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Effects of acid hydrolysis and defatting on crystallinity and pasting properties of freeze-thawed high amylose corn starch

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Abstract

Paste of defatted and/or mildly acid-hydrolyzed high amylose corn starch was freeze-thawed, and then the starch was isolated by vacuum drying for the analysis in crystallization and pasting properties. X-ray diffraction pattern and differential scanning calorimetric analysis showed that the crystallinity of the freeze-thawed starch was increased as the degree of hydrolysis increased. The diffraction pattern revealed B- and V-crystals with patterns with diffraction peaks at 17, 20, and 23–25° (2θ), which were developed by amylose recrystallization during the freeze-thawing. The crystal melting enthalpies, for dual endothermic transitions above 100 °C, which resulted from the melting of amylose–lipids complex and amylose double helices were raised by the treatment. The isolated and dried starch formed a paste by aqueous heating under the ambient pressure, and its paste viscogram exhibited substantially higher resistance to shear-thinning, and rapid setback upon cooling. Acid hydrolysis, however, reduced overall paste viscosity, possibly due to the increased crystallinity. Enzyme-resistant starch content in the acid hydrolyzed starch was increased by the freeze-thawing, but not by acid hydrolysis. It was slightly increased by defatting.

Keywords: Freeze-thawing; Acid hydrolysis; High amylose corn starch; Resistant starch

1. Introduction

Unlike normal starches, the starches from amylose-extended mutants of barley or maize contain unusually high amylose content, from 40 to 70% (Eliasson & Gudmundsson, 1996). These starches display unique physical characteristics, useful for specific applications: resistant to swelling, rapid gelling, etc. (Moore, Tuschmoff, Hastings, & Schanefelt, 1984). Amylopectin in the starch of amylose-extended mutants is more stable to thermal treatment than that in the parent normal starch, since it has longer chains that could form more stable amylopectin crystals (Eliasson & Gudmundsson, 1996). In addition, the longer side chains allow the starch to retrograde readily, resulting in higher enthalpy for the melting (Gudmundsson & Eliasson, 1990). Due to the retrogradation tendency, high amylose starches are recently used as natural sources for dietary fiber that can be added to processed foods such as bread, breakfast cereals and various extruded products (Brown, Macnamara, Power, Hazzard, & McNaught, 2000).

It has been reported that repeated freeze-thawing cycles accelerated starch retrogradation in a paste or gel (Jacobson & BeMiller, 1998; Shi & Seib, 1992; White, Abbas, & Johnson, 1989; Yuan & Thompson, 1998). Jacobson and BeMiller (1998) claimed that the repeated freeze-thawings for a waxy maize starch paste (20% solids) could lead to a retrogradation equivalent to that obtained by an isothermal holding at 4 °C. Shi and Seib (1992) and White et al. (1989) also reported similar effect from freeze-thawing with waxy maize starch paste. The dissolution and recrystallization of ice cause starch components in paste system to relocate in concentrated regions, and thus starch chain associations are facilitated (Eliasson & Kim, 1992).

Mild hydrolysis of starch chains could accelerate starch retrogradation in a paste or gel (Kikumoto & French, 1983; Kitahara, Eitoku, Suganuma, & Nagahama, 1997). Morrison, Tester, Gidley, and Karkalas (1993) showed ^{13}C-cross-polarisation magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR) data in which double helix content of barley starch in a paste was increased by acid hydrolysis,

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as a result of amylose retrogradation. Jacobs, Eerlingen, Rouseu, Colonna, and Delcour (1998) also reported an increase in the amount of amylose double helices by lintnerization. Not only the crystal content, but the storage modulus of oat starch gel increased and the phase angle decreased when the starch was lintnerized (Virtanen, Autio, Suortti, & Poutanen, 1993). It was suggested that the increased elasticity was mainly due to the associations between partially hydrolyzed amylose chains.

