CHAPTER IV

RESULTS AND DISCUSSION

Starch Powder Studies

1. Physicochemical Properties of Native Starch

The native starches used in this study were the high-grade commercial starches (corn, glutinous rice and tapioca starch). Anyway all types of native starches used were rechecked for the physicochemical properties according to the compendial standard. It was found that all types of starting native starches were complied with USP 23.

The differences of physicochemical properties among commercial native starches were presented in **Table 6**. The results could be explained that each starch is unique in terms of granule organization and structures and behaviors of starches from different sources are limited, and that not all granules of a single starches preparation behave identically (BeMiller, 1997). Amounts and structure of other constituents differ from plant source to plant source and probably from location to location. So it is essential to direct the research on starch source toward pharmaceutical technology of starches by extensive investigation on development and modification of various starches available locally for pharmaceutical purpose.

Table 6 Properties of native corn, glutinous rice and tapioca starch according to USP XXIII.

Specifications	USP Standard Limit	Corn Starch Test	Glutinous Rice Starch Test	Tapioca Starch Test
Identification				
I. translucent, whitish jelly	conform	conform	conform	conform
II. reddish violet to deep blue	conform	conform	conform	conform
pH	4.5-7.0	5.7	6.6	5.4
Loss on drying	≤14.0%	12.1%	11.1%	12.5%
Residue on ignition	≤0.5%	0.1%	0.3%	0.1%
Iron	≤0.002%	0.001	0.000	0.002
Oxidizing substances	≤0.002%	< 0.002	< 0.002	< 0.002
Sulfur dioxide	≤0.008%	0.004%	0.005%	0.003%

2. Acid Treated Starches

2.1 Preliminary study

Since the primary objective in acid modification is to reduce the hot paste viscosity of starch, the conversion process is monitored by measurement of viscosity by Brabender viscoamylograph

The reaction conditions of acid treated starches, i.e. acid concentration, temperature and time of the treatment were varied to obtained the acid treated starch with two levels of viscosity.

Three types of mineral acid, hydrochloric acid and autophosphoric not more than 7% or sulfuric acid not more than 2%, have been approved to use in food starches by the Ministry of Industry, Thailand. The hydrochloric acid and sulfuric were usually used in the earlier study (Lintner, 1886 cited in Shildneck and Smith, 1967). The reason for selecting hydrochloric acid used in this study was that the sulfuric acid formed salts with the non starchy substances and that these salts inhibited the rate of hydrolysis; chloride salts had no inhibitory effect, and hydrochloric in excess, was necessary to guarantee a normal hydrolysis rate and complete hydrolysis. And as pointed out in the previous research, there is a marked difference between the hydrolysis rates with hydrochloric acid and with sulfuric acid when both are used in comparable amounts, the rate constant being larger for hydrochloric acid than for sulfuric acid. The ratio depends on both the acid concentrations and temperature; with 0.1 N acid about 100°C, the catalytic activity of sulfuric acid is about 56% of that hydrochloric acid. This was shown that the hydrochloric acid could also strongly affect the gel and viscosity characteristics (BeMiller, 1965).

Since all or nearly all hydrogen bonds in starch molecule are relatively weak. By action of the aqueous acid at the temperature below the gelatinization point, starch granule are degraded with cleavage of some or all the macromolecules but little change in the external form or birefringence of the granule. (see **"The Polarizing Microscope of Starch"**) Initial attack is in the amorphous region. This degradation leads to a reduction in the viscosity of starch (Rhower and Klem, 1984).

The type and extent of morphological change undergone by starch granules during hydrolysis have been well documented. In general, hydrolysis agents either

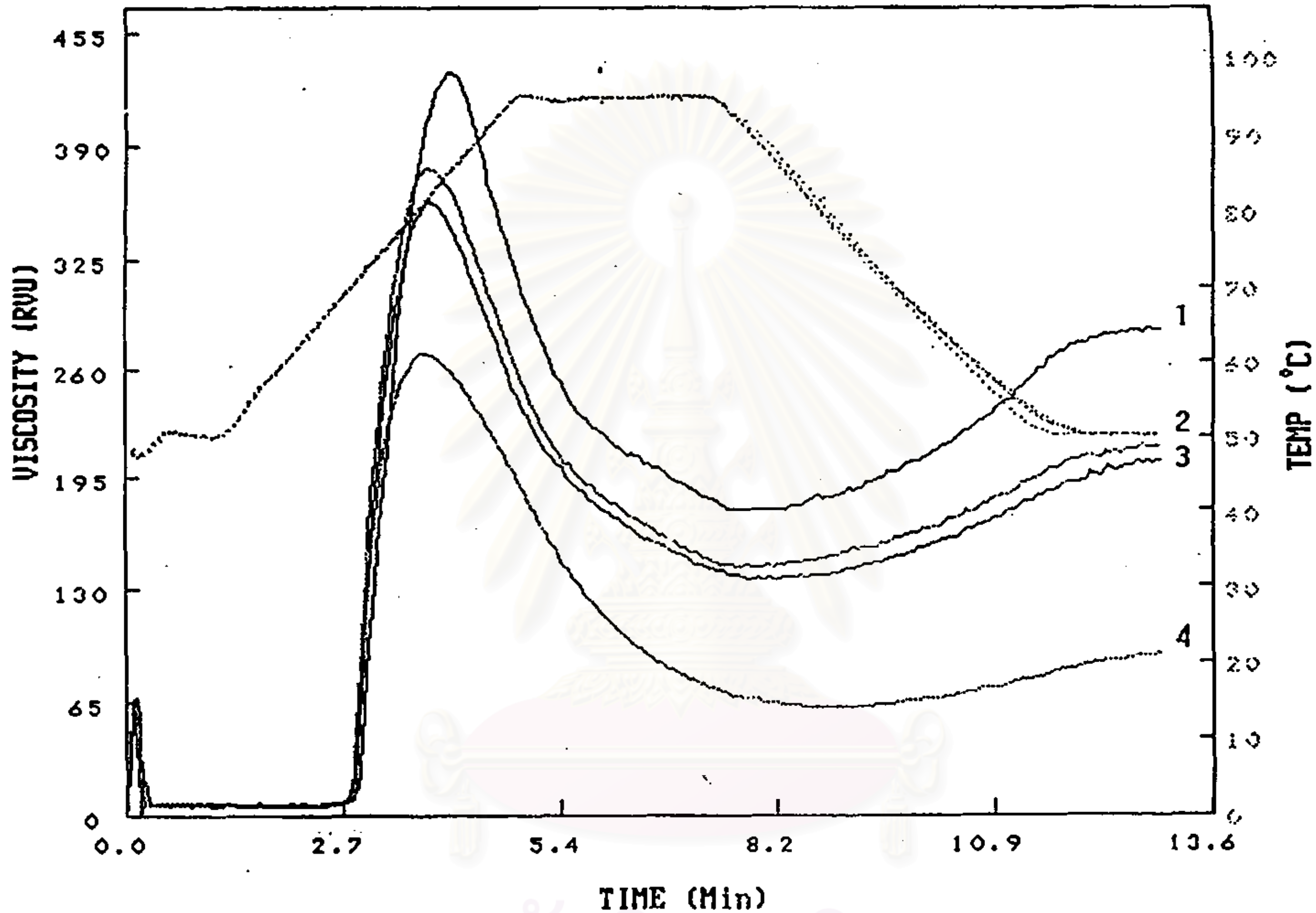


Figure 6 The viscosity of tapioca starch in various types of acid (Oates, 1997)

1 : tapioca starch   2 : tapioca starch + lactic acid   3 : tapioca starch + hydrochloric acid   4 : tapioca starch + sulfuric acid

erode the entire granule surface or sections of it (exocorrosion) or digest channels from selected points on the surface towards the center of the granule (endocorrosion). Initial hydrolysis in the case of most starch granules is superficial and dependent on the type of starch. Starches from some tropical tubers such as tapioca starch have specific susceptible zones that become pitted owing to endocorrosion. Pits become enlarged and canals of endocorrosion sink into the interior, and numerous channels are formed around the granules. Starch granules from rice are hydrolyzed by the formation of random and deeply pitted canals that enlarge through the granules at each shell level. Following the initial attack, in many types of starches, hydrolysis agent will hydrolyse one or more paths to the center of granule with subsequent enzyme attack proceeding outwards over a broader front. It is clear that during all stages, from initial attack to later digestion, some religions of the granule are more readily digested than others. Those area that are susceptable to attack are the less organized amorphous rings, whearas the crystalline lamellae offer resistance to erosion (Oates, 1997).

