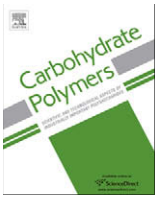
Carbohydrate Polymers 80 (2010) 215–221

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Characterization of remaining granules of acetylated starch after chemical surface gelatinization

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ARTICLE INFO

Article history:
Received 27 September 2009
Received in revised form 29 October 2009
Accepted 9 November 2009
Available online 13 November 2009

Keywords:
Acetylation
Waxy potato
Starch
Chemical gelatinization

ABSTRACT

One acetylated waxy potato starch and three acetylated normal potato starch samples were treated with aqueous calcium chloride (4 mol/L) for surface gelatinization. The remaining granules after removal of gelatinized starch were investigated on size distribution and level of acetylation. Their crystal structure, thermal property and morphological change were studied with X-ray diffractometry, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Greater proportions of the acetyl groups were present at the periphery than at the core of the granule. Remaining granules obtained after higher degree of gelatinization showed greater relative crystallinity and gelatinization temperature. Morphology of gelatinized starch and remaining granules differed for acetylated waxy and normal potato starch samples. The results suggest that structural divergence exists not only between acetylated waxy and normal potato starches, but also within one granule.

1. Introduction

Acetylation is a type of esterification at the hydroxyl groups of the starch. Among a great variety of starch esters, acetylated starch is the one that is most actively marketed (Fleche, 1985). Acetylated starches are particularly useful in flour based noodles, extruded and coated snacks, bakery products and in various frozen or cold stored ready-to-eat menus (Bergthaller, 2004).

Liu, Ramsden, and Corke (1999) reported that amylose content affects properties of acetylated starch: acetylation with vinyl acetate increased the swelling power and freeze–thaw stability of non-waxy rice starch, but decreased these properties of waxy rice starch. The effect of granule size toward derivatization reactions was reported for acetylated potato and sweet potato starches by Chen, Schols, and Voragen (2004). Starch samples were fractionated by sieving into different size granule fractions after modification with acetic anhydride. Small size granule fractions showed higher degrees of substitution (DS) than the large size granule fractions.

The chemical fine structure of acetylated starch has been investigated from several aspects, i.e. the acetylation position in the glucose residues, and the distribution of acetyl groups in amylose and amylopectin populations. The substitution pattern of highly acetylated starch was determined by high resolution nuclear magnetic resonance (NMR) spectroscopy, and the results showed that both O-2 and O-3 positions were substituted likewise (Heins, Kulicke, Käuper, & Thielking, 1998). Biliaderis (1982) investigated acetylated distarch phosphate derivative of smooth pea starch and proposed that the acetyl groups located predominantly in certain parts of amylopectin. Acetylated potato and sweet potato starches was fractionated into different size fractions to study the influence of granule size on the molecular structure (Chen, Huang, Suurs, Schols, & Voragen, 2005; Chen et al., 2004). For both amylose and amylopectin populations, acetyl groups were unevenly distributed. Acetyl groups located more closely to the non-reducing ends for amylose originating from small size granule fractions when compared to amylose from large sized granules. Acetyl groups were also found to be different for amylopectin from different granule size fractions and located near the branching point, in the external chain and in the internal chain regions.

In our previous work, the effect of reagent type (acetic anhydride and vinyl acetate) on properties and chemical fine structure was studied for yellow pea and cowpea starches. Modification with vinyl acetate resulted in much higher peak viscosities than modification with acetic anhydride for the same starch with same granule size and same DS. Granule size had a greater effect on reactivity when modified with acetic anhydride (a rapidly reacting reagent) than with vinyl acetate (a slowly reacting reagent). Vinyl acetate resulted in higher DS for amylopectin populations than acetic anhydride. The distributions of acetyl groups along the amylose and amylopectin chains were more clustered for modification with vinyl acetate as compared with modification with acetic anhydride. It is postulated that acetylation occurs more homogeneously

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doi:10.1016/j.carbpol.2009.11.011

throughout the granule when vinyl acetate is used as reagent, while the reaction with acetic anhydride to a large extent takes place in the outer lamellae of granule (Huang, Schols, Jin, Klaver, and Voragen, 2007b; Huang, Schols, Jin, Sulmann, & Voragen, 2007a; Huang, Schols, Jin, Sulmann, and Voragen, 2007c).

