compared to native counterparts. Their versatile nature and properties allow manufacturers to use drum dried starches in production of products which are heat liable (Majzoobi et al., 2010).

3.3. **Extrusion**

Extrusion involves the processing of raw ingredients by applying a combination of stress, pressure and temperature which eventually alters the physical characteristics of starches. Single screw as well as double screw extruders both could be used to make extruded products. When starch slurry is subjected to high temperature during extrusion, it leads to gelatinization of starch (Hagenimana et al., 2006). Feed moisture content of starch (9-17% or 16-22%), screw speed (200-300 rpm), barrel temperature (100-160˚C), compression, die sections of extruder plays an important role for final product. Low feed moisture content can be used for extrusion of pregelatinized starches. It results in higher flavor retention as well (Kollengode, Hanna et al., 1996; Kollengode and Hanna, 1997).

3.4. **Spray drying**

Pregelatinized starches could also be prepared by heating starch slurry in jet cookers and extruders followed by spray drying. Contact time of particle with hot air is kept minimum. Spray drying is commonly used equipment for producing pregelatinized starch long time ago as it efficiently converts liquid droplets into amorphous particulates without disrupting its granular integrity. It is normally applicable for tablet formulation or where minuscule surface area is required (Laovachirasuwan et al., 2010). However, shape retaining products can also be prepared by final drying by this method. Feed flow rate, inlet temperature, concentration of slurry, air flow rate affects the nature or free flow properties of drying matter. This strategy for drying is especially profitable b/c drying by this method produces spherical granular particles that are demanded in various products (Eduard and Karl, 1967). When using drum drying, extrusion and alcoholic-alkaline methods for preparation of pregels, the starch has a hard stone like structure usually in millimeters which is then ground using sophisticated and high input mills. This method is therefore far more superior than drum drying and extrusion (Fu et al., 2012).

3.5. **Autoclaving**

Autoclaving is another but commercially less practiced way of preparing pregelatinized starches. Autoclaving duration (130˚C, 25psi, 20-30 min) and slurry concentration (5-7 % w/w) has a profound impact on morphological and physiochemical properties of pregels. However, this process accounts more for high amylose containing starch as compared to waxy (high amylopectin) sources. Philosophy behind this is the formation of cohesive and gummy mass due to amylopectin-ethanol interaction. Ethanol was used for precipitation/
dehydration purpose (Patindol et al., 2013). Autoclaving and extrusion both led to decrease in bulk density. This reduction might be due to disruption of crystalline network and extent of starch gelatinization. Low moisture level and high temperature in extrusion has led to lowest BD (Bulk Density) and vice versa (Hagenimana et al., 2006; Patindol et al., 2013).

4. MORPHOLOGICAL CHARACTERISTICS OF INSTANT STARCHES

Examination of morphological characteristics of starches assists in understanding difference between starches isolated from different sources and also helps to study the impact of physical/chemical modification on the external structure and size of starch granules.

Instant starches prepared from drum drying showed irregularly laminal, loss of granule shape and structure. It is mainly due to breaking of hydrogen bonds holding molecules together due to high temperature applied during preparation step (Yan and Zhengbiao, 2010).

Starch granules lose their integrity, melt, and re-associate to form complex when treated through extrusion to form PG starch. During each stage of extrusion, structure of granule is changed resulting into porous shaped sponge. Also crystallinity is lost due to high rate of shearing and heating in extruder. Irregular stone like structure with holes were observed in SEM microphotographs (Yan and Zhengbiao, 2010).

Morphology of granule treated with alcohol-alkaline CWS was much better with smooth granular surface. Indented appearance increased due to this treatment. Alkali swells the granules but alcohol inhibits as the aim is to swell the granule but not to burst. Due to use of an organic solvent (alcohol) these two forces balance each other and resultant CWS is formed where granular structure is retained but crystallinity is completely lost. Waxy starches show higher swelling of granules as amylopectin is responsible for swelling; whereas amylose serves as a connector for holding granules intact. During swelling of granules it imparts tension on neighboring granules and crystallinity is destroyed due to increased tension. At this stage amylose performs key role by intertwining with amylopectin in order to maintain the integrity of starch granules (Yan and Zhengbiao, 2010).

Granule surface exhibit different changes by treatment. Surface wrinkling was also observed in normal maize and tapioca. Surface wrinkling is mostly due to swelling and shrinkage of granule when treated with water and ethanol. Large granules are more likely to be affected by alcoholic alkaline treatment in contrast to small granules. Ratios of starch: water: ethanol is a key factor and a critical area of interest. Water content is directly associated with swelling however, changing ratio will lead to deformation and bursting of granules from hilum region (Zhang et al., 2012).

Alcohol dried PG starches showed sharp vesicles and cavities. However, drum dried starches exhibit disintegrated laminar structure. Dents were also observed on granules after spray drying, and honey comb like structure was noticed after freeze drying of rice starch pastes. Bulk density also decreased after alcoholic treatment or extrusion when making PG/CWS starches (Patindol et al., 2013).