Cowie and Greenwood (1957, cited in BeMiller, 1965) have examined the effect of 0.2 M HCl acid at 45°C on the granular structure of potato starch, a tuber starch. They observed that, under the conditions used, there was no swelling of the granules, whose birefringence properties were also unchanged. This was interpreted as meaning that the acid treatment preferentially affected the amorphous rather than the crystalline region of the granule.

Figure 7- 9 show the viscosity Brabender viscoamylograph obtained from acid treated corn, glutinous rice and tapioca starches by seven process conditions (**Table 3**) comparing with native starch.

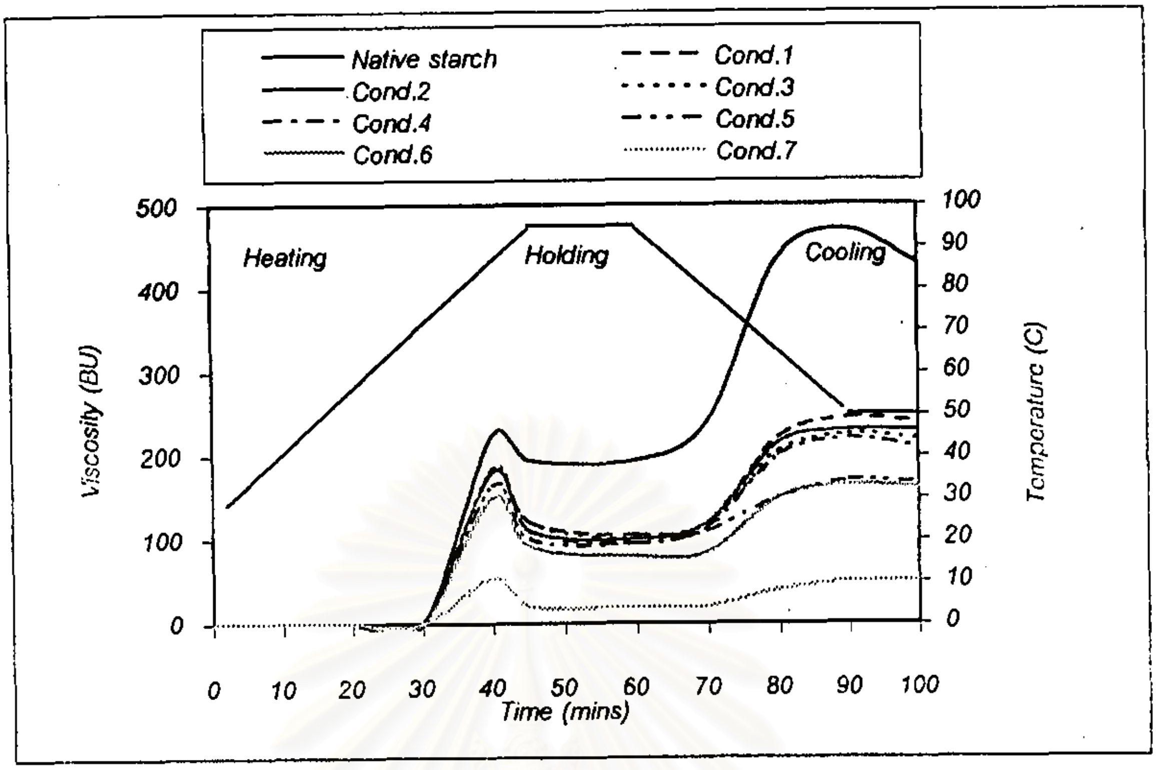


Figure 7 Influence of acid treated conditions on viscosity of corn starch

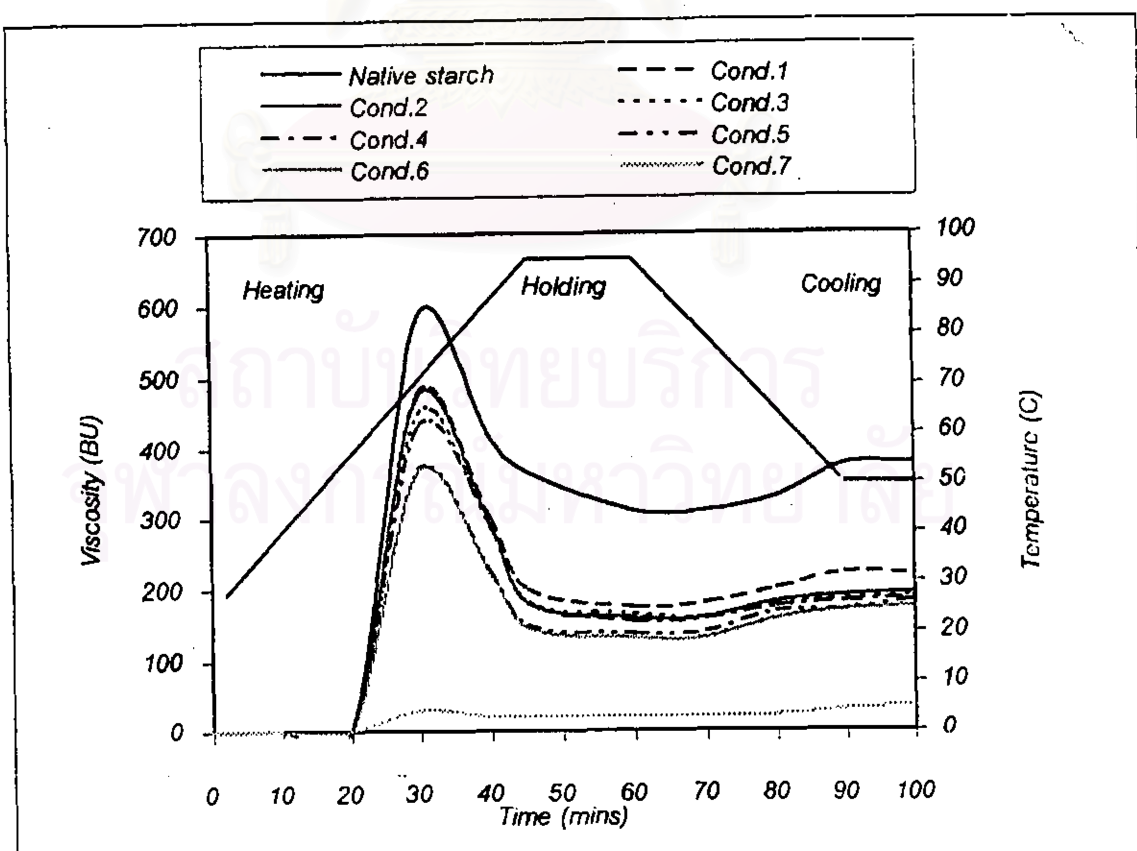


Figure 8 Influence of acid treated conditions on viscosity of glutinous rice starch