Starch associations, in the retrogradation process, produce the thermally stable enzyme-resistant starch, which is classified as the RS3 type (Englyst, Kingman, & Cummings, 1992). The usual process for RS3 formation is cyclic heating and cooling procedures, generally referred to as annealing (Thompson, 2000). Berry (1986) reported that debranching of potato amylopectin with pullulanase before the heating and cooling cycles substantially increased the RS3 content. Lee, Mun, and Shin (1997) and Vasanthan and Bhatty (1998) hydrolyzed amylomaize starch by acid, prior to the annealing, to enhance the enzyme resistance.

To increase amylose crystal content, defatting has been also used. Eerlingen, Cillen, and Delcour (1994) and Russell, Berry, and Greenwell (1989) suggested that RS3 content increased by defatting, because it allowed more amylose chains to form double helices.

In our previous work (Jeong & Lim, 2003), repeated freeze-thawings (−20 °C for 24 h, and then 25 °C for 4 h) were used effectively to induce retrogradation of high amylose corn starch in an aqueous gel. But it found that the retrogradation occurs most prevalently during the first cycle of freeze-thawing. In the present study, acid-hydrolyzed and/or defatted high amylose corn starch was subjected to a freeze-thawing treatment, and the amylose double helix content and pasting properties of the starch powders isolated from the gel were examined.

2. Materials and methods

2.1. Materials

High amylose corn starch (~70% amylose) was a gift from Cerestar USA Inc. (Hammond, IN). Defatting was done by refluxing the starch with 85% methanol for 24 h by the method of Schoch (1964). Alpha-amylase and amyloglucosidase were the products of Novo Nordisk (Thermonyl 120L, Bagsvaerd, Denmark) and Sigma Chemical Company (crystal form, St Louis, MO), respectively.

2.2. Acid hydrolysis

The native or defatted starch was hydrolyzed by stirring the starch dispersion in 2.2 M HCl (50 g in 500 ml) at 35 °C for 0.5, 1, or 2 h according to the method of Colonna, Buleon, and Lemarie (1988). The hydrolysis residue was isolated by centrifugation, neutralized by washing with sufficient amount of water, and then dried (40 °C, overnight).

2.3. Sample preparation by freeze-thawing

Starch dispersion in water (10% solids) was heated at 125 °C for 10 min in an autoclave mixer (BEP 280, Büchi AG, Uster, Switzerland) with mechanical stirring (200 rpm). The gelatinized starch paste was transferred into petri dishes (50 mm diameter, 10 mm depth) and cooled at room temperature for 1 h. The starch gel was frozen by storing at −20 °C for 24 h, and then thawed at 25 °C for 4 h. The gel was vacuum-dried (25 °C) overnight and then the dried starch was ground to a powder, which was sieved through 100 mesh screen.

2.4. X-ray diffractometry

The X-ray diffraction patterns were obtained with the vacuum-dried starch powders (~3% moisture), using a diffractometer (MAC Science Co. MO3XHF22, Japan) at 40 kV and 30 mA with 0.154 nm CuK radiation (Ni filter). The scan rate was 0.5°/min.

2.5. Differential scanning calorimetry (DSC)

Crystal melting was examined with a differential scanning calorimeter (DSC6100, Seiko Instruments, Chiba, Japan). The indium and tin standards were used for temperature and enthalpy calibrations. Starch sample (approximately 9 mg) was weighed in a large-volume silver pan (70 μl) and then distilled water (approximately 40 mg) was added. The water was allowed to evaporate on balance until the starch solid and water ratio reached 1:4 (w/w). The pan was hermetically sealed and heated at a rate of 10 °C/min from 10 to 240 °C. An empty pan was used as reference.

2.6. Paste viscosity

Paste viscosity of the freeze-thawed starch powders was measured by a Rapid Viscoanalyser (Newport Scientific Instruments and Engineer, Australia). Starch suspension in water (10% solids) was heated from 25 to 95 °C at a heating rate of 3.5 °C/min, held at 95 °C for 10 min, cooled to 50 °C at 3.5 °C/min, and then held at 50 °C for 10 min.

