Nano Crystalline Starch And Its Alternatif Implementation

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***Abstract*:**
Starch, normally consisting of amylose and amylopectin, is a partially crystalline polymeric substance. Native starch granules may give A-, B-, C-, and V-type X-ray diffraction patterns. A-type crystalline structure occurs in cereal starches, whereas B-type structure is found in tuber, root, and amylose-rich starches. The C-type polymorph is a mixture of A- and B-type polymorphs and occurs in some tuber and legume starches. The V-type diffraction pattern is given by amylose lipids, iodine, and alcohol complexes. Upon heating in water, starch undergoes gelatinization, which breaks up its crystalline structure. During subsequent cooling and storage, recrystallization or retrogradation of gelatinized starch occurs. Process technology responsible to the strach product characteristics and to be advance develop in the next product. Hydrolysis and partial hydrolysis is one great chance to be advanced development to produce nano cristalline starch. One of alternative technology throughout nano crystalline starch technology process production. In this paper would be review and discuss more about nano starch technology, its process production, characteristics and alternative its implementation in the advance product such as composite, or another alternative advanced developments.

***Key words*:** Nano, starch, process, alternative implementation

1. Introduction

Starch, normally consisting of amylose and amylopectin, is a partially crystalline polymeric substance. Native starch granules may give A-, B-, C-, and V-type X-ray diffraction patterns. A-type crystalline structure occurs in cereal starches, whereas B-type structure is found in tuber, root, and amylose-rich starches. The C-type polymorph is a mixture of A- and B-type polymorphs and occurs in some tuber and legume starches. The V-type diffraction pattern is given by amylose lipids, iodine, and alcohol complexes. Upon heating in water, starch undergoes gelatinization, which breaks up its crystalline structure.

The convensional model for the inner structure of starch is that it is formed from two regions- crystalline and amorphous lamella, which together form the crystalline and amorphous growth rings [1]. The dominant component of the cystalline region in native starch granules is thought to be amylopectin lamellae [2,3], which pack together to form double helix crystal structure [4,5]. In Crystallites of starch, parallel stranded double helical structure is found in pairs, and all chains are packed in arrays.

During subsequent cooling and storage, recrystallization or retrogradation of gelatinized starch occurs. Process technology responsible to the strach product characteristics and to be advance develop in the next product. Hydrolysis and partial hydrolysis is one great chance to be advanced development to produce nano cristalline starch. One of alternative technology throughout nano crystalline starch technology process production.

In this paper would be review and discuss more about nano starch technology, its process production, characteristics and alternative its implementation in the advance product such as composite, or another alternative advanced developments.

2. Materials And Methods

All of scientific paper about nanao crsystalline starch process production, characteristics, and implemenation collect, discuss and analysis also adjust what the benafit could be reached and advanced develop it. In this paper would be review and discuss more about nano starch technology based on the scientific data.

3. Results And Discussion

Process Production

Research in the starch nanocrystal increased related with increasing the benefit of its mataerials. Based on [6], summarized the articles dealing with starch nanocrystals as shown in the Figure 1 below.