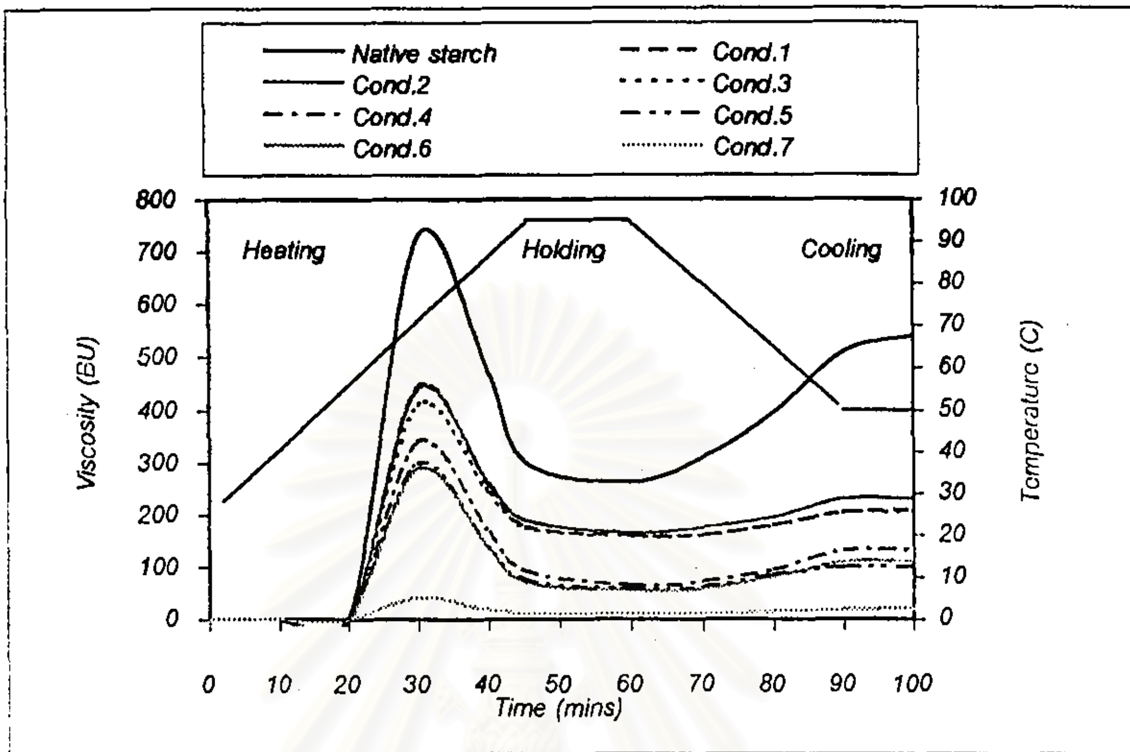


Figure 9 Influence of acid treated conditions on viscosity of tapioca starch

Cond.1: 0.5% v/v hydrochloric acid, 35°C, 0.5 hour

Cond.2: 0.5% v/v hydrochloric acid, 35°C, 1.0 hour

Cond.3: 0.5% v/v hydrochloric acid, 35°C, 2.0 hour

Cond.4: 1.0% v/v hydrochloric acid, 35°C, 0.5 hour

Cond.5: 1.0% v/v hydrochloric acid, 50°C, 0.5 hour

Cond.6: 2.0% v/v hydrochloric acid, 35°C, 0.5 hour

Cond.7: 2.0% v/v hydrochloric acid, 50°C, 0.5 hour

The Brabender viscoamylograph curves present that the concentration of acid, temperature during treatment and reaction times upon acid modification of starch are very important factors which affected viscosity of acid treated starches obtained, the higher acid concentration, higher temperature and/or longer reaction time, the lower will be the viscosity.

In this experiment, the attempt has been made to reduce the viscosity of starch at two levels in comparing with native starch in order to find the suitable viscosity of pregelatinized starch prepared to have less effect on the disintegration of tablet formulated with theses modified starches. The conditions selected were:

1. Acid modified starch produced at HCl acid concentrated 0.5 %, at 35°C for 0.5 hour, possessed properties suitable high level viscosity acid treated of all starches but lower than native starches

2. Acid modified starch produced at HCL acid concentrated 2 %, at 50°C for 0.5 hour, possessed properties suitable low level viscosity acid treated of all starches

2.2 Scale-up

The three types of starting native starches were measured for the viscosity by Brabender viscoamylograph prior to acid modification (**Figure 10**). The reaction conditions of acid treated starches, i.e. acid concentration, temperature and time were varied to obtain the acid treated starch with two levels of viscosity selected above and employed these conditions when prepared in the large batch size (1600 g) and rechecked the viscosity by Brabender viscoamylograph. The result are presented in

Figure 11 for corn starch, **Figure 12** for glutinous rice and **Figure 13** for tapioca starch. It was found that there is a little change of viscosity of starch when compare with the small batch size. So the conditions which were selected could be used to prepare acid treated starch for the further experiment. The selected acid treated conditions to obtain suitable two types of viscosity level of all native starches used, corn, glutinous rice and tapioca starch were the same.

All of the acid treated starches obtained were pulverized by pin-mill using screen No. M3 (0.3 N) after that the viscosity were determined by Brabender viscoamylograph as shown in **Figure 14-16**. The Brabender curve types are not different from the ones before milling but they all have a little change in viscosity, which seem to be a little lower. These may be the cause of the smaller in size of starch powder.

The Brabender amylograph is the most widely used for determining the viscosity of a starch paste. Viscosity curves obtained were due to the swelling of starch granules that occurred during gelatinization. There were three important zones during the measurement, the initial viscosity was the viscosity at 30°C, and the time since initial stage to 95 °C is called heating period. This stage is very important since the usable pasted will be obtained in this period. The paste stability at 95°C for 15 min which is called holding period, and then cooled down to 50 °C (cooling period) to measure the setback that occurs on cooling the hot paste (Zobel, 1984).

When a concentrated aqueous suspension of starch is heated, the individual granules gelatinize and swell freely until they imbibe virtually all the available water.

As a result, the swollen granules become increasingly susceptible to disintegration by mechanical shear. In addition, the bonding forces within the granule become more tenuous and hence, the fragibility of the granule toward thermal or mechanical breakdown increase during the entire cooking cycle.

Brabender viscosity curves have specific characteristics and difference for each starch. The paste viscosity normally rises rapidly to a peak value and then decreases more slowly. The temperature at which the viscosity begin to rise is termed the "pasting temperature"

The drop in viscosity from a maximum value to the obtained after 1 hr holding period at 95°C indicates the stability of the paste to breakdown during cooking.

Brabender curves of starch pastes could be divided into two types, single-stage and two-stage Brabender amylograph curves. The differences between two types of curves are upon the swollen of each starch granules, corn starch gives definite two-stage Brabender amylograph curve. Under the similar conditions, glutinous rice and tapioca starches give uniform single stage curves.

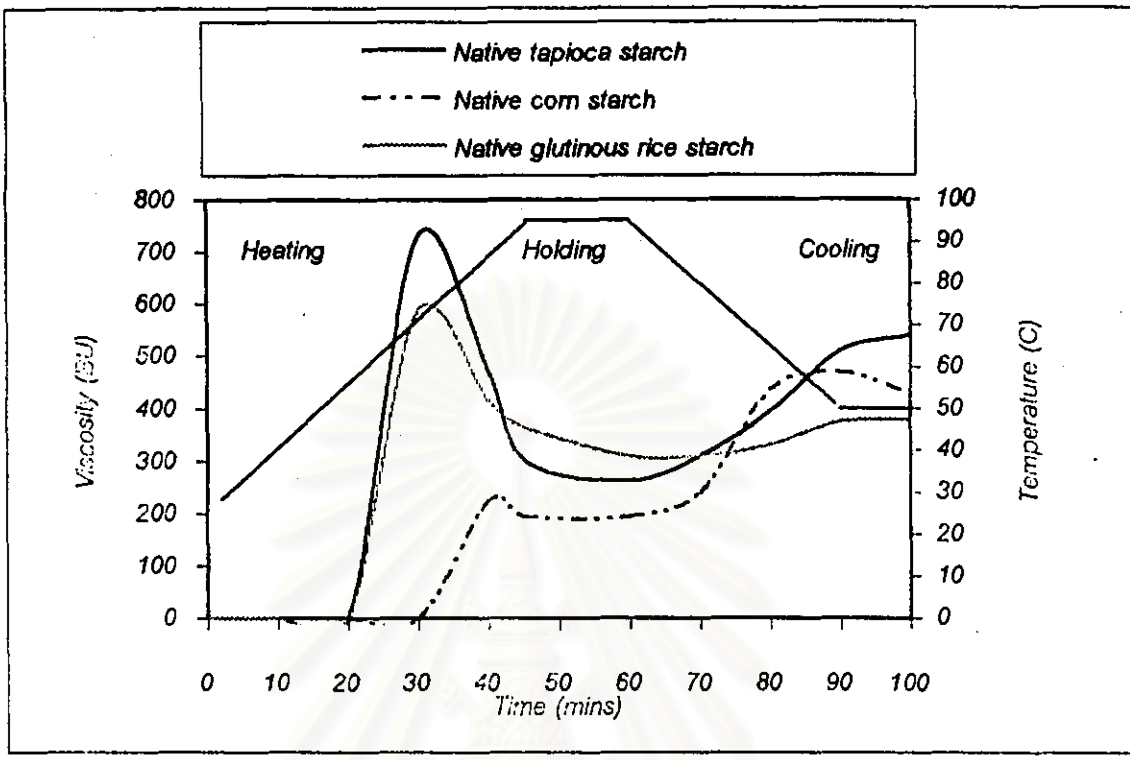


Figure 10 The Brabender viscosity of native corn, glutinous rice and tapioca starch

