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Characterization and utilization of acid-modified cross-linked Tapioca starch in pharmaceutical tablets

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Abstract

Tapioca starch was cross-linked in the presence of alkaline sodium trimetaphosphate solution. The cross-linked tapioca starch was hydrolyzed by 6% (w/v) HCl solution at room temperature for 192 h. The final product was dried by centrifugal spray dryer to obtain agglomerated acid-modified cross-linked tapioca starch. Spray-dried native tapioca starch, cross-linked tapioca starch and acid-modified tapioca starch were also studied parallel with that of acid-modified cross-linked tapioca starch. It was found that cross-linking didn't increase the relative crystallinity or the melting enthalpy of tapioca starch. Compression of both native and cross-linked tapioca starches gave tablets with a very low crushing strength. Acid hydrolysis introduced to remove the amorphous regions in order to increase the crystallinity of both types of starches, resulting in tablets with a higher crushing strength. In this respect tablets prepared from acid-modified cross-linked tapioca starch were better than those prepared from acid-modified tapioca starch.

Keywords: Tapioca starch; Acid-modified starch; Cross-linked starch; Acid-modified cross-linked starch

1. Introduction

Tapioca starch is an important carbohydrate in tropical countries, worldwide. It has a unique bland flavor and gives a stringy cohesive paste when gelatinized (Bean & Setser, 1992). However, its price in the world market is low when compared to starches from other sources. Therefore it is of interest to add value by finding other uses. In this present work, the potential of tapioca starch for use as a filler in pharmaceutical tablets is investigated. Native tapioca starch possesses many desirable filler properties. It is as dry, white, odorless, tasteless, insoluble and neutral, however it has poor flowability and compressibility. The latter two parameters are of particular importance for tablets prepared by direct compression, (Atichokudomchai, Shobsngob, Chinachoti, & Varavinit, 2001; Bos, Bolhuis, Van doorne, & Lerk, 1987).

Direct compression refers to a process by which the tablets are compressed directly from a powder blend of the active drug and suitable excipients. Usually, the excipients include a filler, a disintegrant and a lubricant. For good tablets to be formed, the powder blend has to flow uniformly and form firm compaction. Good flowability ensures uniformity in die fill and thus uniformity in tablet weight. It also facilitates blending of fine powders encountered in direct compression blends. The filler should furthermore yield tablets of adequate crushing strength without having to apply an excessive compression force (Bolhuis & Chowhan, 1996; Shangraw, 1989).

It is well known that acid hydrolysis of native starches at temperatures lower than the gelatinization temperature can increase the relative crystallinity of the starch. Acid preferentially attacks amorphous regions, while the crystalline regions remain intact. (Chun, Lim, Takeda, & Shoki, 1997; French, 1984; Komiya & Nara, 1986; Vasudeva, Zakiuddin Ali, & Divakar, 1993). In our previous study, native and acid-modified tapioca starches, hydrolyzed with 6% (w/v) HCl at room temperature for various reaction times, were compressed into tablets at various compression forces. It was found that native tapioca starch provided tablets with low crushing strength while the crushing

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strength of tablets prepared from acid-modified tapioca starches increased inline with crystallinity. Tapioca starch hydrolyzed for 192 h provided tablets with an adequate crushing strength without applying excessive compression force (Atichokudomchai et al., 2001). The purpose of this investigation was to study the quality of tablets produced from acid-modified tapioca starch and acid-modified cross-linked tapioca starch. Native and cross-linked tapioca starches were hydrolyzed with 6% (w/v) HCl at room temperature for 192 h. The drying process of all starches studied was by spray drying in order to allow formation of agglomerated starch granules, which provided flowability suitable for direct compression. The starches were compressed into tablets using magnesium stearate as a lubricant. Crushing strength, disintegration time and friability (%) of the tablets were evaluated.

2. Experimental

2.1. Materials

Tapioca starch was a product of Choheng Co., Ltd (Thailand). The chemical compositions of the starch were 0.08, 0.19 and 0.39%(w/w) of protein, lipid and ash content, respectively (Atichokudomchai et al., 2001). Sodium trimetaphosphate, sodium hydroxide, sodium carbonate and hydrochloric acid were analytical grade obtained from Merck (Germany). Magnesium stearate was obtained from the Vithayasom Co. Ltd, (Bangkok, Thailand).

2.2. Methods

2.2.1. Preparation of spherically agglomerated native tapioca starch (control)

Spherically agglomerated native tapioca starch was prepared by suspending 400 g (dry starch basis) of native tapioca starch in 600 ml distilled water, then spray drying with a centrifugal typeMobile Minor Spray Dryer (Gea-Niro, Denmark) at inlet and outlet temperatures of 160 and 60 °C, respectively. The agglomerated native starch granules were sieved through 100-mesh sifter to obtain fine spherically agglomerated starch.

2.2.2. Preparation of cross-linked tapioca starch

Crosslinking reaction of tapioca starch was performed by suspending 300 g of the starch in 600 ml solution of 5% (w/w dry starch basis) sodium trimetaphosphate (STMP), 1.8 g NaOH and 9 g Na_2CO_3. The starch suspension was stirred at room temperature for 3 h, then adjusted to pH 6.5 with 0.2N HCl, washed with distilled water (5000 ml) in a disc type separator (Loher, Germany). The cross-linked starch slurry was spray-dried following the procedure stated earlier to obtain fine spherically agglomerated cross-linked starch.