2.7. Resistant starch content

The resistant starch (RS) content was determined by enzymatic-gravimetric assay (Association of Official Analytical Chemists, 1995). Starch (1.0 g dry basis) in 0.05 M MES–TRIS (Morpholino ethanesulfonic acid–Tris(hydroxymethyl)aminomethane) buffer (pH 8.2, 40 ml) was heated with a heat-stable α-amylase (50 μl), in a boiling

water-bath for 30 min while stirring. After cooled to room temperature, the starch hydrolyzate solution was adjusted to pH 4.5 with 0.325 M HCl, and added with amyloglucosidase (300 μl). The mixture was then incubated for 30 min at 60 °C. The resistant starch was recovered by adding 95% ethanol (4 × of the solution). The precipitate was vacuum-filtrated (3G2, Iwaki glass Co., Japan), and washed successively with distilled water, 78% ethanol, 95% ethanol and acetone. The residue was dried overnight in an oven at 105 °C and then weighed as the RS.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the freeze-thawed native and defatted high amylose corn starch powders isolated from the paste, at different periods of acid hydrolysis, are given in Fig. 1. The freeze-thawed high amylose corn starches showed the diffraction patterns with the peaks at 5, 15, 17, 20 and 22–23° (2θ), which were typical diffraction lines for

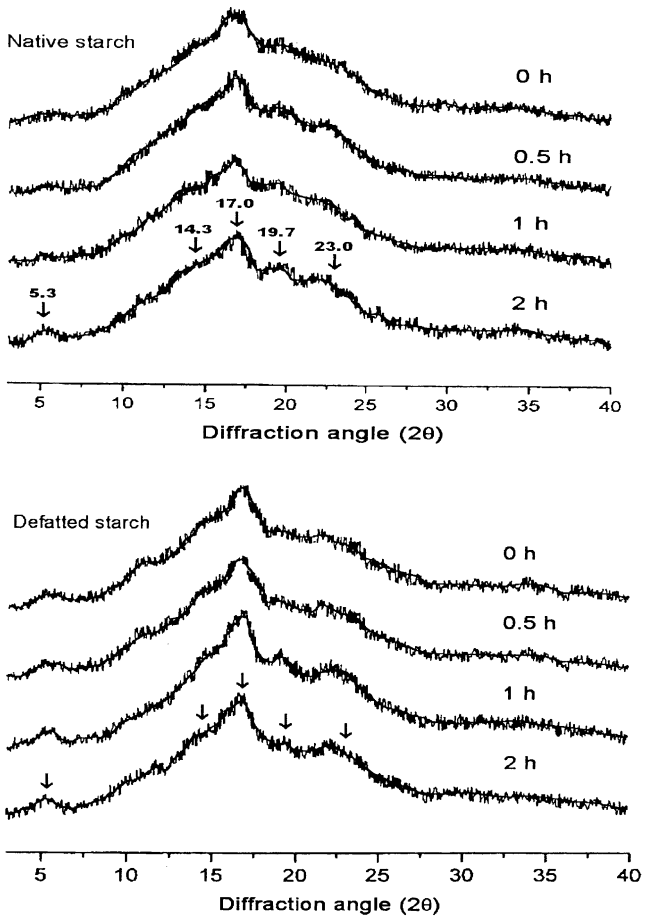

Fig. 1. X-ray diffraction patterns of acid-hydrolyzed native and defatted high amylose corn starches, isolated after freeze-thawing, at different periods (0–2 h) of acid hydrolysis.

combination of B- and V-type crystallites. Similar diffraction pattern was observed with the same starch treated by repeated freeze-thawing cycles without hydrolysis (Jeong & Lim, 2003). This result was in accord with the finding by Sievert, Czuchajowska, and Pomeranz (1991) with autoclaved and cooled high amylose corn starch. Native granular starch of high amylose maize typically exhibited a diffraction pattern of B- and V-crystallites, similar to that of the freeze-thawed starch. But the crystallinity for the isolated starch, based on the diffraction intensity, was much lower. But the recrystallized pattern induced by the freeze-thawing was similar to that of the parent starch.