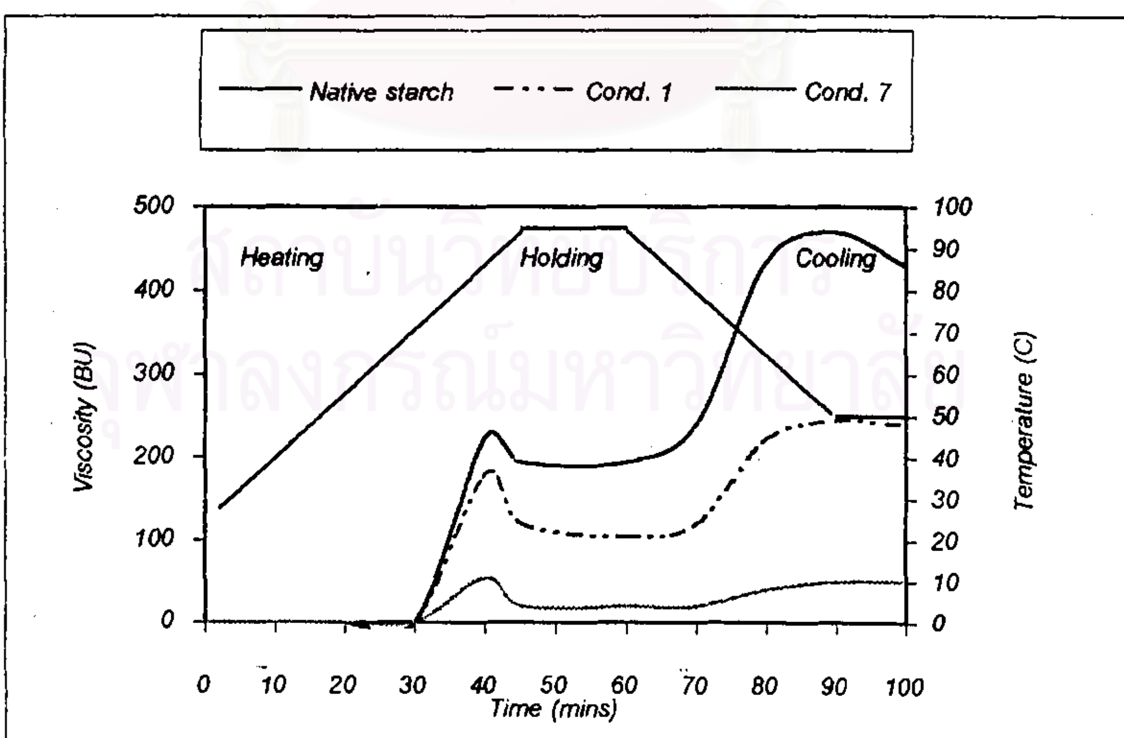


Figure 11 The selected viscosity of acid treated corn starches after scale up

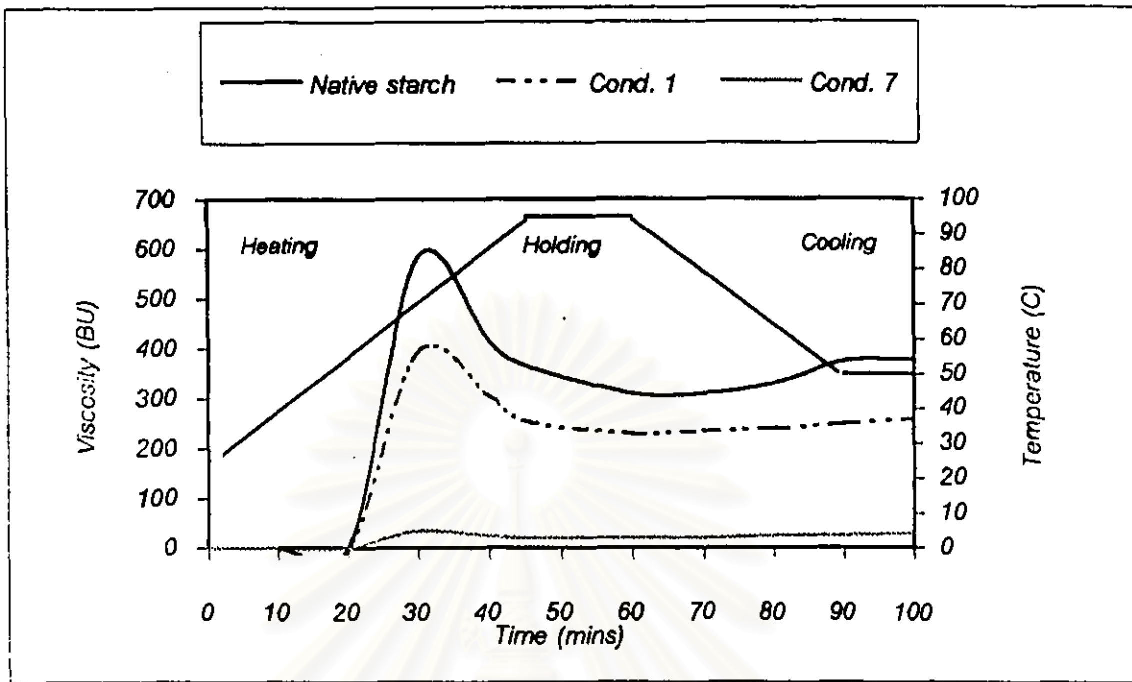


Figure 12 The selected viscosity of acid treated glutinous rice starches after scale up