2.2.3. Preparation of acid-modified and acid-modified cross-linked tapioca starches

400 g (dry basis) of native or cross-linked tapioca starch was hydrolyzed by suspending in 600 ml of 6% HCl solution at 25 °C for 192 h without stirring. After hydrolysis, the suspension was neutralized with 10%(w/v) NaOH solution, and washed three times with distilled water. The water was then removed by centrifugation (Sorvall RC 3B Plus, Du Pont Company, Delaware, USA) at 207 g for 2 min followed by decanting. The modified starch was then spray-dried following the procedure stated earlier to obtain acid-modified or acid-modified cross-linked starch.

2.2.4. Scanning electron microscopy (SEM)

The starches were mounted on scanning electron microscopy (SEM) stubs with double-sided adhesive tape and coated with gold. Images were taken using a JEOL JSM-5410LV microscope (JEOL, Tokyo, Japan). The accelerating voltage and the magnification are given on the micrographs.

2.2.5. Size distribution of the spherically agglomerated starches and the starch granules

The size distribution of the spherically agglomerated native, cross-linked, acid-modified and acid-modified cross-linked starches were measured by suspending 5 g of the spray-dried starch in 10 ml solution of 99% ethanol. The starch suspension was stirred at 3500 rpm and immediately passed through a laser diffraction spectrometer (Malvern instruments Ltd, Malvern, UK). The granular size distribution of the starches were measured by suspending 5 g of the spray-dried starch in 10 ml distilled water. The starch suspension was sonicated for 30 min to disrupt the agglomerates using a Ney ultrasonik cleaner tank (Ultrasonik 3Q/H, Ney Company, Bloomfield, CT). Power was set at 50% of the maximum 175 W (out put frequency 50/60 Hz). After that the starch suspension was stirred at 3500 rpm and suddenly passed through the laser diffraction spectrometer. The volumetric weighted means of all samples were recorded.

2.2.6. Amylose and phosphorus content measurement

The amylose content was measured by the iodine affinity method (Knutson, 1986). Phosphorus content was determined from the starch ash. The starch was mixed with 1% (w/w) Na_2CO_3 and ignited in a furnace at 600 °C. The phosphorus content in the ash was determined colorimetrically according to the method described by Murphy and Riley (1962). The degree of substitution (DS) was calculated using the following equation by (Paschall (1964)):

$$DS = \frac{162P}{3100 - 102P}$$

where P = %phosphorus (dry basis) of the phosphorylated starch.

Table 1
Composition of native (NT), cross-linked (CT), acid-modified (AT) and acid-modified cross-linked (AC) tapioca starch

Starch sample	Moisture (%wet basis)	% Amylose content[a,b]	% Relative crystallinity[a,b]	%Phosphorus content[a,b]	Degree of substitution (DS)
NT	10.0	33.4 ± 1.4a	38.9 ± 0.2a	0.02 ± 0.01a	0.001
CT	9.9	33.6 ± 0.5a	38.5 ± 0.8a	0.09 ± 0.00b	0.005
AT	9.9	10.8 ± 0.1b	54.4 ± 0.6b	0.12 ± 0.00c	0.006
AC	10.0	13.2 ± 0.5c	52.9 ± 0.6c	0.13 ± 0.01d	0.007

[a] Mean ± Standard deviation.

[b] Means with the same letter in each column are not significantly different ($\alpha = 0.05$).

2.2.7. X-ray powder diffraction measurements

Monochromatic Cu Kα radiation (wavelength = 1.542 A) was produced by a Bruker D8 (German) X-ray powder diffractometer. The starch powders were exposed to the X-ray beam with the X-ray generator running at 40 KV and 30 mA. The scanning regions of the diffraction angle 2θ were 4–30°, step interval 0.02, scan rate 2°/min. The sollet and divergence slit was 1°. The receiving slit was 1° and scattering slit was 0.15°. The measurements were made at 25 °C. Relative crystallinity (%) of the starches were measured following the method of Komiya and Nara (1986).

2.2.8. Gelatinization properties

Gelatinization properties of native and acid-modified tapioca starch were analyzed using a Differential Scanning Calorimeter (DSC7, Perkin Elmer, Norwalk, CT). The starch samples at starch to water ratio of 1:2 were prepared. Each starch suspension was then transferred to an aluminum pan (Perkin Elmer) and hermetically sealed. Following equilibration at room temperature for 24 h, the samples were heated from 40 to 120 °C at 5 °C/min. An empty pan was used as the reference and the DSC was calibrated using indium. All measurements were done at least in triplicate. The onset (To), peak (Tp) and conclusion (Tc) temperatures and the melting enthalpy (ΔH) in J/g of dry starch were recorded.