As the starch was subjected to longer period of acid hydrolysis (i.e. 2 h), the overall peak intensity for the treated starch increased. The starch chains of reduced chain length formed by the acid hydrolysis had increased chain mobility, and thus readily tended to recrystallize during the freeze-thawing treatment. Similar results were reported by Vasanthan and Bhatty (1998), in which acid hydrolysis (0.5–6 h) of high amylose corn starch could lead to increased crystallinity by the formation of double helices. Atichokudomchai, Varavint, and Chinachoti (2002) also suggested that hydrolysis increased the proportion of short amylose and amylopectin chains, which readily formed double helices.

When the residual lipids were removed by refluxing in alcohol (defatted starch in Fig. 1), the overall crystallinity of the starch products became higher. As the lipids that could form complex with amylose were removed, more amylose chains became available to form amylose double helices, instead of V-type single amylose–lipids helices.

Sievert et al. (1991) examined X-ray diffraction profiles of repeatedly autoclaved high amylose corn starch, and found that the peak intensity at 20° was decreased by the autoclaving. They suggested that the intensity decrease resulted from the melting of amylose–lipids complex during the treatment. In our results, the 20° peak intensity was decreased by defatting, but increased by acid hydrolysis. Accordingly, Morrison et al. (1993) reported that the residual amount of amylose–lipids complexes (single V_6-amylose helices) increased by acid hydrolysis. It was because the amylose–lipids complex was resistant to the acid hydrolysis. In accordance with their result, the peak at 20°, representing the single V_6-amylose–lipids complexes, remained even when the acid hydrolysis time was 1 or 2 h, indicating that it contained the single helices of amylose–lipids complexes. Moreover, the defatted starch displayed the 20° peak, which indicated that the some lipids still remained after defatting.

From the overall X-ray diffractograms, the high amylose starches could recrystallize by freeze-thawing, into a Bv-type structure, typical for retrograded starch, with broad and diffused diffractograms. And the crystalline formation was enhanced by mild acid hydrolysis prior to the freeze-thawing treatment.

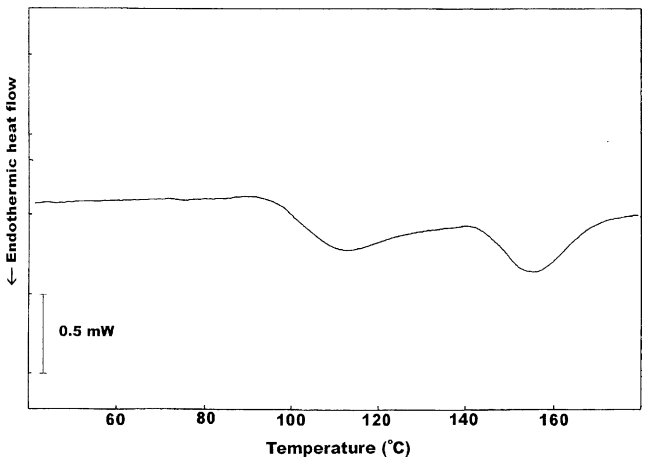

Fig. 2. DSC thermogram of recrystallized native high amylose corn starch produced by freeze-thawing after acid hydrolysis for 2 h.

3.2. Thermal characteristics

Two endothermic peaks were found in the DSC thermograms for native and defatted starch samples (Fig. 2). The endotherm in a temperature range about from 150 to 170 °C was attributed to the melting of amylose double helices, and the endotherm below 130 °C reflected the melting of amylose–lipids complexes. The thermal transition corresponding to melting of amylopectin crystals (40–70 °C) was not observed in the thermograms for the high amylose corn starch samples (Fig. 2).