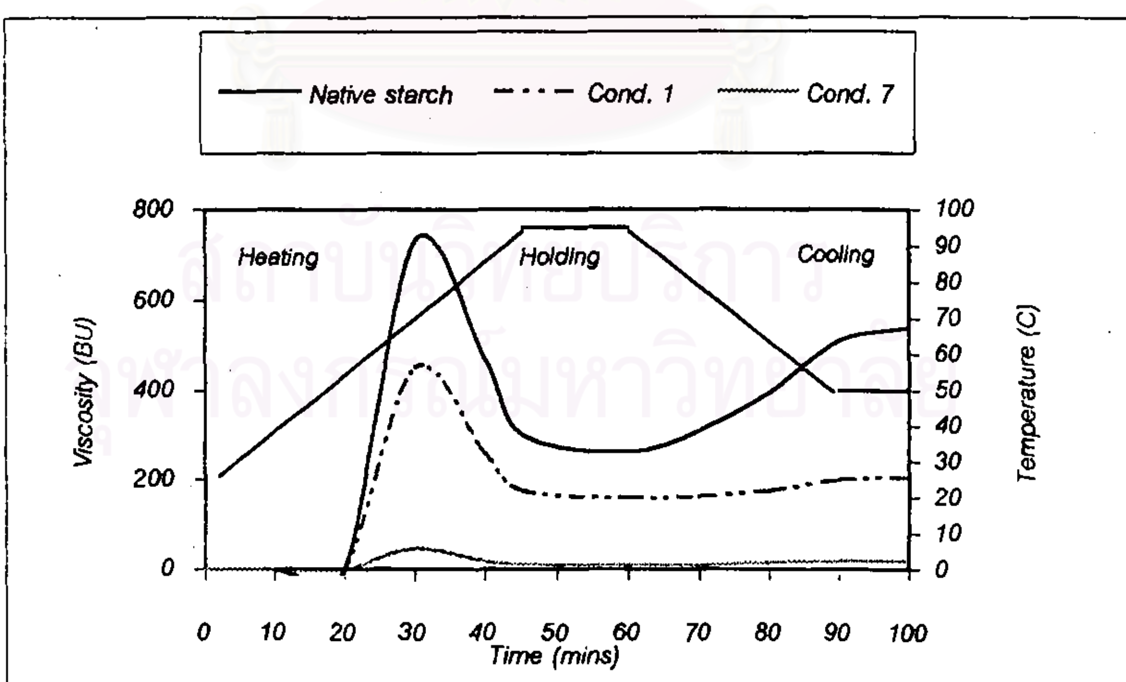


Figure 13 The selected viscosity of acid treated tapioca starches after scale up

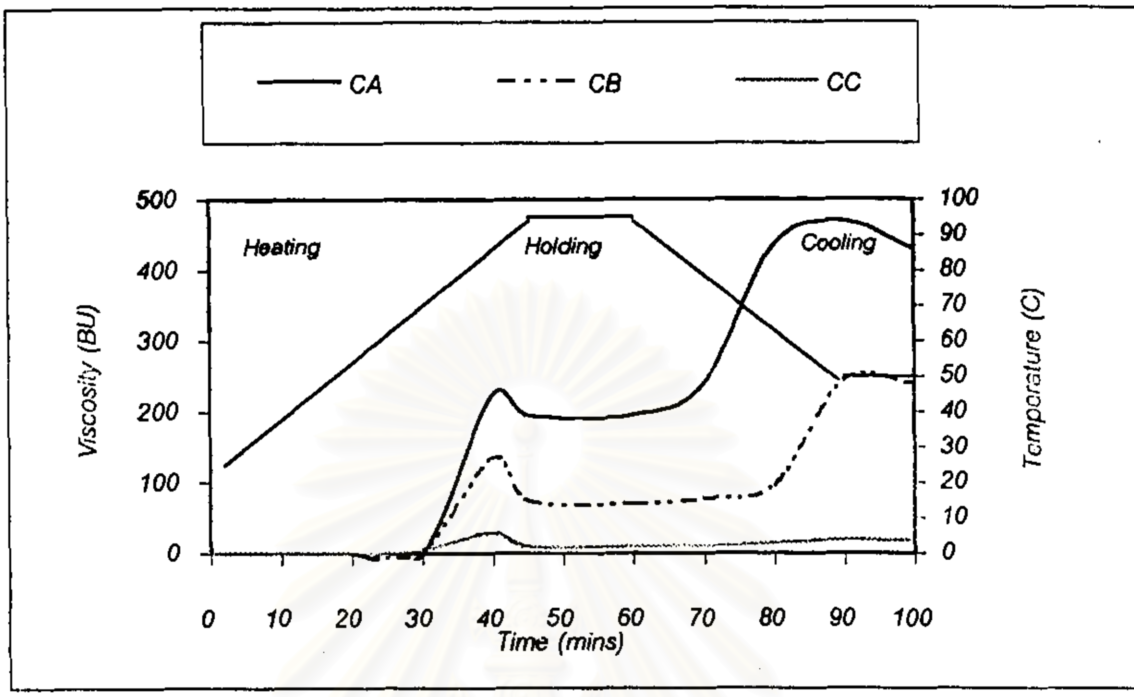


Figure 14 The Brabender viscosity of acid treated corn starches after pulverizing by pin-mill

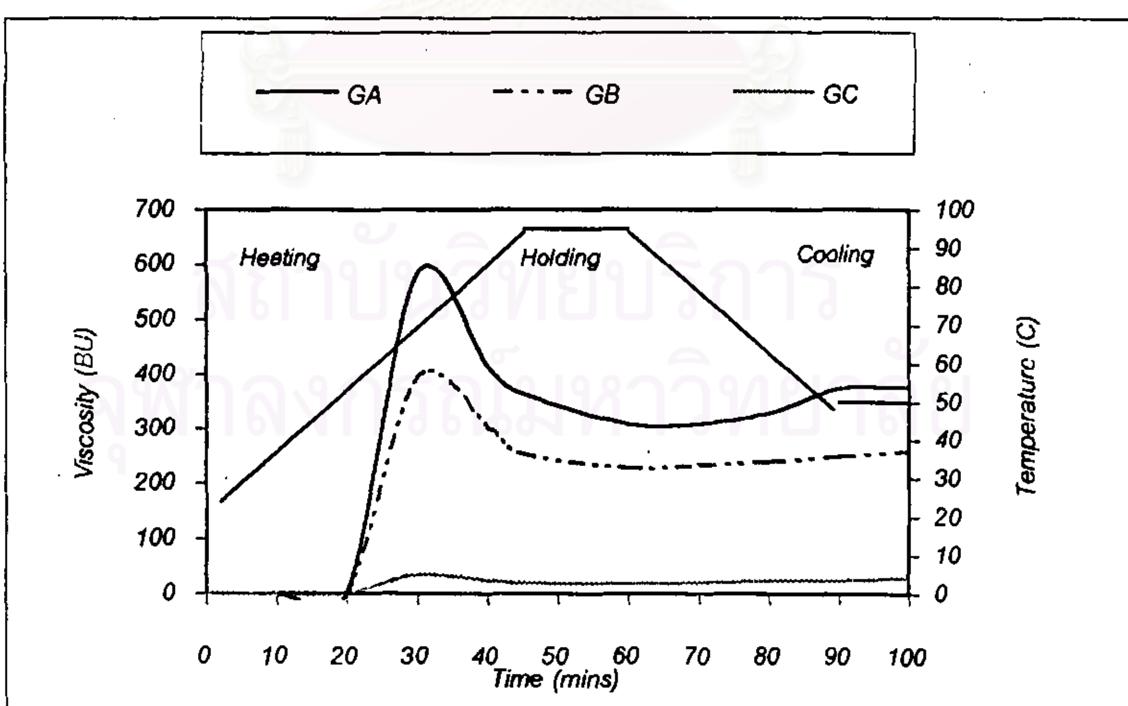


Figure 15 The Brabender viscosity of acid treated glutinous rice starches after pulverizing by pin-mill

