Cold water swelling starch: methods to prepare and recent applications

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Abstract. Cold water swelling starch (CWSS) offers advantage of unique properties over its origin. Among methods available to prepare CWSS, heating starch in ethanol can be considered to be the simplest one. The unique features of CWSS are depending on its starch origin and degree of conversion; therefore, its application should be specific depending on the feature of CWSS. This review summarizes methods to produce CWSS, advantage of producing CWSS by heating starch in ethanol method, the most important features of CWSS that influence its applicability, and exploration on CWSS applications. We expect that this review will be beneficial for food industries that utilize modified starch as ingredient in their products as well as researchers who seek potential applications of CWSS.

1. Introduction
Starch is one of the most abundant biopolymers built from two major components namely amylose and amylopectin. Amylose is a macromolecule primarily linear glucose chains linked each other by α-(1-4) glycosidic bond while amylopectin is a highly branched molecule with α-(1-4) linked D-glucose as backbones and branches of glucose chains interlinked with backbones by α-(1-6) glycosidic bond [1]. The proportion as well packing arrangement of amylose and amylopectin within the starch structure influence the properties of the native starch.

Native starches are inherently unsuitable for most applications due to limited characteristics such as insoluble in cold water, loss of viscosity at high cooking temperature, and low thickening power post cooking [2]. Therefore, most starch need to be modified either by chemical or physical modification prior to application in food industry. Modified starch can be used in many food products as thickeners, gelling agents and encapsulating agents. It also can be used for other non-food applications such as in papermaking industry. Some modified starch can also be used as a wet-end additive in coating binders. In textile industry, modified starch is an important ingredient for warp sizing of textiles also glass fibre sizing [3].

Due to certain safety considerations such as the requirement to produce no chemical residue after starch modification process, some food industry prefer to use physically modified starch over chemical modified ones. The most common argument is that physical modified starch is considered safer for human consumption [4]. Instantane gelatinized starch is an example of physically modified starch which can be produced either by pre-gelatinized starch (PGS) and cold water swelling starch (CWSS) methods.
PGS can be prepared by heating starch in excess of water at above the gelatinization temperature of starch while CWSS can be produced by certain methods to swell starch granules at some extent [5]. The CWSS gives more superior properties compared to PGS. The CWSS offers greater solubility, viscosity, smoother texture and more tolerance for further processing [6].

2. Methods to produce cold water swelling starch

Effort to develop starch products that is soluble in cold water has been started since the mid of 1950. Knowledge on the starch granule morphology and pasting behavior of native starch brought out the ideas to produce instantaneous soluble starch. Powell E L [7] reported that pre-gelatinized starch could be prepared by drum drying, extrusion, and conventional cooking followed by spray drying processes. The pre-gelatinized starch product exhibits inferior properties such as graininess, less sheen and less flexible for further processing; thus the product has lower quality than the freshly cooked-up product. However, method of pre-gelatinized starch cooking is still implemented to prepare certain food products such as instant porridges.

Lindqvist I [8] was the first who revealed the ability of starch to gelatinize in cold water after it was treated with potassium iodide (KI) and potassium thiocyanate (KSCN). Pitchon E, et al. [9] introduced a process to prepare CWSS using a special spray drying technique. The starch slurry was atomized in an enclosed chamber from one nozzle, and then at the same time, the other nozzle injected a high-pressure steam to cook up the starch. The product showed indented spheres and swelled well upon rehydration. The major disadvantages of this technique were the high capital cost to construct the spray dryer and the high operational cost of spray dryer.

The first patent of CWSS preparation process was filed by Eastman J E and Moore C O [10]. In their method, normal starch was slurried in an aqueous alcohol and then it is subjected to high temperature in a pressurized autoclave. The CWSS obtained by this method exhibited higher solubility than that of normal starch. However, this method could not be applied for waxy starch because the starch completely gelatinized during the conversion process. Eastman J E [11] successfully polished up his previous method to convert waxy starch to become CWSS. The CWSS product obtained by this method was claimed to be chemically unmodified. The CWSS product can be set to become a sliceable gel without cooking or chilling when it was blended with aqueous sugar syrup. The CWSS product was also claimed to be useful for ingredient of many instant food products such as pie fillings, jellies, demouldable desserts, and puddings.