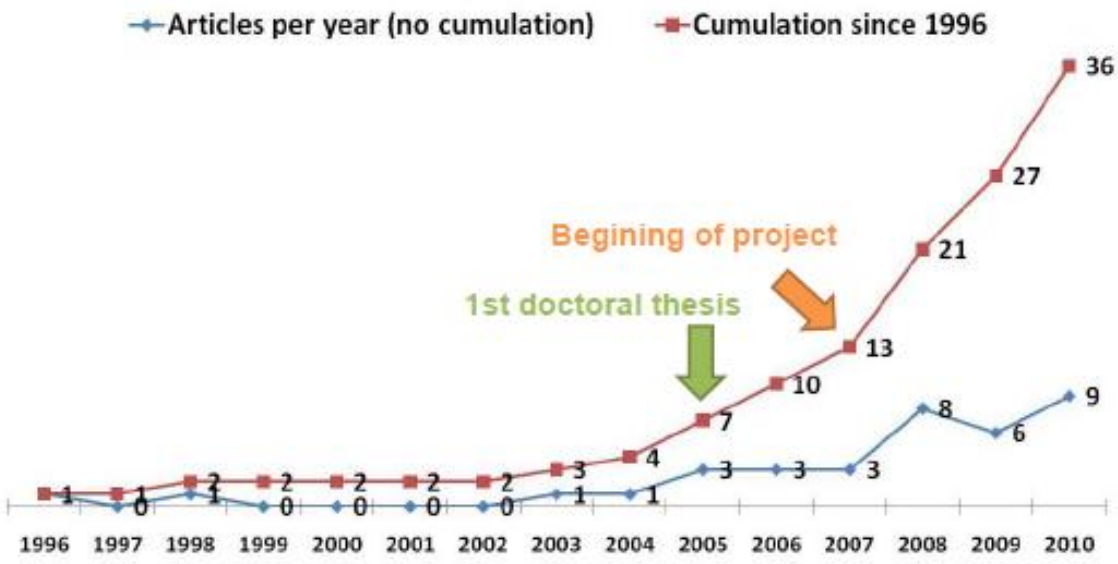

Figure 1.Articles dealing with starch nanocrystals [6]

Starch is a natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy. It is the second most abundant biomass material in nature. The starch structure has been under research for years, and because of its complexity, an universally accepted model is still lacking. However, the predominant model for starch is a concentric semicrystalline multiscale structure that allows the production of new nanoelements: (i) starch nanocrystals resulting from the disruption of amorphous domains from semicrystalline granules by acid hydrolysis and (ii) starch nanoparticles produced from gelatinized starch [7].

The derived of nano starch process production, colud be separate in three types which are nano crystalline, nano particle and nano colloids. Nano crystalline produced commonly hydrolysis used to anzymatic and acid process production. While nano particle through regenation and precipitation. Nano colloids processed throughout mechanical treatment as shown in the Figure 2 below.