The transition peak for the melting of amylose–lipids complex showed slight increases both in melting temperature and in enthalpy by the acid hydrolysis (Table 1). The defatted starch samples showed a small endotherm for the amylose–lipids complex melting, only after the acid hydrolysis was performed for 1 h. As confirmed by the X-ray diffraction data, it proved that minor amount of lipids remained even after the defatting treatment. It was noteworthy that the amylose–lipids complex appeared after 1 h of acid hydrolysis. It agreed with the finding by Morrison et al. (1993) and Jacobs et al. (1998), in which lintnerised starch had more tendency to form amylose–lipids complex. The acid hydrolysis might produce the amylose chains of reduced chain lengths, which had increased mobility and thus complexed more readily with lipids.

Another possibility might be from the release of long B-chains from amylopectin by the acid hydrolysis. Those chains could behave like short amylose chains, capable of forming the lipid complex and double helices.

Both native and defatted starch samples showed the same trends of melting enthalpy increase but melting temperature decrease for the recrystallized amylose double helices as the hydrolysis time increased. Morrison et al. (1993) suggested from ^{13}C-CP/MAS NMR data that the amount of retrograded amylose (double helices) in barley starch increased after partial hydrolysis.

Freeze-thawing induces the water to be released from starch gel matrix, and thereby increases regional concentration of starch chains, so that the amylose chains are given more possibility for physical associations. By the acid hydrolysis, the amylose chains of reduced length obtained the mobility, and thus crystal formation could be enhanced (Table 1).

The defatted starch showed higher melting enthalpy for the amylose double helices, compared to the native starch. As shown in X-ray diffraction results, DSC data revealed the increased tendency for amylose chains to recrystallize by the defatting (Eerlingen et al., 1994; Jeong & Lim, 2003). The DSC data also suggested that the changes in X-ray diffraction pattern by the acid hydrolysis were mainly due to the formation of amylose double helices.

3.3. Paste viscosity

The viscosity profiles while pasting the freeze-thawed native and defatted starch powders (10% dry solids) are shown in Fig. 3. As reported by Jeong and Lim (2003), high

Table 1
Melting characteristics of retrograded native and defatted high amylose corn starches produced by freeze-thawing, at different periods (0–2 h) of acid hydrolysis

Samples	Amylose–lipids complex[a]				Amylose double helices[a]			
	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native								
0 h	94.1 ± 0.6	104.5 ± 1.4	125.6 ± 2.0	2.347 ± 0.072	154.4 ± 1.2	161.1 ± 1.1	172.3 ± 2.5	2.409 ± 0.138
0.5 h	98.9 ± 1.0	108.5 ± 0.2	120.9 ± 1.9	2.209 ± 0.104	152.4 ± 0.9	159.6 ± 1.8	170.4 ± 3.1	2.559 ± 0.107
1 h	98.9 ± 2.2	109.8 ± 1.7	122.2 ± 2.5	2.512 ± 0.152	152.1 ± 0.1	159.3 ± 1.3	173.4 ± 2.2	2.851 ± 0.211
2 h	103.0 ± 0.1	110.4 ± 0.5	126.9 ± 1.8	2.673 ± 0.154	148.7 ± 0.3	157.3 ± 0.7	169.1 ± 0.9	3.238 ± 0.197
Defatted								
0 h	–	–	–	–	153.5 ± 0.9	160.5 ± 1.4	175.1 ± 1.9	3.248 ± 0.154
0.5 h	–	–	–	–	151.9 ± 2.1	158.8 ± 0.5	172.0 ± 2.5	3.959 ± 0.212
1 h	93.2 ± 2.1	106.1 ± 3.1	115.1 ± 2.5	0.974 ± 0.279	151.6 ± 0.4	159.6 ± 0.8	171.1 ± 1.4	4.040 ± 0.034
2 h	90.4 ± 1.5	101.1 ± 0.7	112.3 ± 2.4	1.509 ± 0.351	149.9 ± 1.5	159.6 ± 1.7	171.8 ± 2.1	5.124 ± 0.241

[a] T_o, T_p and T_c indicate the temperature of the onset, midpoint and end of melting, respectively.