Rajagopalan S and Seib P A [12] successfully patented another method to prepare CWSS. In their method, starch slurry of a mixture of starch, water and polyhydric alcohol was heated in an atmospheric pressure. The successful keys of the method depended on the type of starch, type of polyhydric alcohol, temperature and the proportions of starch, water, and polyhydric alcohol. Aqueous propan-1,2-diol was the most preferable medium, although aqueous ethylene glycol, glycerol and any other four positional isomers of butandiol were also useful. Aqueous butandiol was the most effective reagent to convert hydroxypropylated starch to CWSS, while aqueous glycerol was the most effective reagent when the starting material was potato starch. This finding was significant in terms of energy conservation for CWSS processing. They claimed that the method can be applied to produce CWSS from many starch sources such as cereal, tuber, root, and legume starches. They also reported that the CWSS products had cold water solubility up to 95%.

Another patent related to CWSS preparation method was released by Jane J and Seib P A [13]. They claimed that the new method was capable to prepare CWSS from waxy rice or high amylose starches which could not be achieved by another previous method. In their method, they used a mixture of ethanol and alkali. The alkali (primarily NaOH) was functioned to swell the starch granules; meanwhile, the ethanol was used to prevent the starch granule from disintegration. The treated starch was then neutralized with HCl, washed and dried at 80°C. They found that higher percentage of used NaOH will produce CWSS with higher solubility.

A new approach in CWSS preparation method was introduced by Wang J, et al. [14] in which they used polyethylene glycol to gelatinize the starch. In this method, polyethylene glycol acts as a grafting
agent to create micro pits on the starch granule surface. Therefore, allowing water molecules to penetrate inward and swell the starch granule.

3. Advantage of producing CWSS by heating starch in ethanol method

Simple CWSS preparation method was demonstrated by Zhang B, et al. [15]. A mix of starch and aqueous alcohol was heated in a rotary evaporator in order to facilitate uniform mixing and at the same time it is functioned to evaporate the reactant. The development was mainly intended to avoid the use of harsh chemical such as NaOH. Unfortunately, this method was not applicable to prepare CWSS from waxy starch because the starch granules underwent rapid swelling and gelling upon conversion. Dries D M, et al. [16] prepared CWSS by heating a mixture of water-ethanol in a leak-proof Schott bottle. The method is relatively simple to obtain CWSS in a lab scale. Also heating starch in ethanol can be considered to be the simplest and green process for preparing CWSS. After the conversion process the ethanol can be completely removed from the CWSS product by dehydration [15, 16].

4. The most important features of CWSS that influence its applications

4.1. Solubility and water absorption in cold water

Solubility in cold water is one of the most essential properties of CWSS. Pre-gelatinized starch and CWSS are both known as instantaneous soluble starch product; however, CWSS has lower solubility than pre-gelatinized starch. Majzoobi M, et al. [17] reported that the solubility of CWSS from maize starch was 6.24% while that of pre-gelatinized starch from maize starch was 8.45%. Decreasing or increasing the pH of solution tends to increase the solubility of CWSS [5]. Moreover, increasing the solubilization temperature also increases the solubility of CWSS [18].

The water absorption capacity of CWSS reflects the ability of CWSS to absorb and hold water within its matrix. Pre-gelatinized starch shows higher cold water solubility than CWSS, but CWSS exhibits higher cold water absorption capacity than pre-gelatinized starch. Jane J, et al. [19] reported that CWSS from maize starch had water absorption capacity of 12.33 g/g while pre-gelatinized starch was 9.85 g/g. Hedayati S, et al. [5] also reported similar result in that the water absorption capacity of CWSS from maize starch reached 13.35 g/g which was higher than that of pre-gelatinized starch (10.04 g/g). The water adsorption capacity of CWSS and pre-gelatinized starch increased at high pH and decreased at low pH [5]. CWSS that still preserve its granular form and CWSS that losses its granular form have almost similar water absorption capacity values, however, both CWSS have different mechanism to absorb water [20]. Upon water absorption, CWSS with granular form absorb water via fissures on the granule surface meanwhile, water is entrapped within the three-dimensional structure of starch components of non-granular CWSS.