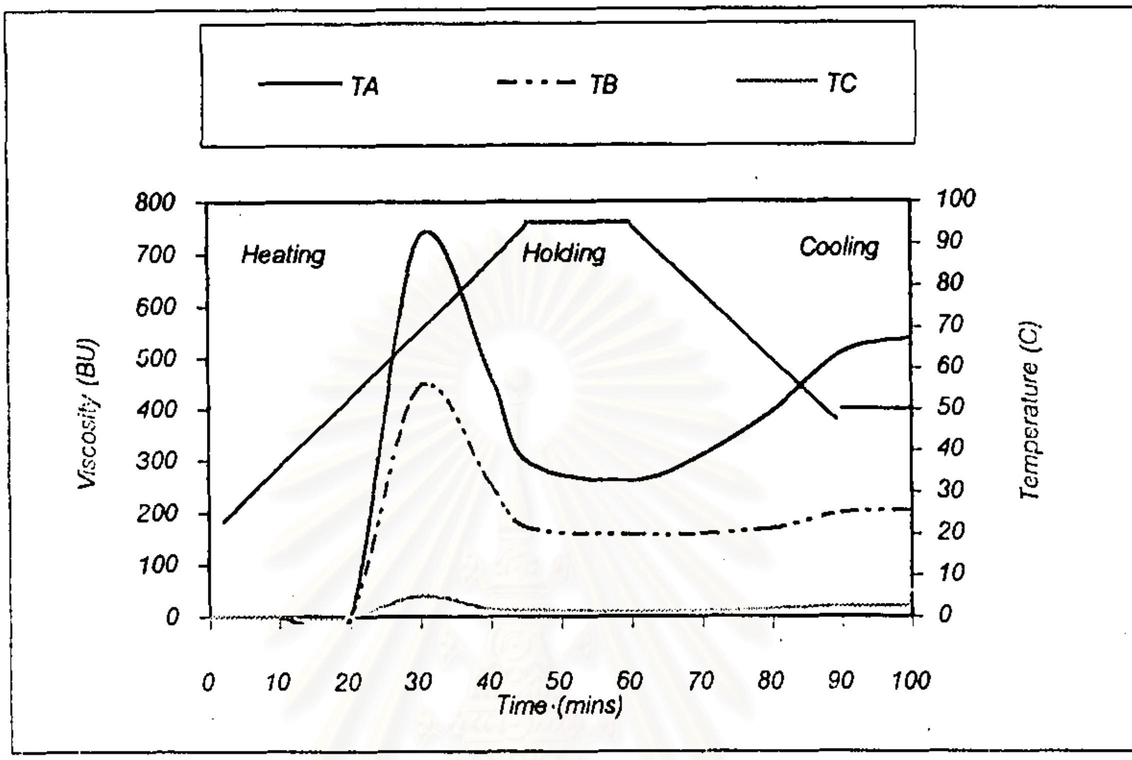


Figure 16 The Brabender viscosity of acid treated tapioca starches after pulverizing by pin-mill

3. Pregelatinized Starches

Pregelatinized starches were prepared from native starches and acid treated starches from 2 using double drum dryer. All starches were prepared in pasted form prior to pregelatinization. The process was divided in two steps, first was cooking starch paste, which was completely gelatinized, and then feeding the starch paste to drum dryer for the drying step. The dry starch obtained was fully pregelatinized straches (Daranee Pencharoen, 1999).

All types of starches were completely gelatinized at a temperature not higher 95°C (Charley, 1982). Regarding the study by Makino and Kitamori (1995), it was found that the complete gelatinization of corn starch was performed when cooking the starch paste at 90°C for 30 min.

In this study , the starch paste at concentration of 10%w/w was prepared by heating in the water bath, temperature of starch paste was controlled in the range of 90-100°C for 30 min. It was reported during the study that the starch pasted of acid treated starches were more liquefied than that of their native starches, and could be prepared in the maximum concentration of 40% w/w. While the native starches pasted were too viscous to stir and it could not be in practical use. To control the factor of starch paste concentration, 10%w/w starch pasted of all starches were selected.

Conditioning of. the distance between drums, drum speed and steam pressure were adjusted to obtain satisfactory physical properties of drum dried products and loss less products.

The corn and tapioca dry film products having a uniform particle size in range of about 0.1 to 2 cm while the glutinous rice has smaller particle size range about 0.1 to 0.5 cm. This might be the nature of glutinous rice that is stickness so the pastes may be more sticky to the rolls and difficult to scrap off. Anyway, after milling by pin mill the pregelatinized starches, pregelatinized of acid treated starches obtained in each type of starches were not difference in appearances. There were a little different of color shade among three types of starches, the corn starches were looked more yellowish, the tapioca starches colored white to off-white while the glutinous rice starches were the most white. This might be cause of their nature of native starches.

Compare with native starch, the coarseness hand feel property of all pregelatinized starches were rougher which were similar to the commercial pregelatinized starches (Era-gel, National 1551 and Starch 1500) and also in appearances.

Evaluation of Physical Properties of Acid Treated Starches and Pregelatinized Starches in Comparison with Commercial Pregelatinized Starches.

1. Viscosity Measurement

1.1 Brabender viscoamylograph

The pasting profiles of all types of pregelatinized corn, glutinous rice, tapioca and commercial pregelatinized starches are displayed in **Figure17-20.**

Figure 17 shows the viscosity curves of all type pregelatinized starch which had not been treated by hydrochloric acid prior to pregelatinization. The viscosity curves of TD have a continuous decline from initial point with a sharp decrease and a slight increase in the end of period. This type of curve is similar to that of pregelatinized glutinous rice starch. But the viscosity of the later was higher. Regarding to the viscosity curve of CD, it was different from the others. Because the curve shows lower viscosity at the initial period and higher in the holding and cooling period however lower than of GD and TD. Anyway the maximum viscosity was lower than that of native starch. This such property was complied to the characteristic of simply pregelatinized starch from drum drying indicating that if the obtained pregelatinized starch was in cubical form, it will give high bulk densities, slow rehydation rates in cold water and posses relatively low cold-paste viscosity and relative high hot-paste viscosity (Powell, 1967).The pregelatinized corn starches obtained trend to be cubical particles rather than thin sheets.

Figure 18-21 demonstrated that the pregelatinized acid treated corn and tapioca starches at both levels (CE, CF and TE, TF) did not show clear differences of viscosity curves in contrast to pregelatinized glutinous rice starches, which presented the separated viscosity curves of each levels (GE, GF) comparing with the pregelatinized native starch (GD). The acid could decrease in thickness and stiffness, which has been attributed to the fragmentation of swollen granules in the process of pregelatinization. Reduction in the thickening power that could be the nature of each native starches. The glutinous rice starch contains the highest amylopectin portion causing the more difficulty in reducing the viscosity by acid modification leading to the higher viscosity in pregelatinized starch than the others. With regard to the acid treated levels, the viscosity of pregelatinized starches was ranked as follows: CD > CE ≅ CF (**Figure 18**) for corn starch, GD > GE > GF (**Figure 19**) and TD > TE ≅ TF (**Figure 20**) for glutinous rice starch and tapioca starch respectively. This could be explained that corn starch and tapioca starch, which have lower amylopectin portion than glutinous rice starch could be rapidly decreased in viscosity when their acid treated starches were prepared to pregelatinization. On the other hand, this might be the cause of pregelatinization process which specified that all types of starch must be prepared in the form of starch paste before feeding to the drum dryer which aimed to produce fully pregelatinized starches. This stage of preparing starch pastes could damage the acid treated starch granules that it breaks once the gelatinizedation temperature was reached. This might be related that the pregelatinized starches obtained from both levels viscosity did not give the different of Brabender curves. Anyway these have been confirmed by Haake viscometer. (see "**viscosity measurement by Haake viscometer**")

All types of the pregelatinized starches obtained exhibited the characteristic of pre-cooked starches that retained the ability to reabsorb large amount of water and develop initial viscosity.

It was found that the Brabender curves of CE, CF, TE and TF were nearly similar to that of Era-gel, which exhibited the lowest constant viscosity throughout the measurement. These results became interesting because Era-gel is fully pregelatinized starch while CE, CF and TE, TF are fully pregelatinized corn starches and tapioca starches respectively.

Figure 21 shows the Brabender curves of three types of commercial pregelatinized starches, Era-Gel (fully pregelatinized rice starches), National 1551 (fully pregelatinized corn starch) and Starch 1500 (partially pregelatinized corn starch). Both National 1551 and Starch 1500 gave the similar patterns in viscosity curves with gradual and slight increase in viscosity. The initial viscosity of the National 1551 was higher than the Starch 1500's. These may be the cause of the characteristic of fully pregelatinized starch that could reabsorb larger amount of water than partially pregelatinized starch. In the case of Era-gel which is one of the fully pregelatinized starches but exibited quite different viscosity curve from National 1551. This might be the different in the process of pregelatinization or the different in starch modification prior to pregelatinization.