2.2.9. Preparation of tablets

The tablet formulation was 99.5% starch (as filler) and 0.5% magnesium stearate (as lubricant). The spherical agglomerated starches of native, cross-linked, acid-modified and acid-modified cross-linked starch were compressed with a 8 mm a flat-face-beveled-edge punch on an instrument tablet press (Fette, Germany), which had been calibrated with resistance strain gauges to monitor

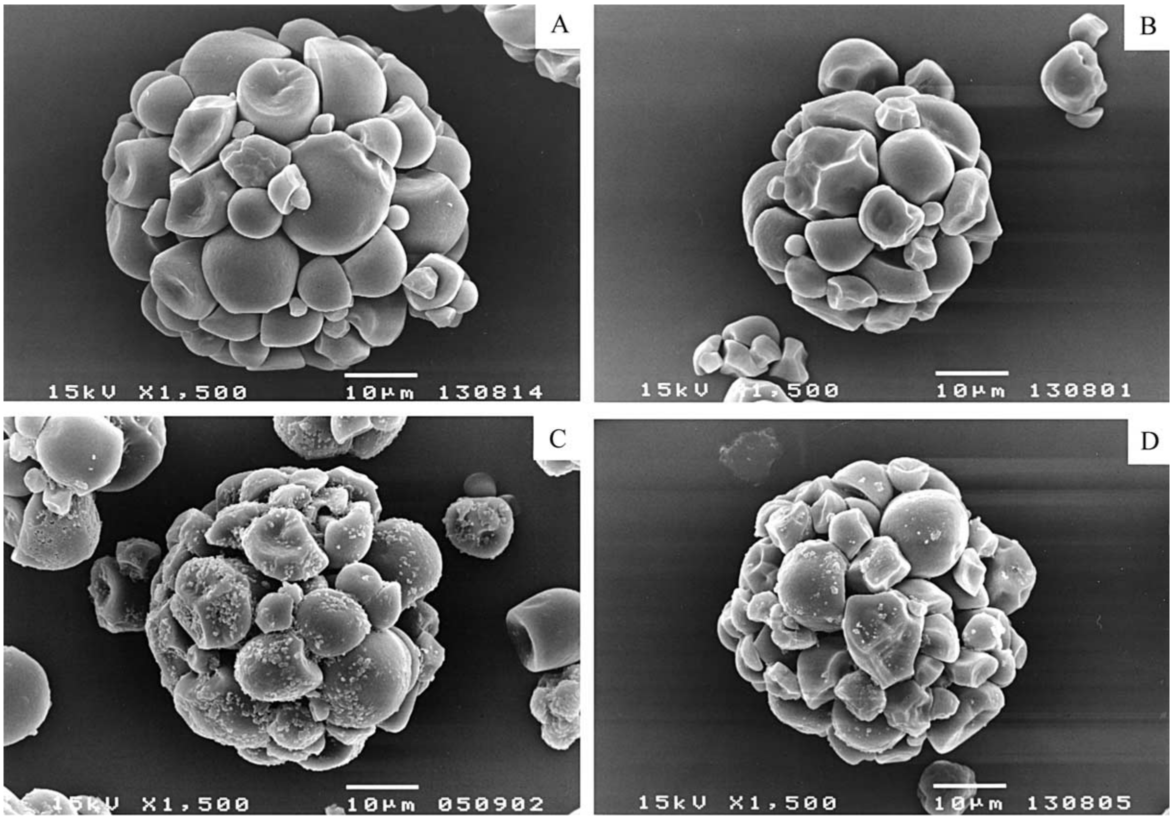

Fig. 1. The scanning electron micrographs (magnificent 1500 ×) of spray-dried native (A), cross-linked (B), acid-modified (C) and acid-modified cross-linked (D) tapioca starches.