Packing arrangement of amylopectin which constructs the native crystallinity of starch is also expressed in the physical properties of the starch. The degree of conversion of CWSS is affected by the native crystallinity of the raw starch. Chen J and Jane J [21] investigated the effect of native starch crystallinity during CWSS conversion by using the cold water solubility as indicator. The cold water solubility of normal maize which is a typical of A-type starch exhibited lower than cold solubility of Hylon 5 which has B-type crystalline, respectively, 22% and 90%. Imberty A and Perez S [22] recorded that B-type starches has space in the unit cell whereas A-type starches is more densely packed. Therefore the structure of B-type is more susceptible to any treatments [23-25]. From their observation Chen J and Jane J [21] supposed that this was because of the effect of crystalline structures of the raw starch which brings consequence the CWSS prepared from B-type starches has higher cold water solubility than those prepared from A-type crystalline starches.
Table 1. Cold water solubility of CWSS prepared from different starch sources which have different native crystalline type [21].

| Sample       | Native crystalline type | % CWSS solubility |
|--------------|-------------------------|-------------------|
| Normal maize | A                       | 22.5±3.5*         |
| Hylon 5      | B                       | 90.3±2.1          |

*Data shown as mean ± standard deviation of duplicate samples

4.2. V-type crystalline structure of amylose-ethanol complex

The V-type crystalline structure is formed when guest molecules resides in the cavity of amylose chain as observed by X-ray diffraction technique. This structure may present as an artifact of a complex between amylose and ethanol during CWSS conversion process. This is because ethanol can be removed from the cavity of amylose by dehydration means [16].

Table 2. Amylose contents of native starches was determined using the Megazyme assay kit and the peak degrees of polymerization (DPpeak) of amylose chain was determined using high performance size exclusion chromatography (HPSEC) [26].

| Starch sources | Amylose content (% dry matter) | DP peak of amylose chain |
|----------------|-------------------------------|--------------------------|
| Maize*         | 23.7                          | 1710                     |
| Rice           | 18.1                          | 1520                     |
| Cassava        | 17.3                          | 4240                     |
| Potato         | 14.8                          | 3520                     |
| Pea            | 26.8                          | 2150                     |

*This value was previously published in [16]

The role of amylose during CWSS conversion has been investigated since early finding of this modified starch [15, 16, 27-29]. Most of them agreed that linear AM chains are the main component responsible for V-type crystal formation in CWSS structure. In the recent paper published by Dries D M, et al. [26], they reported the role of amylose in term of amount and chain length (in term of degree of polymerization, DP) of the amylose during CWSS conversion. They found that V-type crystalline never exceeded the AM contents of the starches. However, they did not find any quantitative relation between the levels of VH-type crystalline with the amylose contents. In contrast, they found a qualitative relation between the chain length of amylose and V-type crystalline in which the VH-type crystalline in the CWSS decreased with increasing amylose DP. The higher the amylose DP, the more strongly V-type crystal formation is hindered. The molecular weight-dependency is well-known in crystallization of synthetic peak polymers [30] and it is explained by the increased occurrence of entanglements for polymers of higher molecular weight. In addition, Dries D M, et al. [16] emphasized that these entanglements are part of the amorphous regions, which explains why starches with a higher amylose DP have lower V-type crystallinity.

Different with amylose that involved in the V type crystal formation, the amyllopectin structure which constructs the native crystalline was loss, in some part, during CWSS conversion. In 1986, Jane J-L, et al. [31] proposed a mechanism to explain the structural transition during formation of CWSS. They hypothesized after native crystal melting; the alcohol rapidly induces single helical formation and V-type crystalline with alcohol being located within the single helix cavities and possibly interstices. Their hypothesis is based on their observation that the endothermic heat of gelatinized starch in aqueous alcohol was lower than in pure water. Jane et al. (1986) also reported that formation of VH-type
crystalline is mainly assigned equally by the presence of amylose and amylopectin based on the comparison of the X-ray diffraction pattern of their sample with a reference sample. In fact this hypothesis cannot be applied for all starch types. Chen J and Jane J [28] found that no V-type crystalline was exist in CWSS from waxy maize starch. Another report by Zhang B, et al. [15] stated that all CWSS prepared from A-, and B-type sources displayed V-type crystalline except for partially converted waxy maize starches. This fact lead to another hypothesis proposed by Dries D M, et al. [16] that crystallinity transition during CWSS formation requires amylose during nucleation of V-type crystalline and the amylopectin contribution is triggered by amylose.