Physicochemical properties of acetylated starches have been reported (Chen, Schols, and Voragen, 2004; Huang et al., 2007a, 2007c; Liu et al., 1999). However, these property studies were carried out based on intact granules of acetylated starch. Little is known about the characteristics of acetylated starch at different granular levels. Therefore, the purpose of this research was to investigate the properties of remaining granules obtained from acetylated waxy and normal potato starch samples (modified with acetic anhydride) after chemical surface gelatinization.

2. Materials and methods

2.1. Materials

Acetylated waxy potato (AWP) starch was kindly supplied by AVEBE Food Innovation Centre (Veendam, The Netherlands). Three acetylated normal potato (ANP) starch samples were used as references. One of them (ANP-1) was a gift from AVEBE Food Innovation Centre (Veendam, The Netherlands). The other two, 170 and 150 (ANP-2 and ANP-3) were products from TianJin TingFung Starch Development Co., Ltd. (TianJin, China). All the four acetylated starch samples were obtained from modification with acetic anhydride in aqueous suspension in such amounts that the degrees of substitution were lower than 0.1. Other chemicals were all analytical grade.

2.2. Fractionation of acetylated starch granules

Acetylated starch was fractionated according to granules size by using two test sieves (30 μm and 50 μm). Each acetylated starch samples was separated into three fractions: larger than 50 μm, 30–50 μm, and smaller than 30 μm. Sieving was conducted as described in a previous report (Huang et al., 2007a). The middle size (30–50 μm) granules were subjected to further chemical surface gelatinization and analyses.

2.3. Chemical surface gelatinization of acetylated starch granules

Chemical surface gelatinization was conducted according to the method of Jane and Shen (1993) with some modifications. Acetylated potato starch granules of 30–50 μm were used for the chemical gelatinization study. Starch sample (2.5 g, dry basis) was suspended in 4 mol/L $CaCl_2$ (17.5 ml) with low speed magnetic mechanical stirring at 20 °C for various minutes. The degree of surface gelatinization was monitored by using a polarized light microscope (BK-POL, Chongqing Optec instrument Co. Ltd., Chongqing, China). When a distinct layer of gelatinized starch (about 30% or 50%) was observed on the granule surface, the reaction was stopped by adding chilled water (200 ml, 4 °C). Immediately the mixture was centrifuge at 3000*g* for 20 min. Sample was washed twice with distilled water, washed twice with anhydrous ethanol, and dried at 40 °C.

The remaining non-gelatinized starch granules was separated from the gelatinized starch by re-suspending the surface-gelatinized starch (ca. 2 g) in distilled water (30 ml) and blended with a commercial blender (v6-2008, German v6 manufacture Electric appliance Development Company Ltd., Xi'an, China) for about 20 min. The mixture was centrifuged at 3000*g* for 10 min. The procedure was repeated one more time with distilled water (200 ml). The remaining non-gelatinized starch granules was washed twice with anhydrous ethanol and dried at 40 °C.

The following equation was used to calculate the degree of starch chemical gelatinization on dry basis.

$$\text{Degree of chemical gelatinization} \\ = (1 - \text{Remaining granules weight}/\text{Original starch weight}) \times 100\%$$

2.4. Particle size distribution and determination of degree of substitution

Particle size distribution was measured in water with a surface potential and particle size analyzer (BDL-B, Shanghai detection technology on the legislation by the detection Instrument Factory, China). The DS values of starch samples were determined using the titration method according to Huang et al. (2007a).

2.5. X-ray diffraction and Differential Scanning Calorimetry (DSC)

The analysis of the crystalline structure of the starches was carried out using a Rigaku diffractometer (D/max2200pc, Japan). The data were processed using Jade5 XRD pattern processing (USA) software. Degree of relative crystallinity was obtained by using the software. The gelatinization temperature was measured using a Differential Scanning Calorimeter (DSC 204, Netzsch, Germany). Starches (10 mg) and 20–30 mg distilled water were weighed, sealed and hold for 5 min at 10 °C, then heated from 10 °C to 150 °C at a rate of 6 °C/min. The Netzsch Thermokinetics software was used for data handling.

2.6. Microscopy

The gelatinization process was stopped before the starch was completely gelatinized. Polarized-light micrographs were obtained with a light microscope (BK-POL, Chongqing Optec instrument Co. Ltd., Chongqing, China) equipped with a camera. Scanning electron micrographs were obtained with a scanning electron microscope (JSM-6700, Tokyo, Japan & S570, Hitachi, Japan). Starch samples were applied on a metal stub, and the starch was coated with gold–palladium (60:40).