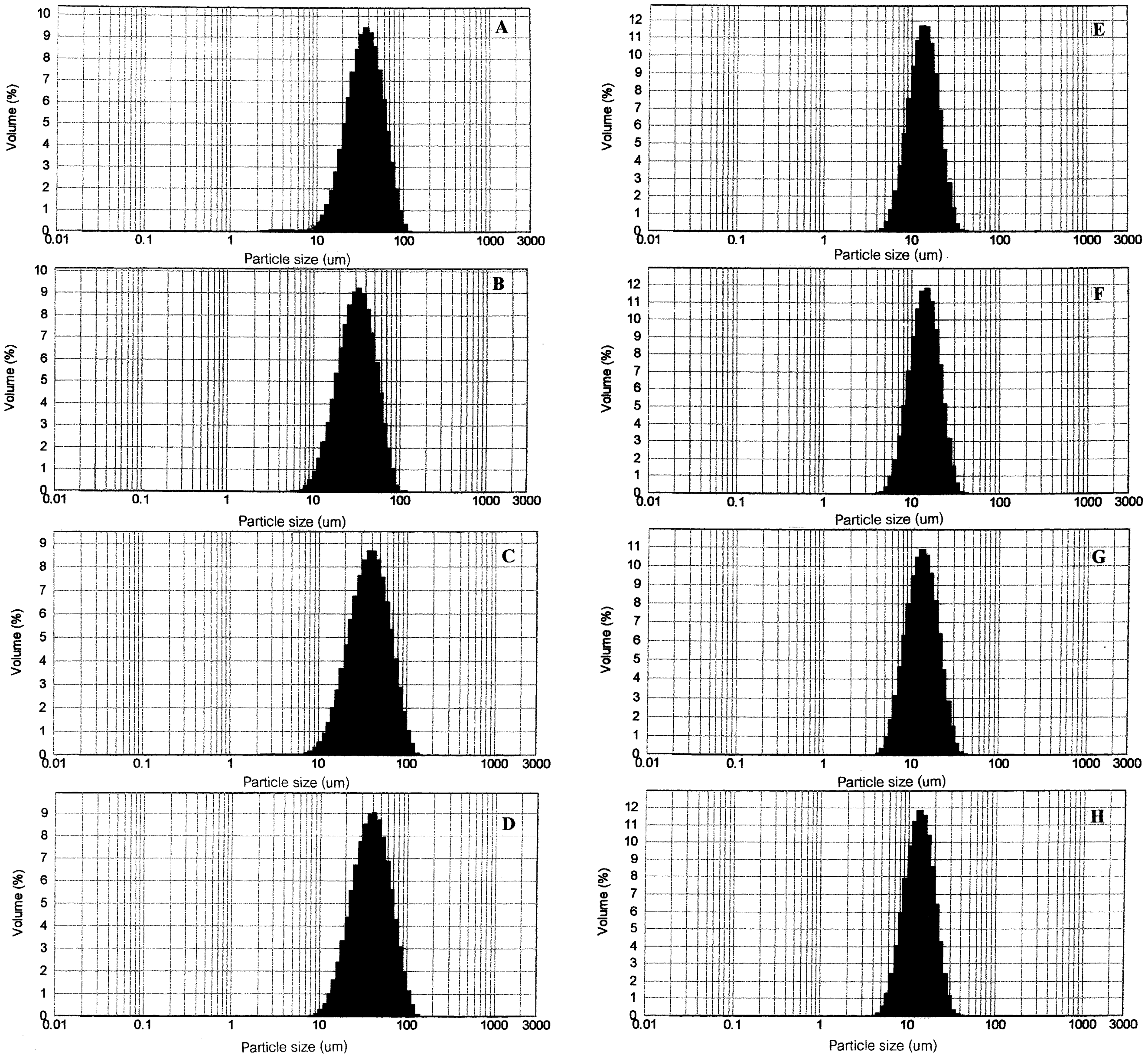

Fig. 2. Volumetric particle size distributions of agglomerated (A–D) and granuler starches (E–H); native (A, E), cross-linked (B, F), acid-modified (C, G) and acid-modified cross-linked (D, H).

compression and ejection forces. The calibration has been described in detail previously (Salpekar & Augsburger, 1974). A single station was used only to help minimize tooling errors. The same circular, flat-faced punches with a die of 8 mm diameter and 300 mg target weight, was used throughout the study.

2.2.10. Tablet evaluation

The crushing strength of tablets was determined with an electronic hardness tester (Schleuniger Model 4M Dr Schleuniger Co., Switzerland). All crushing strengths values reported were given as means of 10 determinations. The friability of tablets were determined by Roche type friabilator (Narongkarnchang, Thailand) (Sjokvist & Nystrom, 1991). The tablet disintegration time was determined with USP disintegration apparatus (Hanson Model AC 24, Hanson Research Corp., USA).

3. Results and discussions

The phosphorus content and degree of substitution (DS) of native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch were shown in Table 1. Native tapioca starch contained 0.02% phosphorus (dry starch basis). Crosslinking with STMP gave cross-linked starch that contained 0.09% phosphorus. After acid hydrolysis, the phosphorus content increased pronouncedly (Table 1).

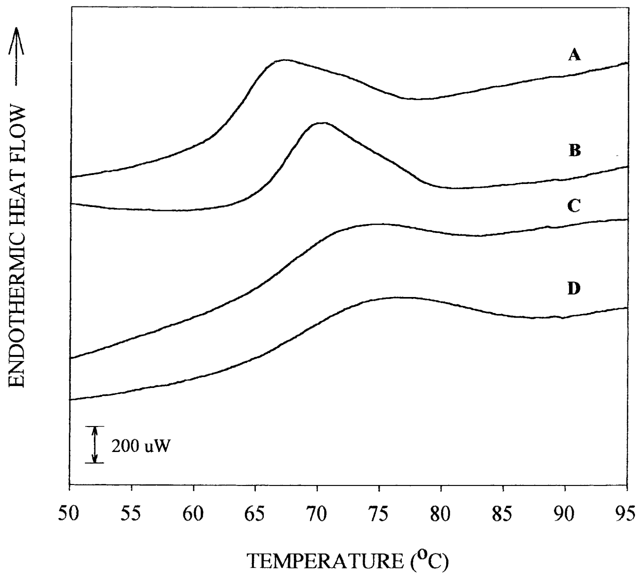

Fig. 3. DSC thermograms of native (A), cross-linked (B), acid-modified (C) and acid-modified cross-linked (D) tapioca starches. All samples contained starch to water ratios of 1:2 and the heating rate was 5 °C/min.