Increase of swelling power, water binding capacity at room temperature as well as at 85˚C is an indication of molecular degradation due to treatments given to granules making it CWS starch (Patindol et al., 2013). In a nutshell, starches prepared by autoclaving, drum drying and extrusion results in formation of flaky structure with complete loss of both crystalline structure and granular integrity. Whereas GCWS starches maintain granular integrity but birefringence is completely lost and therefore it quickly swells at room temperature (Doublier et al., 1986).

Spray dried pregelatinized starches comprised doughnut shaped hollow granules. These changes may be due to consequence of heating & drying process. It also leads to increased water solubility (Laovachirasuwan et al., 2010). When partially gelatinized starch was subjected to spray drying, the surfaces became...
concave like. It is mainly due to the fact that outer hydrated layer vaporized quickly and surface become shrinky and concave (Fu et al., 2012). However honey comb like structures were observed in granules of spray dried samples when fully hydrated (Lee and Rhee, 2007).

5. X-RAY DIFFRACTION

All native starches show strong Maltese cross due to radial orientation. X-ray diffraction results usually show A, B or C type diffraction pattern depending upon the type of crystallites. A type is usually observed for cereals, B type for root and tuber starches, and C type for legume starches. However, PG starches show different diffraction patterns compared to HWS (hot water soluble) starches (Odeku et al., 2008). No maltese crosses were observed, but V-type diffraction pattern was observed (double helical structure A-type was converted into single helical V-type) after alcoholic-alkaline treatment (Jane et al., 1986). Different sources show variable peaks when analyzed through X-ray diffraction pattern. A-type pattern diffused and prominent V-type crystallinity was evolved for gelatinized maize starch. Diffusion of A-type peaks confirmed the loss of native granule order when starch was given aqueous ethanol treatment (Zhang et al., 2012).

Reduced degree of crystallinity was also observed when pregels were produced by drum drying. Pregelatinized starch showed crystallinity of 2.22 % as compared to native wheat starch which was 40.08%. It clearly shows that A- pattern in native wheat starch was completely devastated by drum drying (Majzoobi et al., 2010).

6. THERMAL CHARACTERISTICS

Thermal properties determine the endothermic transitions i.e. onset temperature, peak temperature, conclusion temperature and enthalpy of gelatinization. Native (corn and potato) starches show endothermic peaks b/w 60°C and 80°C. However, these thermal properties differ significantly with source due to differences in amylose content, granular characteristics and percent crystallinity. During gelatinization double helical alignment of starches are disrupted and show melting of crystalline structure in DSC thermograms. Low gelatinization enthalpies may be due to small granules of starch. Cold water soluble/ instant starches normally don’t show any gelatinization endotherm as their structure is already gelatinized (Rajagopalan and Seib, 1992; Singh and Singh, 2003; Kaur et al., 2011). Alcoholic alkaline treatment disrupts the crystalline structure making it unstable. Lower gelatinization enthalpy values (ΔH) of CWS may be due to order-disorder transition inside the granule. Transition temperatures also showed lower values for CWS starches. Higher degree of crystallinity showed higher glass transition temperature (Tg) in native or non treated samples. It is due to the fact that crystallites restricts the segmental movement in glass transition phase (Kaur et al., 2011).

DSC endotherms showed higher gelatinization temperatures and lower gelatinization enthalpy of pregelatinized starch as compared to native counterparts (Okunlola et al., 2015). Gelatinization enthalpy value (AH) decreased significantly with the increase of water content in starch: water: ethanol ratio. Gradual melting of helical structure also takes place (Zhang et al., 2012). However, DSC thermographs (Chen and Jane, 1994) also confirmed absence of gelatinization endotherm between 25°C and 100°C as no peak was observed in instant starches as compared to its native counterpart. Single helical amylose is water soluble at room temperature ±25°C. It is also confirmed by DSC thermograms by not giving gelatinization endotherm between 20°C and 100°C.

When spray dried; transition temperatures of rice starch (To, Tp, Tc) were higher and gelatinization enthalpy becomes lower as compared to non spray dried native ones proving the fact that during spray drying starches are partially gelatinized (Laovachirasuwan et al., 2010). Thus it could be concluded that during pregel preparation, if starches are partially gelatinized it leads to
appearance of endotherm with lower enthalpy values compared to HWS starches. Whereas, if starches are completely gelatinized during any treatment then it subsequently results in absence of endotherm during DSC scans.

7. PASTING PROPERTIES

Pasting profiles of pregel starches prepared by double drum dryer showed higher instant viscosity (560BU) as compared to native one which don’t show any instant viscosity peak at 30°C (Rincón and Pérez, 2002). Amylose content also has a significant impact on starch pasting properties. Pregel from low and medium amylose rice starch showed cold peak viscosity in RVA; whereas high amylose pregel rice starch showed RVA hot peak viscosity. This suggests more severe disruption of starch granules with low amylose content as compared to high amylose starches (Nakorn et al., 2009).

Viscosity profiles reflect the granular changes during heating and cooling cycles at different temperatures. GCWS starches showed higher paste viscosities than HWS starches. Their pasting curves reaches instantly at 300 BU confirming its cold water solubility (Chen and Jane, 1994). Low pasting temperature of GCWS indicates already lost crystalline structure (Kaur et al., 2011).