Table 3. Degree of A-, B, and VH-type crystallinity (%) for native and CWSS determined by wide angle X-ray diffraction (WAXD) [26].

| Starch source | Crystalline type | % crystallinity in native starch | % crystallinity in CWSS |
|---------------|-----------------|---------------------------------|------------------------|
| Maize*        | A               | 27                              | 0                      |
|               | VH              | 2                               | 18                     |
| Rice          | A               | 33                              | 0                      |
|               | VH              | 2                               | 16                     |
| Cassava       | A               | 40                              | 0                      |
|               | VH              | 0                               | 10                     |
| Potato        | B               | 38                              | 0                      |
|               | VH              | 0                               | 10                     |
| Pea           | A               | 13                              | 0                      |
|               | B               | 12                              | 0                      |
|               | VH              | 0                               | 13                     |

*data for maize starch were previously published in [16].

Figure 1. The proposed model of gradual structural transformations of cold water swelling starch prepared by heating in ethanol method [32].

A model developed by Jane J, et al. [27] described the transformations of CWSS as a single step process at the crystalline structural level, while related phenomena at higher structural levels were not considered. Sarifudin A, et al. [32] developed a model that includes the transformations of starch at different structural levels during CWSS conversion. The model of was developed based on the real time observation of structural transformation at crystalline and lamellae levels. They found that when the temperature increased the thermal energy of the system started to rise. It was sufficient to mobilize the mesogen toward a more stable conformation, as indicated by the increase in the crystalline lamellae thickness. The ability of crystalline lamellae to realign into the most perfect register is illustrated by stage III. Above the maximum stress resilience temperature, the crystalline lamella starts to be disrupted which is illustrated by stage IV. Stage VI illustrates the loss of birefringence of the CWSS granules heated at high temperature (100 °C), but they were still in granular form. This might be attributed to the
role of amylose chains and amylose-ethanol complexes to preserve the integrity of the CWSS granules [16, 26].

4.3. Morphology of dried and hydrated CWSS
Conversion to CWSS indeed changes the morphology of native starch. Singh N, et al. [33] reported native corn starch granules appeared less smooth, rounded and angular shaped, meanwhile potato starch granules showed smooth, some were irregular or cuboidal shapes and others were larger oval, and few small granules. The size of corn starch granules were range between 5-7 μm for small granules and 15-18 μm for large granules and for potato starch granules have size between 15-20 μm for small granules and 20-45 μm for large granules. When native starches was subjected to CWSS treatment they underwent morphological changes [34]. They observed that the CWSS of potato starch granules swelled to higher extent more than corn starch granules indicating the effect CWSS conversion on the starch morphology was visually more pronounce for potato starch than that for corn starch. However, the morphological properties of CWSS prepared from different preparation methods do not show much difference between them. Chen J and Jane J [21] that used alcoholic-alkaline treatment for preparing CWSS also observed that there were indentation on the CWSS potato starch granules but the shapes were not rupture. Zhang B, et al. [15] that used rotary evaporation at high temperature for CWSS preparation also noticed that CWSS from potato starch showed bigger size than that of maize starch when observed under light microscope. All reports mentioned that observation of CWSS by using SEM technique indicated that shrinkage in the centre region of the granules can be due to internal fragmentation.

| Sample     | Corn starch granules | Potato starch granules |
|------------|----------------------|------------------------|
| Native     | ![A1](image1)         | ![B1](image2)          |
| CWSS       | ![A2](image3)         | ![B2](image4)          |

*Figure 2.* Native starch and CWSS under scanning electron microscope [15, 33].

Zhang B, et al. [15] reported that native corn starch appeared to have shape polygonal with a distinct Maltese cross in each granule under polarized light microscope. Native potato starch showed smooth, round to oval shaped and it also showed distinct birefringence. As the native starch converted to CWSS, the granules swollen thus increasing the granule size which was correlated with the amount of water adsorbed within the CWSS granules [15]. The CWSS granules started to burst from the hilum region (dark area in the center of most CWSS granules) with wrinkling pattern on the surface. Under polarized light microscope showed majority of granules loss their Maltese cross. However, a diffuse birefringence pattern can still be observed in the outer part of granules. This might be an indication that their native crystalline at the outer layer can still be maintained after CWSS conversion [15, 16].
| Sample               | Corn starch granules | Potato starch granules |
|----------------------|----------------------|------------------------|
| Native               | ![A1](image)         | ![B1](image)          |
| CWSS                 | ![A2](image)         | ![B2](image)          |
|                      | ![A3](image)         | ![B3](image)          |
|                      | ![A4](image)         | ![B4](image)          |

**Figure 3.** Native starch and CWSS under normal light microscope (A1, B1, A3, B3) and polarized light microscope (A2, B2, A4, B4) [15].