The phosphorus content was positively correlated to the relative crystallinity. It is known that the phosphorus in native tapioca starch is phosphate monoesters, which are primarily found in amylopectin clusters (Jane, Kasemsuwan & Chen, 1996; Schoch, 1942; Tabata, Nagata & Hizukuri, 1975). Jane, Xu, Radosavljevic, and Seib (1992) also found that crosslinking of starch chains mainly occurred in amylopectin. Therefore, when the relative amount of crystallinity (mainly amylopectin side chains) increased by acid hydrolysis, the relative amount of phosphorus content in acid-modified and acid-modified cross-linked starches increased (Table 1). Since the relative crystallinity of acid-modified starch was higher than acid-modified cross-linked starch, the phosphorus content was pronouncedly increased for acid-modified starch, but less for acid-modified cross-linked starch when compared to their original starch before hydrolysis (native and cross-linked tapioca starch, respectively) (Table 1).

Before hydrolysis, the relative crystallinity of cross-linked starch was not significantly different from the native starch (Table 1). Therefore the cross links induced between the amylopectin chains (Jane et al., 1992), may only strengthen the existing crystallites without forming new crystalline region. When cross-linked starch was subjected to acid hydrolysis, its relative crystallinity increased but was lower than for acid-modified tapioca starch (Table 1). In contrast, the amylose content of acid-modified cross-linked starch was higher than acid-modified starch. Though crosslinking preferentially occurred in amylopectin, some amylose molecules were cross-linked to amylopectin (Jane et al., 1992). These amylose molecules will be protected from acid hydrolysis. Therefore, amylose hydrolysis decreased after crosslinking resulting in higher percentage of amylose and consequently lower relative crystallinity when compared to that of the acid-modified non cross-linked starch (Table 1).

The scanning electron micrographs of native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch are shown in Fig. 1. All agglomerated starches showed a spherical shape as a result of spray drying (Fig. 1(A–D)). Native tapioca starch granules exhibited smooth granule surfaces (Fig. 1(A)). After being cross-linked, there is no change in the appearance of the starch granule. The surfaces of the cross-linked tapioca starch granules were smooth and similar to that of the native starch granules (Fig. 1(B)). This result was in agreement with that reported by Wurzburg (1986). After hydrolysis for 192 h, the surface erosion of native tapioca starch was observed (Fig. 1(C)). This surface erosion was similarly observed in the case of acid-modified cross-linked starch (Fig. 1(D)) indicating that there was hydrolysis of the amorphous parts, mostly amylose, at the surface of the granules (Atichokudomchai, Shobngob, & Varavinit, 2000).

The size distributions of the agglomerated spherical native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch are shown in Fig. 2(A–D). All of the starches exhibited the same size distribution pattern with a volume mean diameter of 39.7 ± 0.1, 34.8 ± 0.0, 42.0 ± 0.2 and 43.1 ± 0.6 μm, respectively. The agglomerate shape could be broken into individual granules by sonicating in distilled water. The granule size distributions were measured and the results are shown in Fig. 2(E–H). The volume mean diameter of cross-linked starch granules (15.2 ± 0.3 μm) was slightly higher than that of the native starch granules (14.7 ± 0.1 μm), while acid-modified and acid-modified cross-linked showed the same volume mean diameter (14.3 ± 0.0 and 14.3 ± 0.1 μm, respectively).

Table 2
Celatinization temperatures (To, Tp, Tc) and enthalpy of native (NT), cross-linked (CT), acid-modified (AT) and acid-modified cross-linked (AC) tapioca starch obtained from DSC thermograms

Starch Sample	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	Temperature range (Tc–To)
NT	61.5 ± 0.1a	66.6 ± 0.1a	78.5 ± 0.9a	14.3 ± 1.0a	17.0
CT	65.5 ± 1.0b	69.8 ± 0.2b	82.6 ± 0.5b	14.3 ± 0.3a	17.1
AT	59.1 ± 1.0c	72.1 ± 0.07c	85.6 ± 1.3c	13.8 ± 0.9a	26.5
AC	66.0 ± 0.8b	74.7 ± 0.2d	86.7 ± 1.1c	12.3 ± 1.1b	20.7

Mean ± Standard deviation; Means with the same letter in each column are not significantly different ($\alpha = 0.05$).

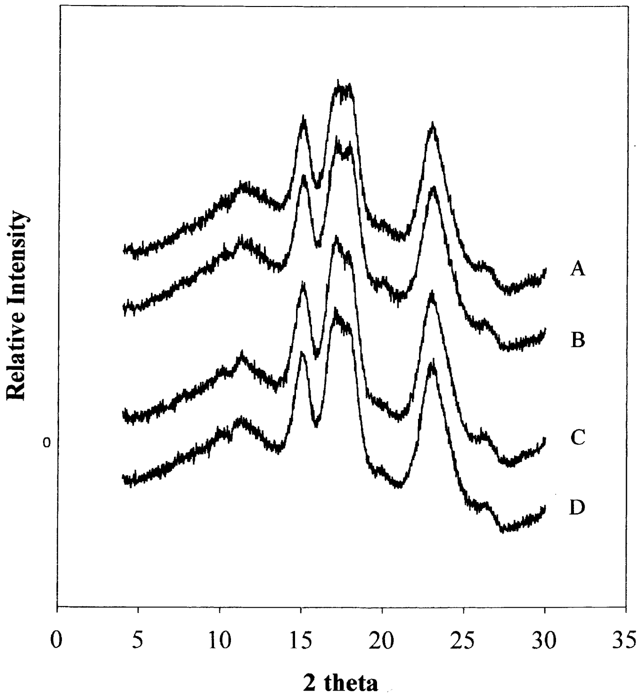

Fig. 4. X-ray diffraction patterns of native (A), cross-linked (B), acid-modified (C) and acid-modified cross-linked (D) tapioca starches.