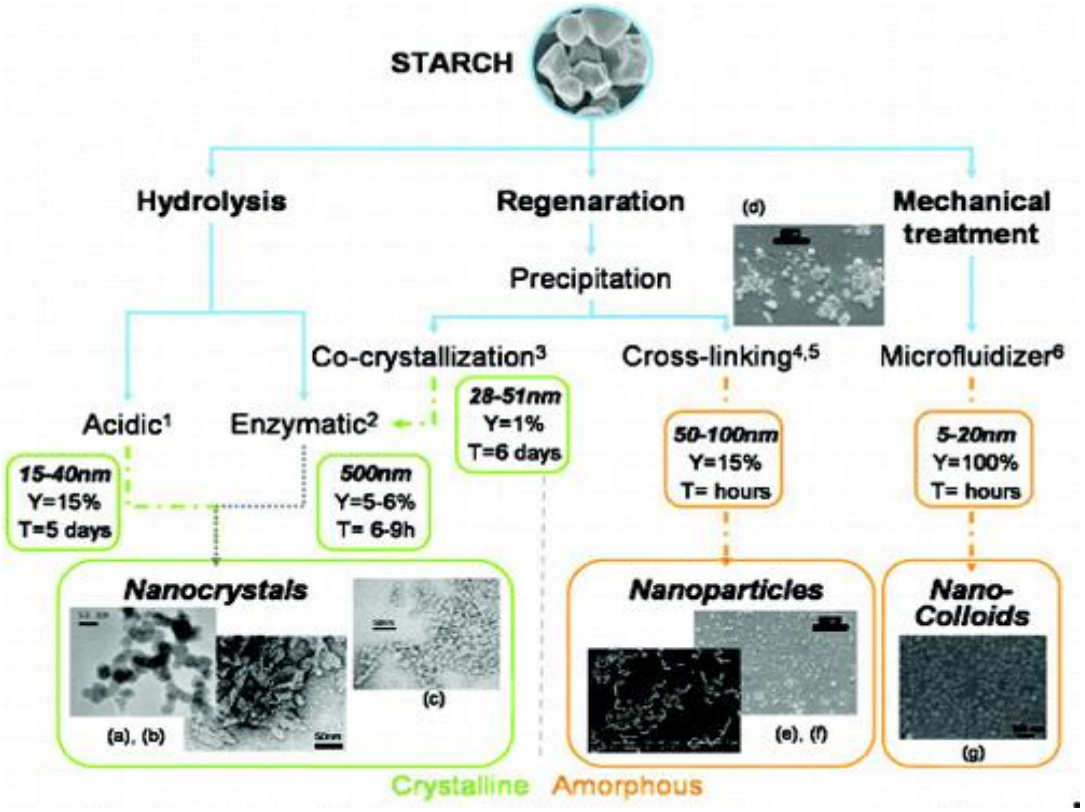

Figure 2. Decreasing cristalinity Process Production [7]

One of detail process production of nano crystal followed by [8] below.

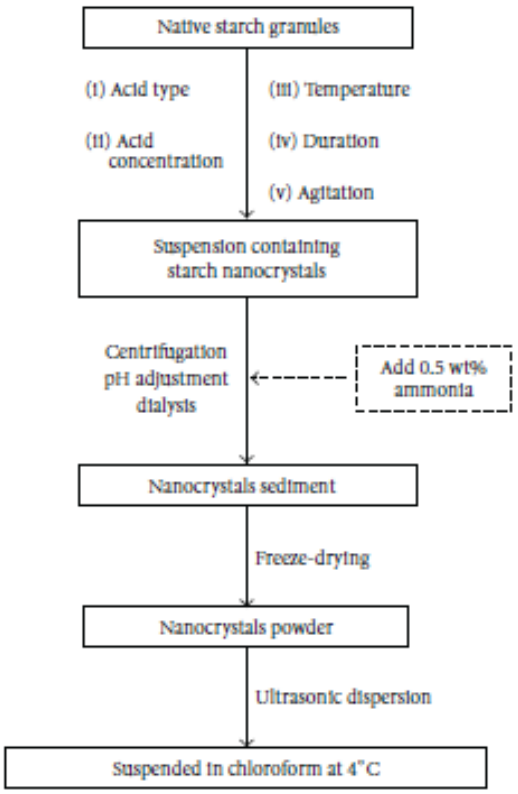

Figure 3. Extraction procedure and preservation method for starch Nanocrystals [8]

The crystalline region of starch granules can be isolated by mild acid hydrolysis or sulfuric acid [9]. It is believed that temperatures below the gelatinization temperature acid molecules preferentially attack the amorphous regions of the granule [10]. Resulting in these regions being more rapidly hydolyzed than the crystalline regions. Below summarized the nano crystalline starch process production from several ways [11]. The others author also held research and summarized as shown below.

Table 1. Technology Process Production of Nano Cristalline Starch

No	Process Production	Result	Autors
1	Stsrch hydrolysis used to 0,5 % concentartion of isoamylase enzyme with different time process production (1 until 24 hours)	3,8 until 10,3 nm	[12]
2	SCA hydrolysis used to isoamylase with 1% isoamlyase concentration in 24 hours process production	10,4 until 11,5 nm	[13]
3	Maizena starch hydrolysis used to Chloric acid with 2,2 mol/ L for 40 days	20 until 40 nm	[14]
4	Maizena starch hydrolysis used to H2SO4 2,87 mol/L	50 nm	[15]

Cai et al [12] and Cai et al [13] processd starch hydrolysis used to Isoamylase enzyme with different concentration resulted 3,6 until 10,3 nm with 0,5% concentration and 10,4 until 11,5 nm with 1% isoamylase enzyme concentration. Enzymatic debranching is another way to release SCA (Short-Chain Amylose). The substrate materials could be glycogen, maltodextrin or starch. According to [16], enzymatically debranched glycogen produced linear chains with average DP = 11. [17] reported that two stage crystallization occured during debranching of a high concentration of maltodextrins by isoamylase.