### 4.4. Pore characteristics of CWSS

Porous starch is a modified starch product which is prepared to enhance the porosity of native starch, thus increasing its water absorption capacity [35, 36]. Another type of starch that exhibits high water absorption capacity is cold water swelling starch (CWSS). Many studies have reported the capability of CWSS to absorb water at low temperatures [16, 29]. CWSS can absorb water up to 12 times more than its weight [17]. Meanwhile, porous starch can only maximally absorb water up to 3 times more than its weight [35]. Therefore, it is advantageous to use CWSS over porous starch in terms of their water absorption capacity.

The capability of CWSS to absorb high amount of water can be an indication that it has high porosity. Model of Jane J, et al. [37] explained that the structure of native starch drastically changes after it is converted to CWSS. The crystalline structure turned to amorphous structure. The amorphous structure provides more free space to reside guest molecules within it [38].

Sarifudin A, et al. [20] reported that CWSS that still has granular form such as CWSS from maize and potato starches contains non-rigid and slit-shaped pores. Meanwhile, CWSS that doesn’t maintain their granular form lost their functional pore. For granular CWSS, water penetrated the granules through the fissures, hydrated the amorphous regions, melted the V-type crystalline structure, and was held within the CWSS granules upon water absorption. For non-granular CWSS, water hydrated the amorphous and V-type crystalline structures, and was entrapped within a three-dimensional network of starch components upon contact with water.
5. Recent applications of CWSS
In the first time of CWSS finding, it was developed in tandem with pre-gelatinized starch to overcome the low solubility of native starch [10]. Due to their capability to adsorb cold water and swell promptly, giving appearance and texture of a cooked-like starch. Therefore, they are commonly used for ready-to-be-consumed product [10]. These modified starches are used as ingredients of instant foods such as pie fillings, jellies, demouldable desserts, and puddings Eastman J E [11].

CWSS has been used to encapsulate active ingredients [39, 40]. They reported that the encapsulated product properties by CWSS were influenced by the encapsulation method. Chen J and Jane J [40] used water as a medium during encapsulating atrazine by CWSS. They reported that chemical interactions between atrazine and starch components did not occur; instead, B-type diffraction appeared as an indication of starch gel retrogradation. Dries D M, et al. [39] used multiple encapsulation stages involving water-ethanol mixture to encapsulate ascorbyl palmitate using CWSS. The method was applied to retain the V-type crystalline structure in the final product.

Boonwatcharapan Y, et al. [41] has investigated alcohol-alkaline-treated rice starch as a tablet disintegrant. They reported that the modified rice starch exhibited higher water solubility and swelling capacity compared to that of native rice starch. They also suggested that the modified rice starch was a good disintegrant for direct-compressed tablet formulations, especially in the presence of water insoluble fillers. The most recent investigation suggested that CWSS is potential for excipients of medicinal tablet [42]. They reported that tablet prepared from CWSS are potential to be used in controlled release system. tablet prepared from granular CWSS showed high friability and low crushing strength indexes, and dispersed and released active ingredients rapidly upon contact with water. Therefore, it is suitable for fast release system. Moreover, tablet from non-granular CWSS exhibited low friability and high crushing strength indexes. Upon hydration, the tablet of non-granular CWSS containing lauric acid eroded gradually and released the active ingredient during tablet erosion. Meanwhile, the tablet of non-granular CWSS containing ascorbic acid swelled slowly during hydration, and the active ingredient diffused out gradually from the swelled tablet. Therefore, the non-granular CWSS is suitable for ingredient of tablet for sustained release system [42].

6. Conclusions
CWSS can be prepared by mixing between gelatinization inducer and anti-swelling agent in certain proportion. However, heating starch in ethanol method is the most simplest method to prepare CWSS since it doesn’t require to do neutralization step also the reactant (ethanol) can be removed completely from the product during dehydration process. The most important features of CWSS are correlated to the capability of CWSS to absorb water and swell instantaneously. CWSS which is commonly used for ingredient of instant product, recently, it is used for encapsulating agent of active ingredients and also binder of medicinal tablet for sustained release system.

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