3. Results and discussion

3.1. Chemical gelatinization of acetylated starch granules

One acetylated waxy potato (AWP) starch sample and three acetylated normal potato (ANP) starch samples were separated into three different size groups (<30 μm, 30–50 μm, and >50 μm). The starch sample of a homogeneous granular size (30–50 μm) was selected to achieve a uniform chemical gelatinization of starch granules from the surface with aqueous calcium chloride (4 mol/L). It was found that starch granules gelatinized faster at a higher temperature. To make the reaction to be conveniently followed with light microscopy and stopped at a suitable degree of gelatinization, treatment with 4 mol/L $CaCl_2$ was performed at 20 °C.

The morphological changes of the granules were observed with polarized light microscope. During the $CaCl_2$ treatment, a layer of gelatinized starch developed at the periphery of the granules and the size of polarization cross was reduced gradually (Fig. 1A–F). Differences were observed between AWP starch and ANP starch. The gelatinized layer on the AWP starch looked like a ring around a circle, whereas the gelatinized layer for the ANP starch resembled crescent or headband. This crescent- or headband-like appearance of the gelatinized layer, also shown by the light micrograph of nor-

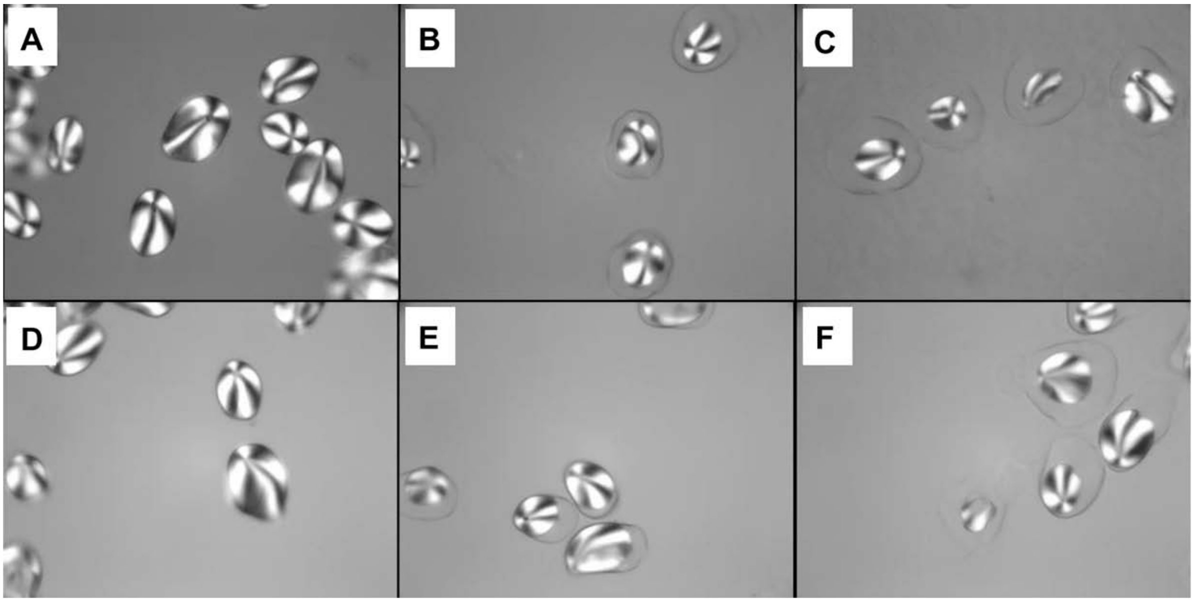

Fig. 1. Polarized light micrographs of starch granules in 4 mol/L $CaCl_2$ solution. (A) AWP, 2 min; (B) AWP, 26 min; (C) AWP, 38 min; (D) ANP-1, 1 min; (E) ANP-1, 34 min; (F) ANP-1, 41 min. AWP, acetylated waxy potato starch (AVEBE, the Netherlands); ANP-1, acetylated normal potato starch (AVEBE, the Netherlands).

mal potato starch granules in 4 mol/L $CaCl_2$ solution (Koch & Jane, 2000), could be explained by concentrated attack of $CaCl_2$ solution on one side of the granule. The results indicate structure diversity between AWP starch granule and ANP starch granule.