While [14] used to chloric acid to hydrolysis maizena resulted 20 until 40 nm crystaline starch. While hydrolysis maizena used to 2,87 mol/L H2SO4 resulted 50 nm nano crystalline starch [15]. Based on its research, nano crystalline starch could be produced throughout several ways both on enzymatic and chemical ways.

Characterisation

Wide-angle-X ray diffraction (WAXD) using synchrotron radiation has been developed as a tool for anlysis of polymers (Riekel and Davies, 2005). Synchrotron WAXD has been applied to study the ultrastructure of starch (Buleon et al, 1998); gelatinization behaviors (Gebhardt et al, 2007) and amylose-lipid interactions (Derycke et al, 2005). WAXD also could be advanced analysis for nano crystalline starch as Cai et al [13] research resulted in Table 2.

Table 2 . Relative crystallinity and approximate average size of polymorph crystallites of short-chain amylose from debranched waxy wheat starch, debranched waxy maize starch, and debranched waxy potato starch as determined by synchrotron wideangle X-ray diffraction.a,b [13]

Samples	Relative Crustalinity (%)	Average Size of Crystalinity (nm)
Debranched waxy wheat	58,7± 0,3	11,5± 0,3
Debranched waxy maize	55,6±0,1	10,9± 0,1
Debranched waxy potato	53,0±1,0	10,4 ± 0,1

Relative crystallinity and approximate average size of polymorph crystallites of short chain amylose from debranched waxy wheat starch, debranched waxy maize starch and debranched waxy potato starch determined by WAXD resulted 11,5, 10,9 and 10,4 nm. This method also used by [12] to analyzed the average size of polymorph crystallites of native waxy maize starch and waxy maize starch debranched in different times as shown below.

Table 3. Average size of polymorph crystallites of native waxy maize starch and waxy maize starch debranched at different times as determined by wide angle X-ray diffraction [12].

Samples	Size (nm)	
	Powder (ca. 4% moisture)	Hydrated (45% moisture)
Native starch[a]	8.1	9.4
Debranched		
1 h	3.8	9.7
2 h	4.0	8.8
4 h	4.8	8.5
8 h	10.3	12.4
16 h	9.5	14.8
24 h	9.8	14.5

[a] The moisture of native waxy maize starch powder was about 11%.

Using WAXD could be identified the size of crystallites in the maize starch and products debranched at different time. At 1,2,4 hours of debranching , the size of crystallites was small (< 5 nm in dry state), but dramatically increased to 10 nm in dry state and 12 nm in hydrated state after 8 hours of debranching. This phenomenon predicted that co crystallization could be produced larger crystallites size process production.

The schematic reducing process production and crystallites size result also defined in [6] as shown in the Figure 4.