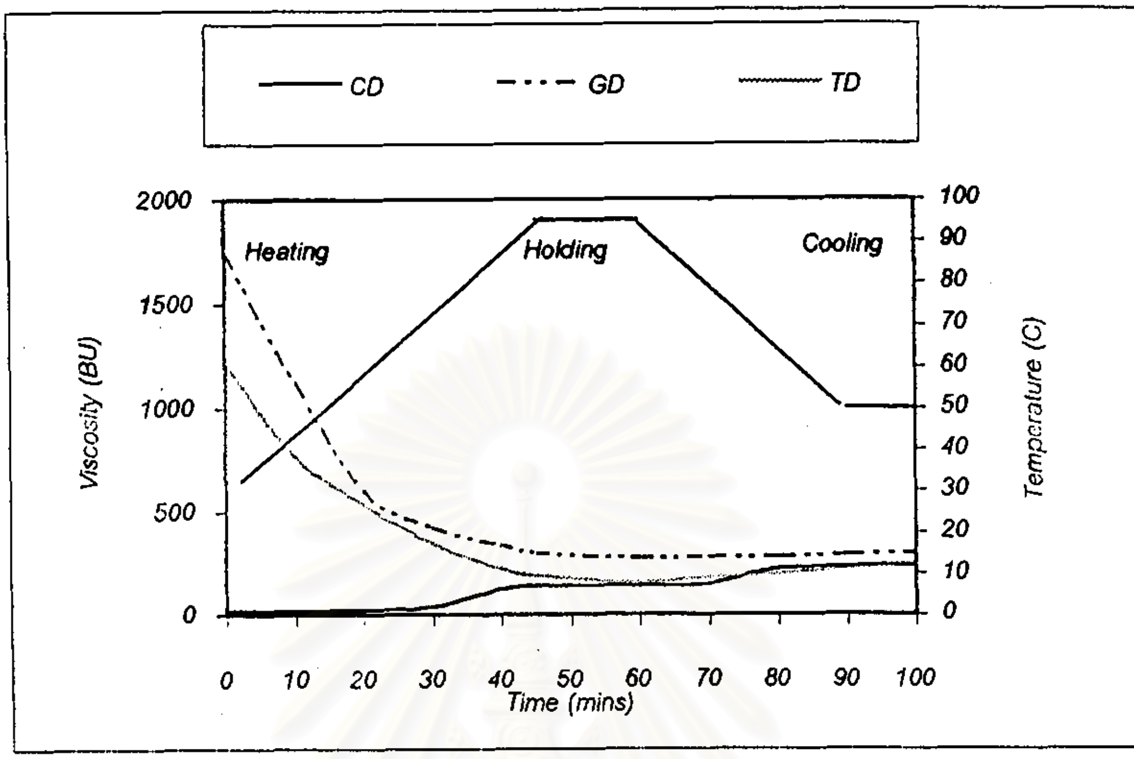


Figure 17 The Brabender viscosity of pregelatinized of native corn starch, glutinous rice starch and tapioca starch

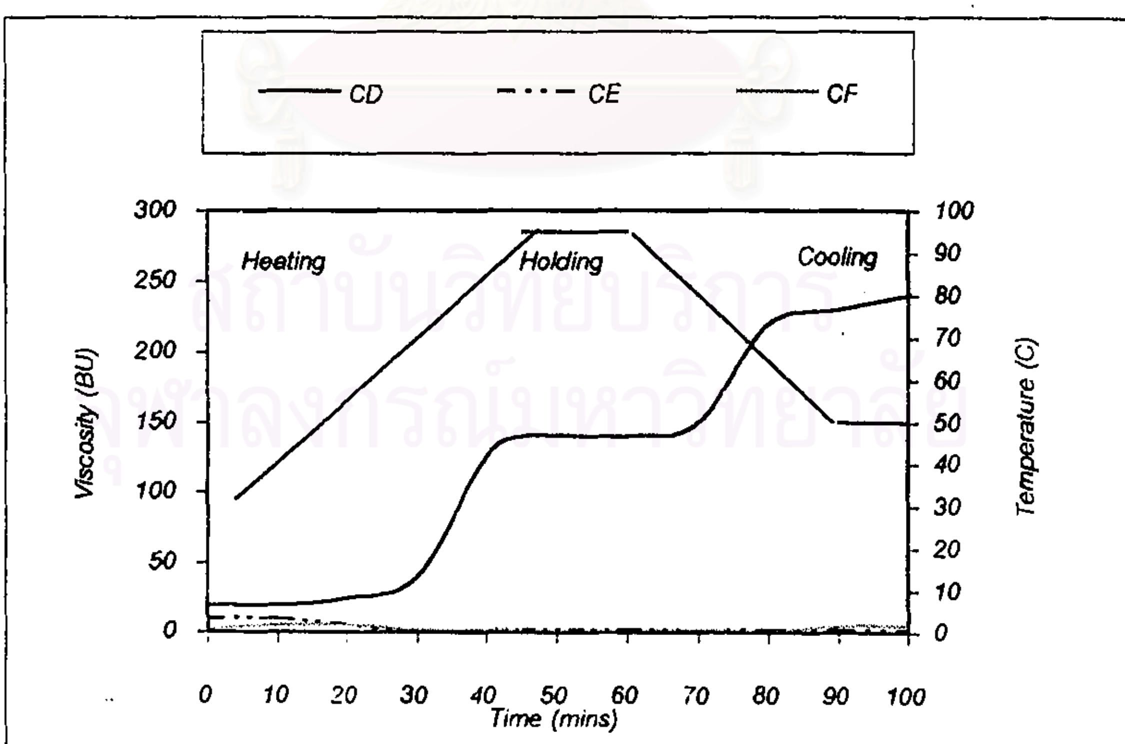


Figure 18 The Brabender viscosity of pregelatinized of native corn starch and pregelatinized acid treated corn starches

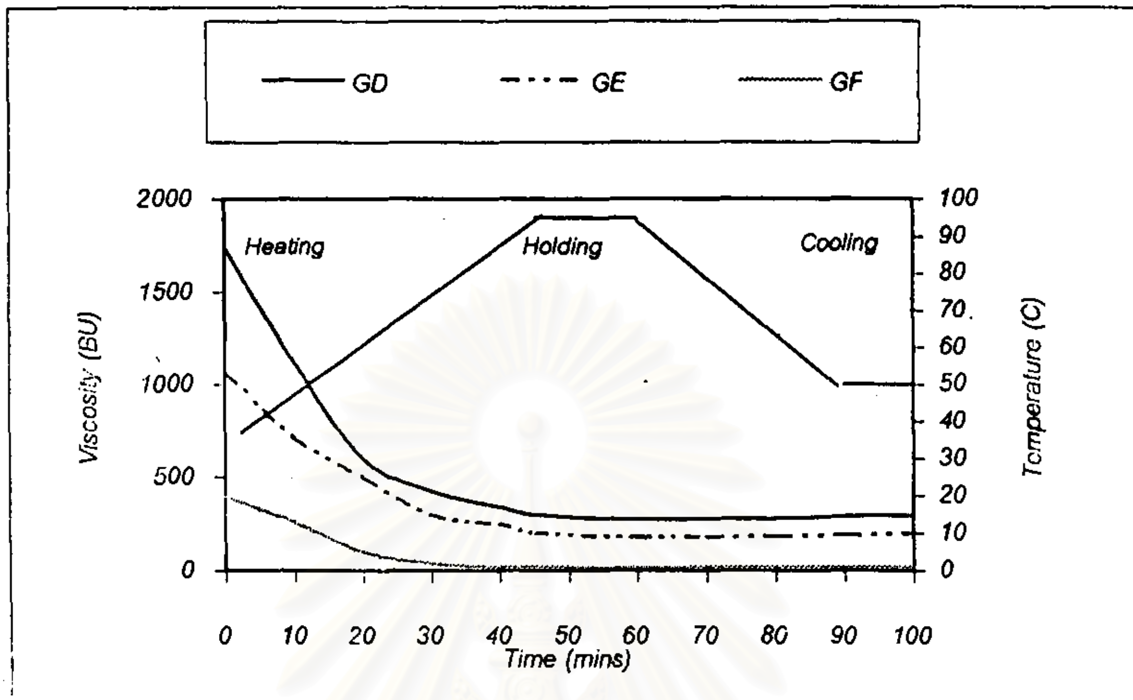


Figure 19 The Brabender viscosity of pregelatinized of native glutionus rice starch and pregelatinized acid treated glutinous rice starches