The degree of starch gelatinization depended on the length of time of exposure to the $CaCl_2$ solution. When the polarization crosses have disappeared in all but perhaps one or two remaining granules in the entire field, this time is recorded as the completion of the gelatinization. The time required for complete gelatinization varied among four acetylated potato starch samples: AWP required the shortest time (46 min), followed by ANP-1, ANP-2, and ANP-3 (54, 59 and 75 min, respectively). Koch and Jane (2000) treated eleven native starches with $CaCl_2$ solution (4 mol/L) at room temperature and found that there was no definite correlation between amylose content and gelatinization time. Hence the rate of surface gelatinization might be influenced by the level of acetylation.

To achieve similar degrees of surface gelatinization, the four acetylated potato starch samples were treated with $CaCl_2$ solution for various times. As shown in Table 1, gelatinization degrees of a given sample were about 30% and 50%. Two types of "peeled" remaining granules, around 70% and 50% of original granules, were prepared after chemically gelatinized starch at the outer layer was mechanically removed from the granule.

3.2. Size distribution of remaining granules

The particle size distributions of four acetylated potato starch (30–50 μm) samples and the remaining granules obtained from chemical gelatinization with 4 mol/L $CaCl_2$ were determined. Mean particle size (D50) was 41.9–43.6 μm for four untreated starch samples (Table 2). The remaining granules showed reduced sizes during the treatment with $CaCl_2$. The D50 were 31.0–35.1 μm for remaining granules obtained after 30–45 min, and 21.5–26.0 μm after 35–60 min. The D50 values of remaining granules with similar chemical gelatinization degrees were alike. While the granule size range of remaining granules obtained after about 50% chemical gelatinization was narrower than that of remaining granules after around 30% chemical gelatinization, and that of untreated starch. An overlap in between could be seen (Fig. 2).

3.3. Distribution of acetyl group at the granular level

Degree of substitution (DS) is an indication of the reaction level. Among the four untreated acetylated potato starch (30–50 μm) samples, AWP starch showed the highest DS value. ANP-1 starch was next, followed by ANP-2 and ANP-3 starch (Table 2). In general, those starches with lower levels of substitution required longer treatment time with 4 mol/L $CaCl_2$ solution to complete the gelatinization. Hydrogen bonds among starch molecules in acetylated starch granules with more acetyl groups were destroyed easier and faster by $CaCl_2$ solution than those in acetylated starch granules with less acetyl groups.

The remaining granules, obtained after longer treatment periods using 4 mol/L $CaCl_2$, with higher degrees of chemical gelatinization, had lower degrees of substitution for all four acetylated potato starch samples. The results indicate that the acetyl groups are distributed unequally within each starch granule. Based on the DS values and degrees of gelatinization, it was clear that 42–48% of the total acetyl groups were present in 26–34% of the granule at the periphery. Greater proportions of the acetyl groups were

Table 1
Degree of starch chemical gelatinization of acetylated potato starch granules after partially gelatinization.

Starch code	Treatment with 4 mol/L $CaCl_2$ (min)	Degree of chemical gelatinization (w/w, %)[e]	Amount of remaining granules (w/w, %)[e]
AWP[a]	30	34	66
	35	48	52
ANP-1[b]	35	31	69
	42	54	46
ANP-2[c]	38	26	74
	45	50	50
ANP-3[d]	45	31	69
	60	52	48

[a] AWP, acetylated waxy potato starch (AVEBE, the Netherlands).
[b] ANP-1, acetylated normal potato starch (AVEBE, the Netherlands).
[c] ANP-2, acetylated normal potato starch 170 (TingFung, China).
[d] ANP-3, acetylated normal potato starch 150 (TingFung, China).
[e] Dry basis.

Table 2
Characterization of untreated starch and remaining granules obtained after treatment with 4 mol/L $CaCl_2$ solution.

Starch code[a]	Fraction[b]	Mean particle size[c] (D50, μm)	Degree of substitution[d]	Relative crytallinity (%) (X-ray)	Peak temperature of gelatinization (°C) (DSC)[e]
AWP	Untreated	43.6	0.0779	13	58.0
	30 min	35.1	0.0633	36	66.6
	35 min	23.1	0.0552	50	69.8
ANP-1	Untreated	41.9	0.0734	15	61.1
	35 min	32.3	0.0552	22	67.0
	42 min	21.5	0.0472	25	70.2
ANP-2	Untreated	42.5	0.0559	15	62.7
	38 min	31.0	0.0433	20	68.6
	45 min	26.0	0.0312	36	72.1
ANP-3	Untreated	42.3	0.0472	13	65.6
	45 min	32.0	0.0363	21	72.2
	60 min	22.8	0.0291	38	75.4