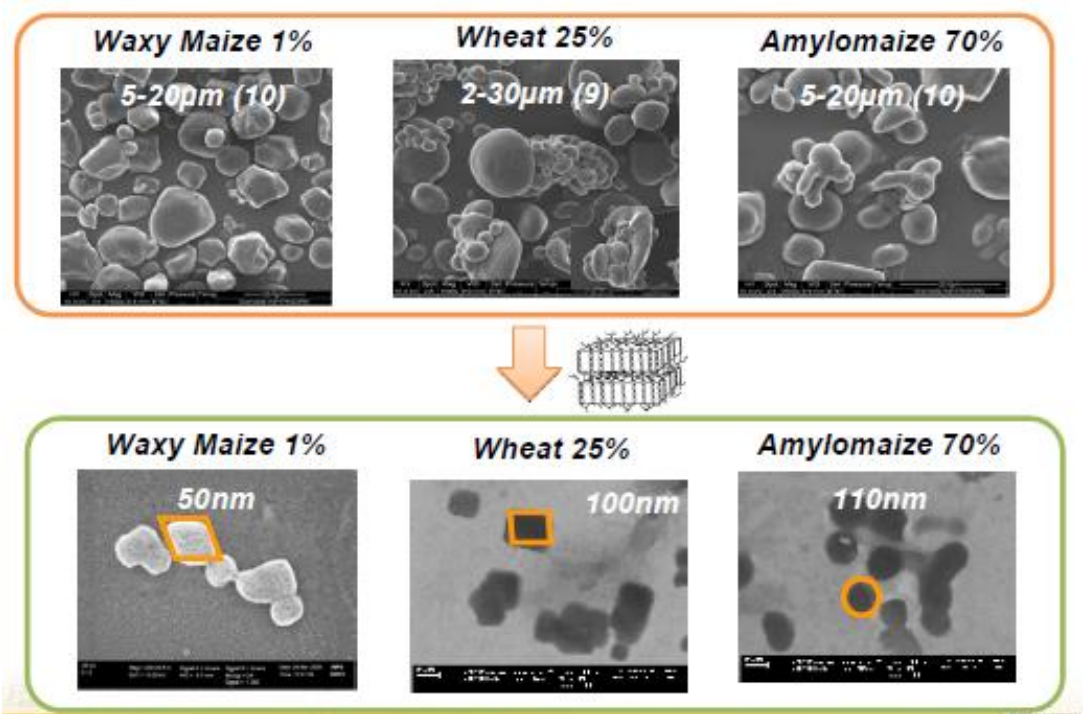

Figure 4. Starch nano crystal reduction [6]

Le core et al [6] identified nano crystal reduction from micro structure. Waxy maize with concentration 1% could be reduced from 5-20 µm reduced to be 50 nm; wheat starch from 2-30 µm to 100 nm; and amylomaize 5-20 µm to 110 nm.

Alternative Implementation

Resistant Starch

The in vitro digestion profiles of native waxy maize starch, waxy maize starch at different debranching times, and isolated crystalline materials. Native waxy maize starch had a very low RS content (<5%). After debranching, RS content increased with time. The rate of increase in RS content was slow from 0 to 4 h but significantly increased from 4 to 24 h. After 24 h at 50 ◦C, a product with 71.4% RS content was formed [12].

Table 4. Levels of rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) content in native waxy maize starch, debranched waxy maize starch produced at different times at 50 ◦C and isolated crystalline materials.

Samples	RDS (%)	SDS (%)	RS (%)
Native starch	29 ± 0.4	66.7 ± 0.4	4.3 ± 0.8
Debranched			
1 h	59.8 ± 0.3	32.9 ± 1.4	7.3 ± 1.7
2 h	58.5 ± 1.7	31.5 ± 0.5	10 ± 1.2
4 h	43.5 ± 0.3	38.9 ± 0.6	17.6 ± 0.9
8 h	33.9 ± 1.1	23.3 ± 0.3	42.8 ± 1.4
16 h	25.1 ± 0.4	8.3 ± 0.9	66.6 ± 0.5
24 h	22.5 ± 0.3	6.1 ± 0.1	71.4 ± 0.4
Isolated crystalline materials[a]	4.9 ± 0	8.2 ± 0.8	86.9 ± 0.8

Gelatinisation of high-amylose starches, or linearization of amylopectin with debranching enzymes, followed by controlled retrogradation have been widely used to generate resistant starch [18,19]. A few authors also investigated hydrothermal and enzymatic treatments of starch to promote the formation of SDS. An illustration of retrograded starch chains and the arrangement of amorphous material, which determine SDS formation, is presented in Figure 5.