The increase in granule size of cross-linked starch might be due to the slightly swelling of the granules, which was possibly enhanced when the phosphate groups were included.

Fig. 3 showed the gelatinization thermograms of native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch, all at water to starch ratio of 2:1 and 5 °C/min heating rate. The onset (To), peak (Tp) and conclusion (Tc) temperatures, the melting enthalpy (ΔH) and the temperature range (Tc–To) are summarized in Table 2. From Fig. 3, it can be seen that the native sample exhibited a deep and sharp endotherm. After 192 h of hydrolysis, the peak became broaden as indicated by the large increase in temperature range (Table 2), while the onset temperature shifted to lower temperature. The decrease in the onset temperature and the endotherm broadening corresponded to the melting of shorter and more heterogeneous double helices of amylopectin, resulting from the loss of molecular order in the second stage of hydrolysis (Atichokudomchai, Varavinit, & Chinachoti, 2002). The melting enthalpy of acid-modified starch was not significantly different from the native starch (Table 2). It is suggested that the partially hydrolyzed amylose retrograded compensating for the decrease in the double helix content which normal occur on with hydrolysis, so that the melting enthalpy did not decrease (Atichokudomchai et al., 2002). The gelatinization endotherm of cross-linked starches shifted to higher temperature when compared to the endotherm of the native starch (Fig. 3). It was known that crosslinking can stabilized the molecular structure of the starch granules causing gelatinization to occur at a higher temperature (Wurzburg, 1986). However, the enthalpy was not significantly changed, suggesting a complete melting of crystalline regions regardless of crosslinking (Chatakanonda, Varavinit, & Chinachoti, 2000). The gelatinization endotherm of acid-modified cross-linked tapioca starch showed a broad feature similar to the endotherm of acid-modified tapioca starch, but with a narrower temperature range (Table 2). The narrower endotherm indicated higher homogeneity in the acid-modified cross-linked granules. The melting enthalpy of acid-modified cross-linked starch was slightly lower than that of acid-modified starch (Table 2). Since amylose was less hydrolyzed after being cross-linked (Table 1), the lower enthalpy might reflect a lower double helix content (Cooke & Gidley, 1992), due to a lower extent of retrograded amylose.

The X-ray diffraction patterns of native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch are presented in Fig. 4. Native tapioca starch showed the A type polymorph with strong peaks at 2θ about 15 and 23° and a doublet at 17 and 18° (Veregin, Fyfe, Marchessault, & Taylor, 1986; Zobel, 1988) (Fig. 4). The cross-linked starch pattern was similar to that for the native starch (Fig. 4). This result indicated that crosslinking had no effect on the repeat distance of crystalline and amorphous lamellae of starch granules (Zheng, Han, & Bhatty, 1999). After acid hydrolysis for 192 h, sharpening of the native and cross-linked starch patterns was observed (Fig. 4).

Table 3 shows the crushing strength (N) at various compression forces (kN) of tablets prepared from native, cross-linked, acid-modified and acid-modified cross-linked tapioca starch. Native and cross-linked tapioca starch possessed poor compressibility since they could only be compressed with magnesium stearate (lubricant) into tablets at 4 kN with a crushing strength of 17.66 and 16.88 N,

Table 3
Crushing strength (N) at various compression forces (kN) of tablets preparing from native (NT), cross-linked (CT), acid-modified (AT) and acid-modified cross-linked (AC) tapioca starch

Compression force (kN)	Crushing strength (N)			
	NT	CT	AT	AC
2.0	eb[a]	eb[a]	13.75 ± 0.06	22.56 ± 0.13
4.0	17.66 ± 0.20	16.68 ± 0.41	64.75 ± 0.28	78.48 ± 0.47
6.0	capping	capping	89.27 ± 0.74	99.08 ± 0.35

[a] Excessive breakage.

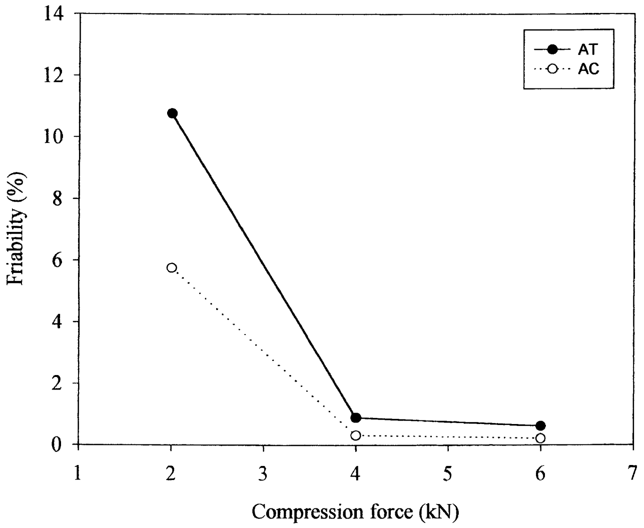

Fig. 5. Friability (%) of tablets prepared from acid-modified (AT) and acid-modified cross-linked (AC) tapioca starches.

respectively. Tablets prepared from acid-modified and acid-modified cross-linked tapioca starch had higher a crushing strength of 64.75 and 78.48 N, respectively.