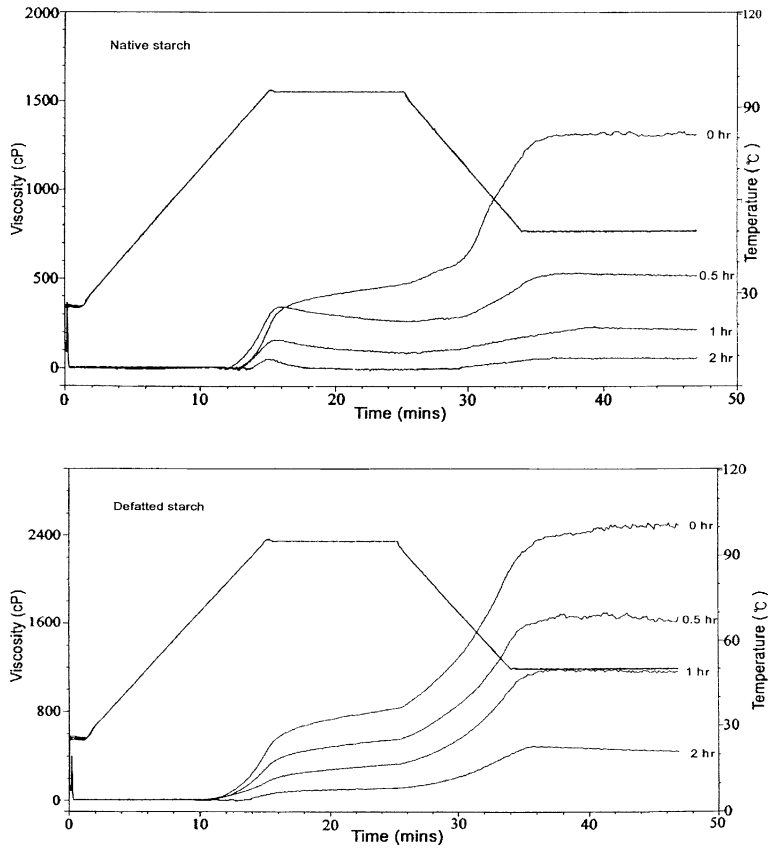

Fig. 3. Pasting viscosity of recrystallized native and defatted high amylose corn starches produced by freeze-thawing, at different periods (0–2 h) of acid hydrolysis.

amylose corn starch powders isolated from freeze-thawing treatment exhibited a paste viscosity pattern similar to that of an ordinary starch, by showing heat-induced swelling and setback in cooling stage. Whereas native granular high amylose corn starch requires pressurized heating, the starch sample from the freeze-thawed gel could form a paste by atmospheric heating. The starches exhibited no or minor shear-thinning but exceptionally high setback. Although viscosity patterns were similar, overall viscosity was higher for the defatted starch than native starch.

Acid hydrolysis decreased paste viscosity, possibly due to the shorter chains produced, but pasting temperature was slightly increased. The increased degree of amylose recrystallization by acid hydrolysis might be attributed to the viscosity change. Because the amylose double helices were not melted in the cooking procedure, the starch particles might be more resistant to swelling. The amylose–lipids complex cause similar effects, by restricting granular swelling (Takahashi & Seib, 1988). Therefore, native starch containing the inherent lipids exhibited a lower paste viscosity than the defatted starch (Fig. 3).