[a] See Table 1 for an explanation of starch codes.
[b] Untreated, original starch granules before treatment; time, time to which the original starch granules was treated in 4 mol/L $CaCl_2$ solution before recovering the non-gelatinized remaining granules.
[c] Values are means of duplicate.
[d] Values are means of triplicate.
[e] Differential Scanning Calorimeter.

present at the periphery than at the core of the granule, suggesting a higher reaction efficiency for the reaction with the hydroxyl groups of the glucosyl residues at the periphery of the granule. For both waxy and normal potato starch samples, granule acetylation started probably at the periphery and proceeded to the core of the granule, since acetic anhydride reacted rapidly before it could penetrate and permeate homogenously throughout the starch granule. For three normal potato starch samples, there may be an additional explanation that amylose was more concentrated at the periphery than at the core of the granule (Jane & Shen, 1993). Amylose was modified to a greater extent than amylopectin has been reported for acetylated starch (Chen et al., 2004; Huang et al., 2007a, 2007b), methylated starch (Steeneken & Woortman, 1994; van der Burgt et al., 2000b), and hydroxypropylated starch (Kavitha & BeMiller, 1998). The finding on the distribution of acetyl group at the granular level supports our previous prediction that reaction with a rapidly reacting acetic anhydride occurred prominently on peripheral surfaces of starch granules (Huang et al., 2007c), which has also been proved by recent results of Steeneken and Woortman (2008).

Huber and BeMiller (2001) and Gray and BeMiller (2004) used microscopy in studies toward the reaction sites within phosphorylated potato starch and hydroxypropyl waxy maize starch at granular level. Highly reactive phosphoryl chloride appeared to react most prominently on peripheral surfaces of potato granules, while reaction with a less reactive propylene oxide analog appeared to occur throughout the granule matrix of waxy maize starch in a more uniform manner.

The chemical gelatinization method has been used for yielding a series of remaining methylated potato and amylopectin potato starch granules and the similar molar substitution of all remaining granules reflects that the methyl substituents are distributed equally within each starch granule (van der Burgt et al., 2000a). The organization of granules influences the substitution pattern since reagents with different reactivity penetrate into the granule with different efficiencies (Bertoft, 2004).

3.4. Crystalline structure and thermal properties of remaining granules

Four acetylated potato starch (30–50 μm) samples and the remaining granules obtained after chemical gelatinization were subjected to X-ray diffractometry and differential scanning calorimetry (DSC) studies. Native starches are biosynthetically assembled as semi-crystalline granules. The type of crystalline structure, labelled as A-, B- or C-type, depends on starch source (van Soest, Hulleman, de Wit, & Vliegenthart, 1996b). Crystals in four acetylated potato starch samples and all the remaining granules determined by X-ray diffraction were all B-type (Fig. 3), which is

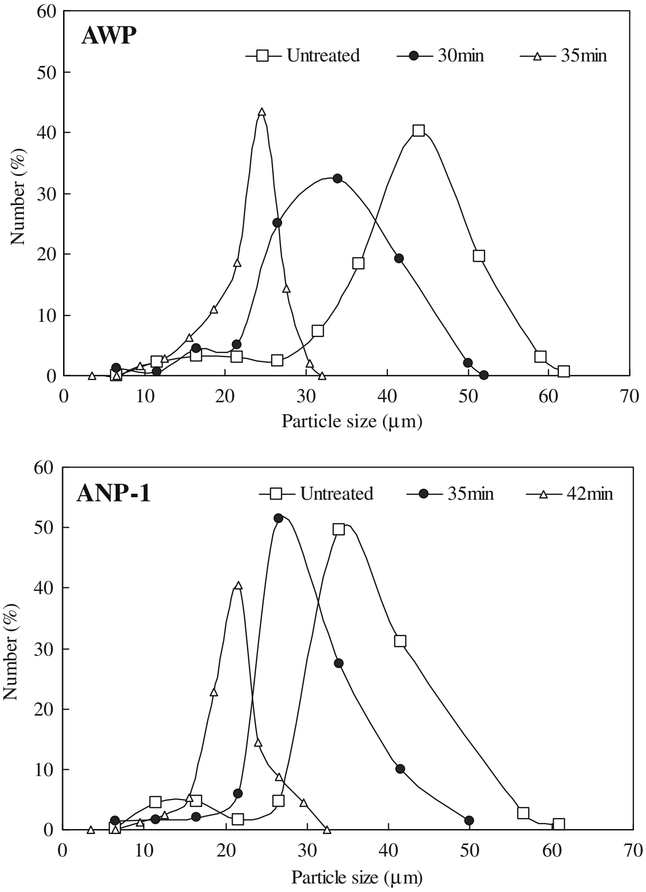

Fig. 2. Particle size distributions of untreated starch and remaining granules obtained after treatment with 4 mol/L $CaCl_2$ solution. AWP, acetylated waxy potato starch (AVEBE, the Netherlands); ANP-1, acetylated normal potato starch (AVEBE, the Netherlands).