In previous work, the crushing strength of the tablets compressed from plain acid-modified tapioca starches increased inline with relative crystallinity. When applying a compression force to the starch granules, the crystalline regions for the more crystalline starches could be forced closer together. The stronger packing structure resulted in an increase in the crushing strength of the tablets (Atichokudomchai et al., 2001). In contrast, for the present work, acid-modified cross-linked starch with a lower relative crystallinity had a higher crushing strength than acid-modified starch (Table 1). Crosslinking introduces intermolecular bridges between starch chains markedly reinforcing hydrogen bonds holding the granule (Rutenberg & Solarek, 1984). As mentioned earlier, it was found that crosslinking mainly took place in amylopectin. Therefore the reinforcement of amylopectin may lead to stronger (closer) packing within the crystalline regions. Thus preparing the tablets from the acid-modified cross-linked starch was likely to have stronger packing than preparing them from acid-modified non cross-linked starch, although it had a lower relative crystallinity.

The friability and disintegration time of tablets prepared from native, cross-linked, acid-modified and acid-modified cross-linked tapioca starches are shown in Figs. 5 and 6, respectively. Acid-modified and acid-modified cross-linked tapioca starch provided tablets with low friability (less than 1% at 4 and 6 kN of compression force) (Fig. 5) and a short disintegration time (less than 3.5 min at 2–6 kN of compression force) (Fig. 6). Acid-modified cross-linked starch exhibited lower friability and shorter disintegration time than those of acid-modified starch when compared at the same compression force.

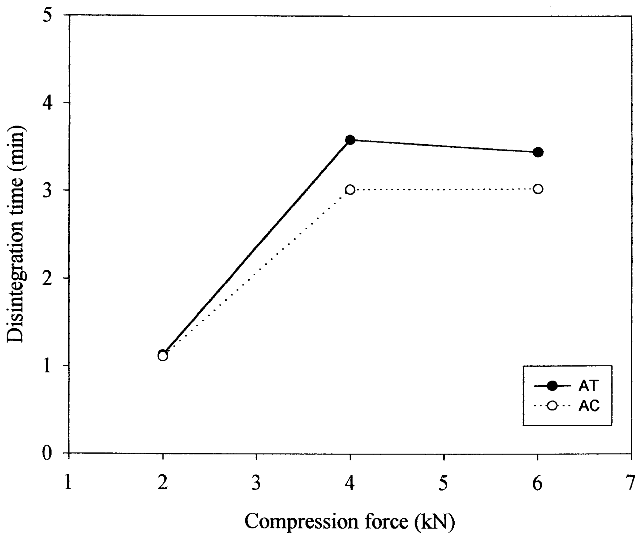

Fig. 6. Disintegration time (min) of tablets prepared from acid-modified (AT) and acid-modified cross-linked (AC) tapioca starches.

For tablets prepared from acid-modified cross-linked starch, the shorter disintegration time might be possibly due to less damage (gelatinized) starch granules in the tablet. The gelatinous layer developing from damaged starch impedes the penetration of water into the tablet and thus prolongs the disintegration (Mitrevej, Sinchaipanid, & Faroongsarng, 1996). Since cross-linking tightened the starch chains, restricting the swelling of the starch granules and increased the gelatinization temperature (Table 2), the cross-linked starch could be less susceptible to damage when subjected to severe conditions, i.e., acid hydrolysis. Thus the tablets compressed from acid-modified cross-linked starch might contain less damaged granules than those of acid-modified starch resulting in a slightly shorter disintegration time when immersed in the water.

4. Conclusion

Crosslinking didn't increase the crystallinity in the starch granules but seemed to have reinforced the packing of crystalline regions as observed from the increase in the gelatinization temperature compared to that of the native starch. However, crosslinking alone cannot increase the crushing strength of the tablets since the amorphous regions still disrupted crystalline packing. Acid-hydrolysis was needed to remove the amorphous regions, resulting in a stronger packing under the application of the compression force. Acid-modified cross-linked tapioca starch provided higher crushing strength than that of acid-modified tapioca starch. Acid-modified and acid-modified cross-linked tapioca starches were shown to be useful as fillers in direct-compression tablet preparation.

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References

Atichokudomchai, N., Shobsngob, S., Chinachoti, P., & Varavinit, S. (2001). A study of some physicochemical properties of high-crystalline tapioca starch. *Starch/Starke*, *53*, 577–581.

Atichokudomchai, N., Shobsngob, S., & Varavinit, S. (2000). Morphological properties of acid-modified tapioca starch. *Starch/Starke*, *52*, 283–289.