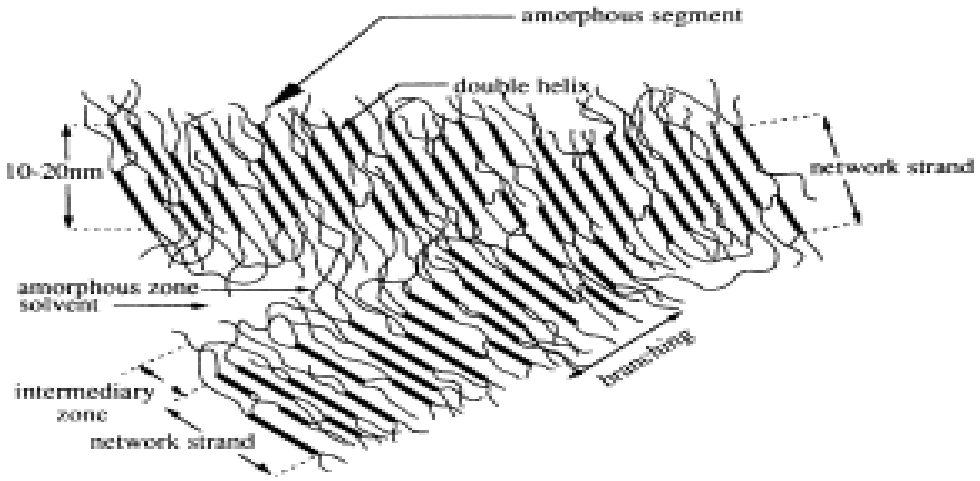

Figure 5. Structure of amylose gels as structural feature of recrystallised SDS [20]

The effect of pullulanase concentration, hydrolysis time and cooling temperature on the SDS content of cooked non-waxy and waxy rice starch was reported [21]. The amylose content and the degree of debranching strongly influenced the kinetics of starch hydrolysis. Debranching of waxy starches resulted in the formation of short amylose chains, favoring the formation of double helices that aggregated into ordered crystalline arrays during cooling. These crystallites are resistant to digestion. In contrast, the presence of longer amylose chains in non-waxy rice starch prevented aggregation and resulted in the formation of a cross-linked network during cooling, leading to a higher digestible material.

Low cooling temperatures favored the nucleation step of crystallization and the formation of SDS, while higher temperatures favored the propagation and maturation steps, resulting into less digestible material. The authors concluded that the resulting SDS fraction might result from the formation of imperfect B-type crystallites with lower density, which are more prone to digestion [22]. The effect of the cooling time on starch digestibility was also reported [22].

Freezing of debranched cooled starches had no effect on digestibility, whereas particle size did. A maximum SDS content of 44% was obtained with waxy rice starch. A similar trend was observed for cooked waxy sorghum starch debranched with isoamylase [23]. The authors confirmed the observation that the resulting SDS fraction might consist of less perfect crystallites and amorphous components. The maximum SDS content obtained was 27%. This technology was patented by [24] who used amylose-containing starches as starting material. SDS was also efficiently generated by [25], using hydrolysis of starches by a-amylase, followed by partial crystallization of the resultant linear chains.

The Others Alternative Implementation

The others alternative implementation of nano starch particle belonged [26] such as Indomethacin matrix, and transdermal drug. All of its alternative implementation as shown in Table 5.

Table 5. Alternative implementation of nano starch particle [26]

Starch Origin	Preparation	Nano Particle	Particle Size	Application	Refference

		Formation			
Tapioca	Copolimerization	Membrane dialysis	65-75 nm	Indomethacin Matrix	[27]
Propyl Starch	Crosslinking	Emulsion Diffusion	180,5-185,3 nm	Transdermal Drug	[28]
Waxy Corn Amylopectin	Polilactic Acid Grafting	Membrane Dialysis	20,7-77,2 nm	Indomethacine Matrix	[29]
Water Soluble Starch	Mini Emulsion Crosslinking	High Pressure Homogenization	100-300 nm		[30]

4. Conclusions

Research in the starch nanocrystal increased related with increasing the benefit of its mataerials. The derived of nano starch process production, colud be separate in three types which are nano crystalline, nano particle and nano colloids. Nano crystalline produced commonly hydrolysis used to anzymatic and acid process production. Based on its research, nano crystalline starch could be produced throughout several ways both on enzymatic and chemical ways. Wide-angle-X ray diffraction (WAXD) using synchrotron radiation has been developed as a tool for anlysis of polymers, to study the ultrastructure of starch, gelatinization behaviors and amylose-lipid interactions. Nano crystallite starch could be increase the resistant starch content in the starch characteristics, which could be advanced develop it. The others alternative implementation of nano starch particle such as Indomethacin matrix, and transdermal drug.

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