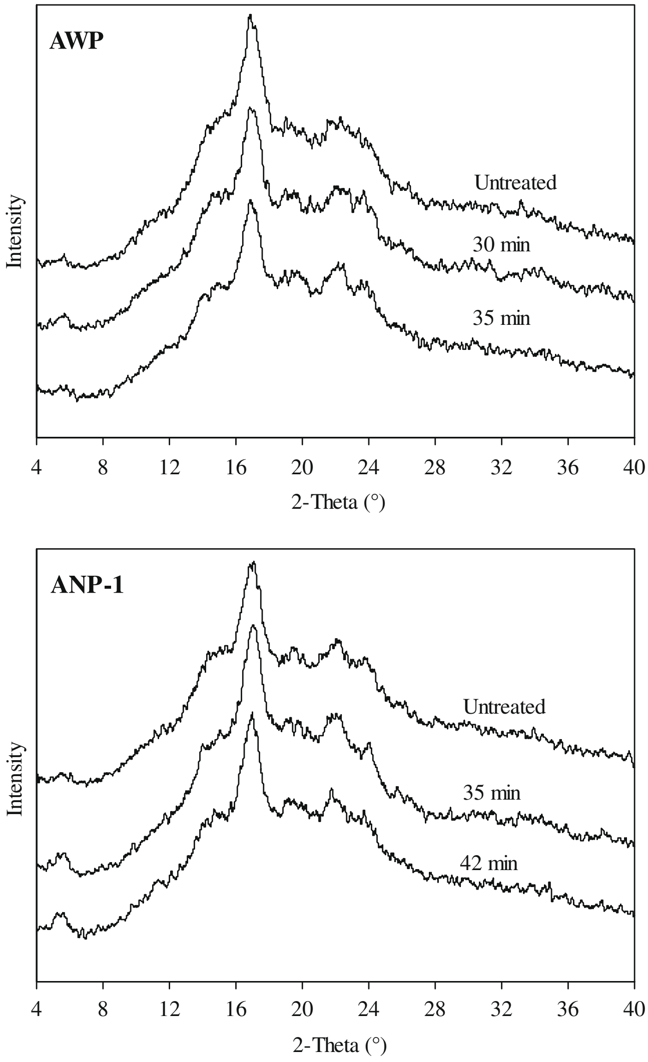

Fig. 3. X-ray diffractograms of untreated starch and remaining granules obtained after treatment with 4 mol/L $CaCl_2$ solution. AWP, acetylated waxy potato starch (AVEBE, the Netherlands); ANP-1, acetylated normal potato starch (AVEBE, the Netherlands).

known as the characteristic pattern of potato starch (van Soest et al., 1996b). At low level of acetylation, no substantial change occurred in crystal structures of granular starch (Chen et al., 2004; Huang et al., 2007a; Lawal, 2004; Wang & Wang, 2002).

X-ray diffraction patterns of remaining granules did not show considerable changes as compared to those of the untreated starches. However, remaining granules obtained after longer 4 mol/L $CaCl_2$ treatment exhibited higher relative crystallinity for all the four tested acetylated starch samples (Table 2). It was reported that acetylation (DS < 0.1) did not change the relative crystallinity of three pea starches (Huang et al., 2007a). Therefore, for acetylated waxy potato starch, the higher relative crystallinity at the core indicates that amylopectin at the periphery has different structure with that at the core. Amylopectin at the core had longer long B-chains than that at the periphery was found for normal potato starch by Jane and Shen (1993). For three acetylated normal potato starch samples, less amylose at the core of the granules (Jane & Shen, 1993) may also contribute to more crystal unit cells containing two double helices and lead to the greater relative crystallinity at the core than at the periphery.

Thermal properties determined by DSC showed that among four samples, acetylated waxy potato starch had the lowest gelatinization temperature. This is in accordance with what was found in gelatinization time: acetylated waxy potato starch gelatinized faster than three acetylated normal potato starch samples.