Atichokudomchai, N., Varavinit, S., & Chinachoti, P. (2003). Gelatinization transitions of acid-modified tapioca starches by differential scanning calorimetry (DSC). *Starch/Starke*, in press.

Bean, M. M., & Setser, S. C. (1992). Polysaccharides, sugars, and sweeteners. In J. Bowers (Ed.), *Food theory and applications* (pp. 70–118). New York: Macmillan publishing company.

Bolhuis, G. K., & Chowhan, Z. T. (1996). Material for direct compaction. In G. Alderborn, & C. Nystrom (Eds.), *Pharmaceutical powder compaction technology* (pp. 419–500). New York: Marcel Dekker.

Bos, C. E., Bolhuis, G. K., Van doorne, H., & Lerk, C. F. (1987). Native starch in tablet formulation: Properties on compaction. *Pharmaceutisch Weekblad*, *9*, 274–282.

Chatakanonda, P., Varavinit, S., & Chinachoti, P. (2000). Relationship of gelatinization and recrystallization of cross-linked rice to glass transition temperature. *Cereal Chemistry*, *77*, 315–319.

Chun, J., Lim, S., Takeda, Y., & Shoki, M. (1997). Properties of high-crystalline rice amylodextrins prepared in acid-alcohol media as fat replacers. *Cereal Food World*, *42*, 813–819.

Cooke, D., & Gidley, M. J. (1992). Loss of crystallinity and molecular order during starch gelatinization: origin of the enthalpic transition. *Carbohydrate Research*, *227*, 103–112.

French, D. (1984). Organization of Starch Granules. In R. L. Whistler (Ed.), *Starch chemistry and technology* (pp. 183–247). New York: Acedemic Press.

Jane, J., Kasemsuwan, T., & Chen, J. F. (1996). Phosphorus in rice and other starches. *Cereal Foods World*, *41*, 827–832.

Jane, J., Xu, A., Radosavljevic, M., & Seib, P. A. (1992). Location of amylose in normal starch granule. I. Susceptibility of amylose and amylopectin to crosslinking reagents. *Cereal Chemistry*, *69*, 405–409.

Knutson, C. A. (1986). A simple calorimetric procedure for determination of amylose in maize starches. *Cereal Chemistry*, *63*, 89–92.

Komiya, T., & Nara, S. (1986). Changes in crystallinity and gelatinization phenomena of potato starch by acid treatment. *Starch/Starke*, *38*, 9–13.

Mitrevej, A., Sinchaipanid, N., & Faroongsarng, D. (1996). Spray-dried rice starch: comparative evaluation of direct compression fillers. *Drug Development and Industrial Pharmacy*, *22*, 587–594.

Murphy, J., & Riley, J. H. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, *27*, 31–36.

Paschall, F. E. (1964). Phosphorylation with inorganic phosphate salts (*Vol. 4*). *Methods in carbohydrate chemistry*, New York: Academic Press Publishers, pp. 214–296.

Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: Production and uses. In R. L. Whistler (Ed.), *Starch chemistry and technology* (pp. 311–388). New York: Acedemic Press.

Salpekar, A. M., & Augsburger, L. L. (1974). Magnesium lauryl sulfate in tableting: effect on ejection force and compressibility. *Journal of Pharmaceutical Sciences*, *63*(2), 289–293.

Schoch, T. J. (1942). Fractionation of starch by selective precipitation with butanol. *Journal of the American Chemical Society*, *64*, 2957–2961.

Shangraw, R. F. (1989). Compressed tablets by direct compression. In H. A. Lieberman, H. A. Lachman, & J. B. Schwartz (Eds.), (*Vol. 1*) (pp. 195–246). *Pharmaceutical dosage forms*, New York: Marcel Dekker.

Sjokvist, E., & Nystrom, C. (1991). Physicochemical aspects of drug release. XI. Tabletting properties of solid dispersions using xylitol as carrier material. *International Journal Pharmaceutical*, *67*, 139–153.

Tabata, S., Nagata, K., & Hizukuri, S. (1975). Studies on starch phosphates. Part 3. On the esterified phosphates in some cereal starches. *Starch/Starke*, *27*, 333–335.

Vasudeva, S., Zakiuddin Ali, S., & Divakar, S. (1993). ^{13}C CP/MAS NMR spectroscopy of native and acid modified starches. *Starch/Starke*, *45*, 59–62.

Veregin, R. P., Fyfe, C. A., Marchessault, R. H., & Taylor, M. G. (1986). Characterization of the Crystalline A and B starch polymorphs and investigation of starch crystallization by high resolution ^{13}C CP/MAS NMR. *Macromolecules*, *19*, 1030–1034.

Wurzburg, O. B. (1986). Cross-linked starches. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 41–54). Boca Raton, FL: CRC Press.

Zheng, G. H., Han, H. L., & Bhatty, R. S. (1999). Functional properties of cross-linked and hydroxypropylated waxy hull-less barley starches. *Cereal Chemistry*, *76*, 182–188.

Zobel, H. F. (1988). Molecules to granules: A comprehensive starch review. *Starch/Starke*, *40*, 44–50.