The starch products were resistant to shear-thinning in the viscograms, which revealed the exceptional tendency in the strong matrix formation of the linear amylose segments, and also possibly long branch chains of amylopectin. The intermolecular interactions among the chain segments hold the integrity of swollen starch particles during shearing. The chain associations continued during the paste cooling, resulting in a high setback and the defatted starch exhibited a higher setback than native starch (Fig. 3). The setback upon cooling is from the associations among the amylose chains leached during the swelling stage. There might be higher degree of amylose leaching in the defatted starch paste than that in native starch paste, because more amylose, free from lipids could be available (Takahashi & Seib, 1988).

3.4. Resistant starch content

Resistant starch has been defined as the fraction of starch not absorbed in small intestine, but digested in the large intestine (Englyst et al., 1992). Retrogradation is the key process to manufacture RS (type 3), in which amylose chains, solubilized during gelatinization, aggregate forming crystalline double helices (Haralampu, 2000). Thus, the high amylose starches are chosen as common sources for the resistant starch preparation (Lee et al., 1997; Sievert & Pomeranz, 1989).

Sievert and Pomeranz (1989) reported that repeated cycles of autoclaving and cooling with amylomaize starch paste induced a melting enthalpy increase and RS

Table 2
Resistant starch (RS) content of retrograded native and defatted high amylose corn starches produced by freeze-thawing, at different periods (0–2 h) of acid hydrolysis

Samples	RS content (%)
Native starch	
Granular	18.91 ± 0.43
0 h	21.01 ± 1.42
0.5 h	19.94 ± 1.36
1 h	20.21 ± 1.99
2 h	20.51 ± 0.44
Defatted starch	
Granular	16.17 ± 1.16
0 h	24.65 ± 1.19
0.5 h	25.30 ± 0.75
1 h	25.15 ± 0.56
2 h	25.39 ± 0.26

formation. Lee et al. (1997) showed that the yield of RS from amylomaize starch slightly increased when autoclaved after acid treatment. According to Jeong and Lim (2003), the RS content could be also increased by repeated freeze-thawing with high amylose corn starch paste.

The RS content in the freeze-thawed starches in this experiment, measured by amylolytic treatment with thermostable α-amylase increased slightly as a result of acid hydrolysis (Table 2), but this was not statistically significant. The crystallinity of the retrograded amylose double helices responsible for the RS, increased on acid hydrolysis according to X-ray diffraction and DSC data. In contrast to the report that the enzyme resistance was positively correlated with melting enthalpy of amylose double helices (Sievert et al., 1991), our results showed no correlation among the samples of different degrees of hydrolysis. In addition to the amount of double helices, the physical conformation of starch matrix isolated from freeze-thawed gel could differ. Gerard, Colonna, Buleon, and Planchot (2001) reported that the resistance to α-amylase was not directly influenced by the crystallinity level, but rather highly correlated with the overall morphology. Therefore, the conformational differences in the starch samples might have additional effect on the enzyme susceptibility.

The defatted starch samples had a higher RS content than native starch samples (Table 2), which agreed with our DSC data, and the earlier studies (Czuchajowska, Sievert, & Pomeranz, 1991; Eerlingen et al., 1994; Jeong & Lim, 2003).

The RS contents of native and defatted high amylose corn starches prior to acid hydrolysis or freeze-thawing were 18.91 and 16.17%, respectively. But with the freeze-thawing treatment, the RS content was substantially increased, even without acid-treatment (0 h). Therefore, RS increase by freeze-thawing treatment, was enhanced by defatting but not by acid hydrolysis.

4. Conclusions

Freeze-thawing a paste of high amylose corn starch produced a retrograded starch product. Mild acid hydrolysis of starch prior to the freeze-thawing treatment allowed more amylose to associate because it generated short amylose chains, suitable for the formation of double helices, and thus increased the degree of retrogradation. By defatting the starch, the acid hydrolysis effect was enhanced, by allowing more amylose to form double helices. Therefore, the amylose crystal formation in retrograded high amylose corn starch, especially after defatting, led to increase in enzyme resistance. Moreover, the high amylose corn starch product isolated from freeze-thawed gel could be pasted by conventional heating. The defatted product formed pastes with higher viscosity and setback.

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