Remaining granules, obtained after surface-gelatinization with $CaCl_2$ solution, showed higher gelatinization temperature than untreated starches. More perfect crystals (Sasaki & Matsuki, 1998; van Soest, Bezemer, de Wit, & Vliegenthart, 1996a) or longer chains in the crystal or a larger crystal size (Matveev et al., 2001) may lead to higher gelatinization temperature. Not only the proportion of crystalline region, but also the molecular architecture of the crystalline region influence the gelatinization temperature (Bao & Bergman, 2004).

3.5. Scanning electron microscopy (SEM)

The morphology of partially gelatinized starch granules and the remaining granules obtained after treatment with $CaCl_2$ solution (4 mol/L) was investigated by using scanning electron microscopy (SEM). There was no obvious difference between acetylated waxy and normal potato starches in granular shapes and sizes (Fig. 4A and E). Scanning electron micrographs of partial-gelatinized starch granules (Fig. 4B and F) showed an undefined shape and gathering of the gelatinized starch, which was different from the light micrographs that a gelatinized layer surrounding the granule. Ethanol was used in preparation of partial-gelatinized starch granules to separate individual granules and caused the precipitation of gelatinized starch. The morphology of the gelatinized starch differed between acetylated waxy and normal potato starches. The paste-like gelatinized starch stuck on the surface of the remaining granule and there was no clear separation of the gelatinized starch and the remaining granule for the acetylated waxy potato starch. Whereas the gelatinized starch, looked like soft film in curl, was distinct from the remaining granule for acetylated normal potato starch. The granular structure of the remaining starch was preserved, as shown in the polarized-light micrographs that the remaining starch retained the polarization cross.

The surface morphology of the remaining granules after the removal of the gelatinized starch is shown in panels C, D, G, and H of Fig. 4. The micrographs showed that the remaining granules were separated quite cleanly from the gelatinized starch. The remaining granule of acetylated waxy potato starch had a rough surface. Whereas the remaining granule of acetylated normal potato starch had a relatively smooth surface and showed a lamella structure (Fig. 4G). This indicates that the surface of acetylated waxy potato starch granule was irregularly corroded, while that of acetylated normal potato starch granule was evenly corroded by salt solution. The results are evidence for the structural divergence between waxy and normal potato at the granular level. Koch and Jane (2000) reported different findings. The micrographs of remaining granules, obtain from waxy potato and potato starch after chemically surface gelatinization, showed that the granule surfaces were rather evenly eroded and that there were holes on the surface of remaining granules for both starches (Koch & Jane, 2000). Variation in cultivars and growing region may cause the structure diversification of starch.

4. Conclusions

Granular structure of starch is preserved throughout the course of acetylation at a low degree (DS < 0.1). The investigation on the distribution of substituent at the granular level for acetylated waxy and normal potato starch samples showed that the distribution of acetyl was uneven within one granule. Greater proportion of the acetyl groups was present at the periphery than at the core of the granule. It is confirmed that reaction with acetic anhydride oc-