Extrusion lead to low viscosity profiles than native ones. Low peak viscosity responds to ratio of gelatinized starch. It may be a possibility that extrusion results in greater gelatinization and degradation that restrained the swelling ability of granules and percolated fractions, thereby decreasing pasting viscosities. It was confirmed by various studies as well (Hagenimana et al. 2006; Zhang et al., 2016). Above pH 7 drum dried pregelatinized starches showed increase viscosity as compared to spray dried and extruded starches (Herman et al., 1989).

8. TEXTURAL CHARACTERISTICS

Native starches have ability to retrograde with passage of time. GCWS exhibited higher paste viscosities and weak gel formation even at room temperature which suggests limited retrogradation capacity during storage (Baik and Jackowski, 2004).

Textural parameters can be tailored by addition of PG starches. For example in a batter aeration creates network of starch granules during mixing of ingredients. This network must be strong to prevent escape of air bubbles during fermentation. This target could be achieved by using PG due to its sticky and gummy property. In terms of firmness; tender, soft and wet crumb can be obtained by using adequate amount of PG as it will bind the water and will not let it to evaporate during baking (Onyango et al., 2011).

Extruded PG starches containing sugars also showed improved paste network, firmness, consistency and cohesiveness (Hedayati et al., 2016). Drum dried PG starches showed weakened internal structure thereby decreasing textural attributes compared to GCWS starches (Hedayati et al., 2016). As GCWS starches has small particles therefore it provides a strong interconnected network; increasing cohesiveness. Whereas, PG starches obtained by drum drying has large particle sizes which prevents consistent paste formation (weakened gel network).

9. APPLICATIONS OF INSTANT STARCHES

Native and modified instant starches have various applications in food products. Some of these are as follows

- Fat replacers
- Coating agents
- Mayonnaise
- Ice creams
- Emulsion stabilizers
- Texture modifiers
- Cheese analogues
- Gluten substitute
- Shape retaining products

Staling and firmness is an important parameter under consideration when employed in freshly baked products. Moisture loss is directly associated with staling. Firmness increases when products stale. Products with high
moisture contents retard staling. Adding hydrocolloids specially pregelatinized / instant starches will help to retain moisture in the product and subsequently retard staling b/c of its higher water binding capacity. It has been confirmed by incorporation of instant starches in microwave-baked cakes as well (Seyhun et al., 2005).

Food coatings serve as a vehicle to impart flavor e.g. sugar coated candies, frying batters, chocolate coated ice creams etc. Functional food coatings improve the functional attributes of products by imparting little or no flavor. Pregelatinized starches also serve as coating agents without affecting the original characteristics of food. Coating film provides homogenous and sheen effect to product by imparting barrier against oxidative deterioration and oil absorption capacity. Different products like potato chips can be coated with PG starch which prevents oil uptake, increase crispiness, decreases reconstitution time (frying accomplished) and imparts better functional characteristics than uncoated fresh french fries (Louis, 1970; Thorpe and Kunerth, 2005). Pregelatinized starch can act as a gluten substitute as well (Toufeili et al., 1994).

Increasing demand of fat mimetics have paved their way into markets today. They provide sensorial properties like oil (e.g. slippery mouth feel); thus, helps in replacing oil in food. Pregelatinized starches play an important role in this regard. Instant starches can act as a fat replacer (3-7% of total product weight) in variety of products eliminating the harmful effect of fat on our health (Sajilata and Singhal, 2005).

Cheese is a nutritious product consumed worldwide. But it has high caloric content. Its caloric value can be reduced with PG. Although PG also acts as a total or partial caseinate replacement. Casein being high in cost is a major concern to food processors. Gelling and emulsion stabilizing properties of caseinate can be somehow achieved by using pregel starch. As emulsifying properties not only depends on the oil content being used, rather also depends on the amount of caseinate being replaced by derivitized PG (Zwiercan et al., 1986).

Shape retaining products like custards, puddings and similar products can also be prepared by mixing starch with edible organic carboxylic acids or edible thickeners and finally drying with spray drier (Eduard and Karl, 1967).

CONCLUSION

The significance of instant starches can never be neglected for food industries. Their versatile nature and compatibility with various foods allow the manufacturer for its application in food, beverages and ready to eat products. Pregelatinized / instant starches’ multifunctional attributes have paved their way into international markets. They are used as fat-replacers, thickeners, as adhesives in batter, as coating agent and as texturizers. The instant starches save money by reducing energy cost (heating and cooling), precludes the need of heating assembly, thereby reducing the total production time. Its cooked-up nature resulted in production of ready to eat version of most popular food products. Instant starches are now marketed by different companies with diversified traits to suit different applications. They are made by using single or combination of methods to produce different gel structures. The specific properties of pregels have benefited snack, baking, sauce, mayonnaise, cheese, noodles and various other industries by increasing yield, improving machining properties, improving water binding capacity, conferring improved flavor and texture and by acting as fat-mimetic to reduce the caloric load.

5. REFERENCES

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