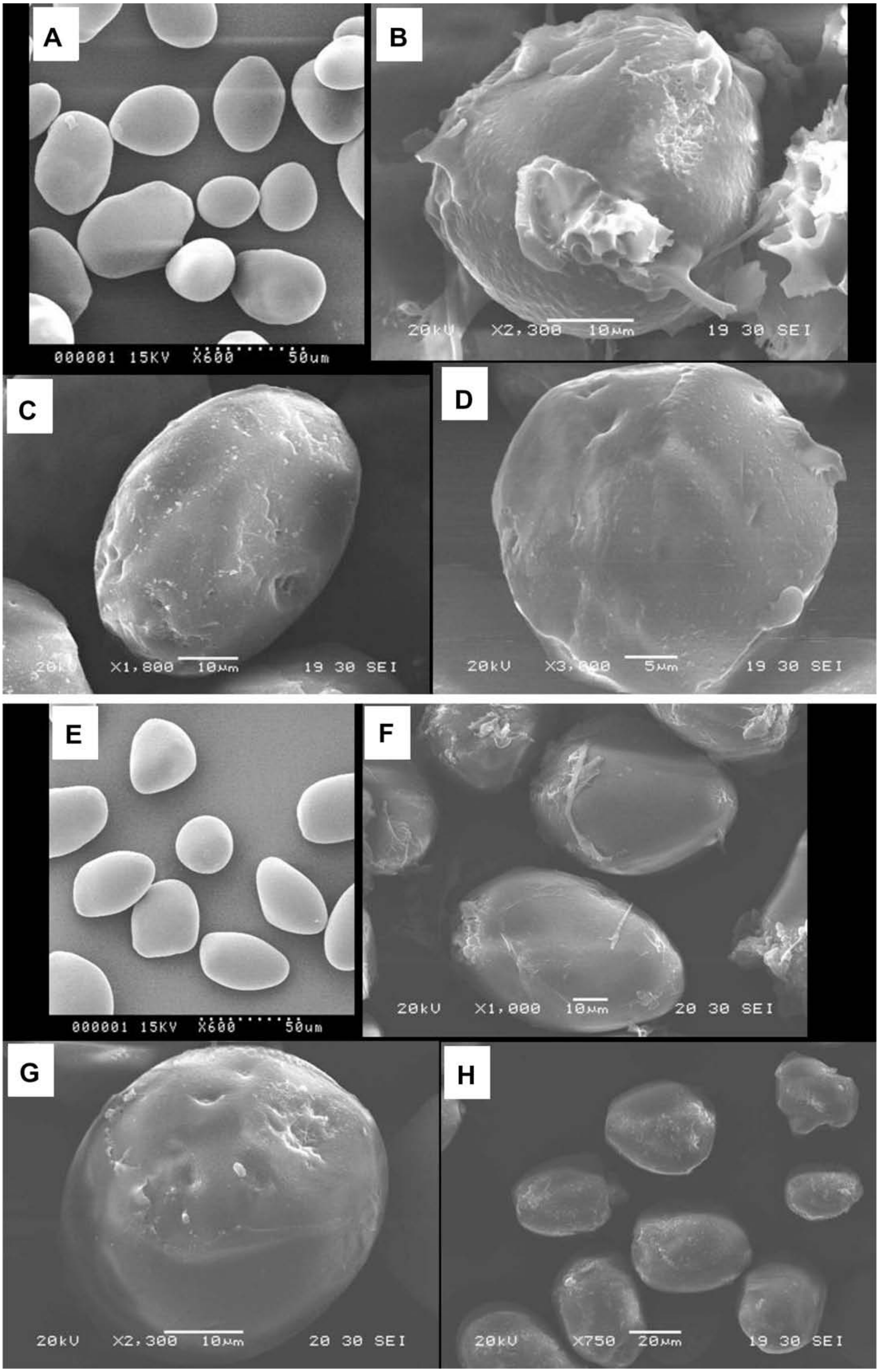

Fig. 4. Scanning electron micrographs of untreated starch, and surface-gelatinized granules and remaining granules obtained from treatment with 4 mol/L $CaCl_2$ solution. (A) AWP, untreated starch; (B) AWP, surface-gelatinized granules, 30 min; (C) AWP, remaining granules, 30 min; (D) AWP, remaining granules, 35 min; (E) ANP-1, untreated starch; (F) ANP-1, surface-gelatinized granules, 35 min; (G) ANP-1, remaining granules, 35 min; (H) ANP-1, remaining granules, 42 min. AWP, acetylated waxy potato starch (AVEBE, the Netherlands); ANP-1, acetylated normal potato starch (AVEBE, the Netherlands).

curred prominently on the periphery of starch granules. Acetylated waxy potato starch gelatinized faster than acetylated normal potato starch when treated with 4 mol/L $CaCl_2$ solution. The chemical gelatinization time was related to the level of acetylation: the higher the DS, the less the gelatinization time. Not only gelatinized starch but also remaining granules showed different morphology for acetylated waxy and normal potato starch, suggesting structural divergence at the granular level. Remaining granules obtained after higher degree of gelatinization showed greater relative crystallinity and gelatinization temperature, suggesting that amylopectin structure at the core was different from that at the periphery.

Acknowledgements

The financial supports of the National Natural Science Foundation of China (20776082) and the Shaanxi University of Science and Technology (BJ07-02) are gratefully acknowledged. The authors are grateful to AVEBE Food Innovation Centre (Veendam, The Netherlands) for providing acetylated waxy and normal potato starch samples. TianJin TingFung Starch Development Co., Ltd. (TianJin, China) is acknowledged for providing two acetylated normal potato starch samples. The authors also thank Professor Min Zhang (College of chemistry and chemical engineering, Shaanxi University of Science and Technology, Xi'an, China) for her help in using the polarized light microscope.

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