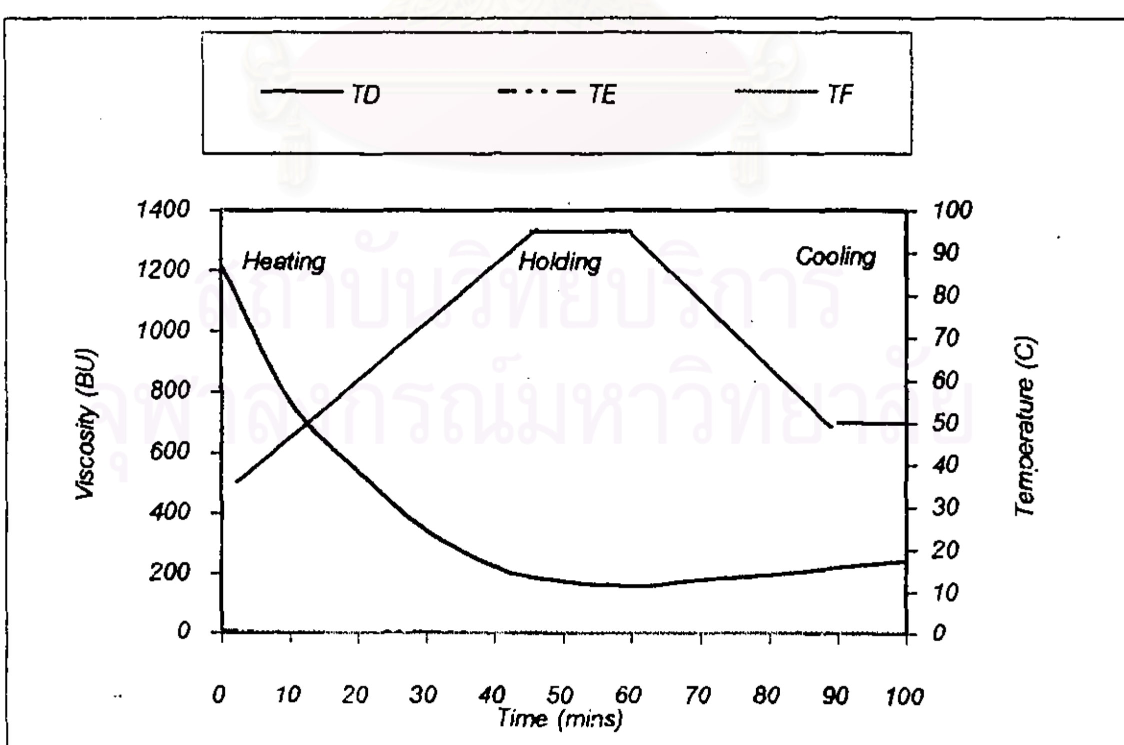


Figure 20 The Brabender viscosity of pregelatinized of native tapioca starch and pregelatinized acid treated tapioca starches

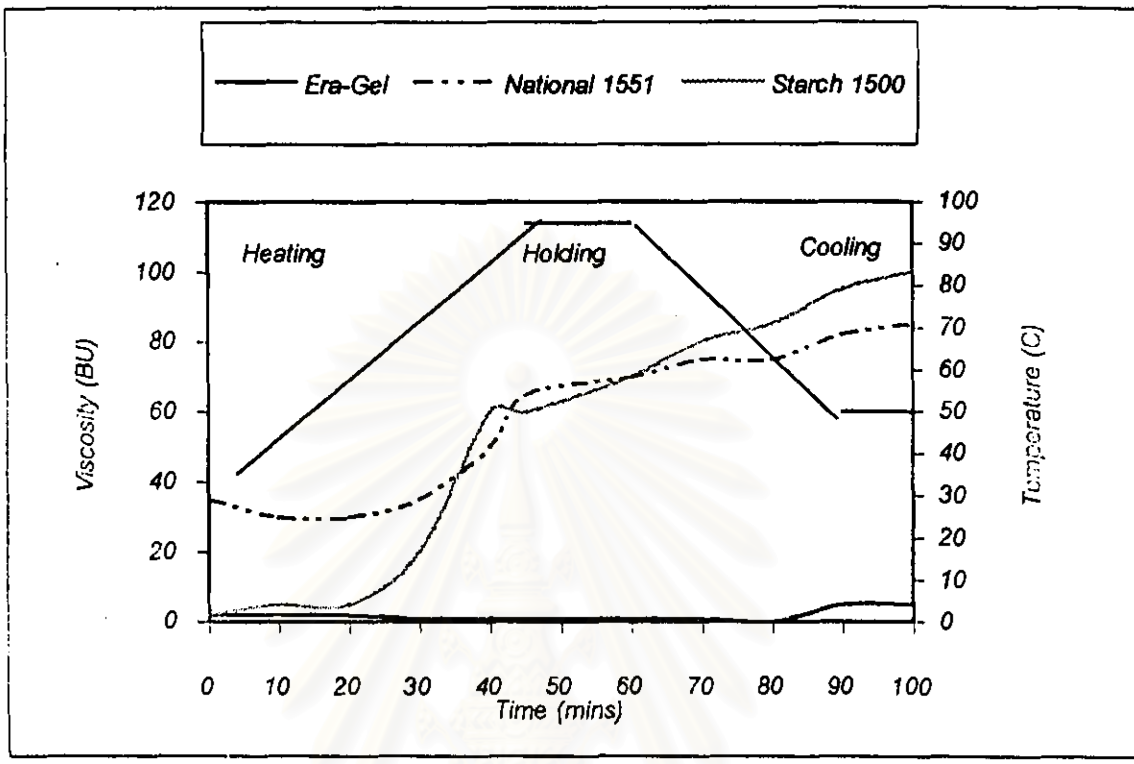


Figure 21 The Brabender viscosity of commercial pregelatinized starches

1.2 Viscosity measurement by Haake viscometer

The starch samples exhibited an entirely different viscosity at 25 °C by Haake viscometer, as shown in **Table 7** and **Figure 22-24**.

Native starches had the lowest viscosity, the order of the viscosity values was GA > TA > CA. There was no difference in apparent viscosity at 25°C in all types of acid treated starches. It would be of interest to discuss that thin-boiling starches differed from native starch in the only way that their cooked solutions are lower in viscosity. But in the room temperature of 25°C, nothing about viscosity was changed from native starch. It could be explained that by the action of the aqueous acid at the temperature below the gelatinization temperature point, starch granule are degraded with damage of some or all macromolecules but little change in the external form of the granule. This may be the reason why the acid treated starches acted like the native starch in many ways such as birefringence, viscosity and swelling capacity at room temperature.

Regarding the commercial pregelatinzed starches, the order of viscosity values was N > E > S. This could be explained that Starch 1500 has both unmodified granules and physically ruptured starch granules, it is considered as a partially pregelatinized starch, thus it could reabsorb in limited of amount of water, in contrast of National 1551 and Era-gel which both are fully pregelatinized starches that could reabsorb a large amount of water. The order of all types of pregelatinized starches agree with the results from Brabender viscoamylograph (see **'viscosity measurement by Brabender viscoamylograph'**)

Table 7 Apparent viscosity by Haake viscometer of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Viscosity* (mPa.s) (SD)
Corn starches	
CA	0.49 (0.03)
CB	0.51 (0.06)
CC	0.52 (0.06)
CD	21.60 (4.89)
CE	4.93 (0.84)
CF	3.49 (0.17)
Glutinous rice starches	
GA	0.81 (0.05)
GB	0.94 (0.06)
GC	1.05 (0.06)
GD	294.22 (26.86)
GE	213.68 (6.05)
GF	26.79 1 17
Tapioca starches	
TA	0.73 (0.22)
TB	0.63 (0.04)
TC	0.60 (0.18)
TD	350.30 (23.38)
TE	3.82 (0.07)
TF	2.19 (0.29)
Commercial pregelatinized starches	
E	9.58 (3.14)
N	25.62 (1.72)
S	3.54 (0.13)

* Average and standard deviation were calculated from three determinations.

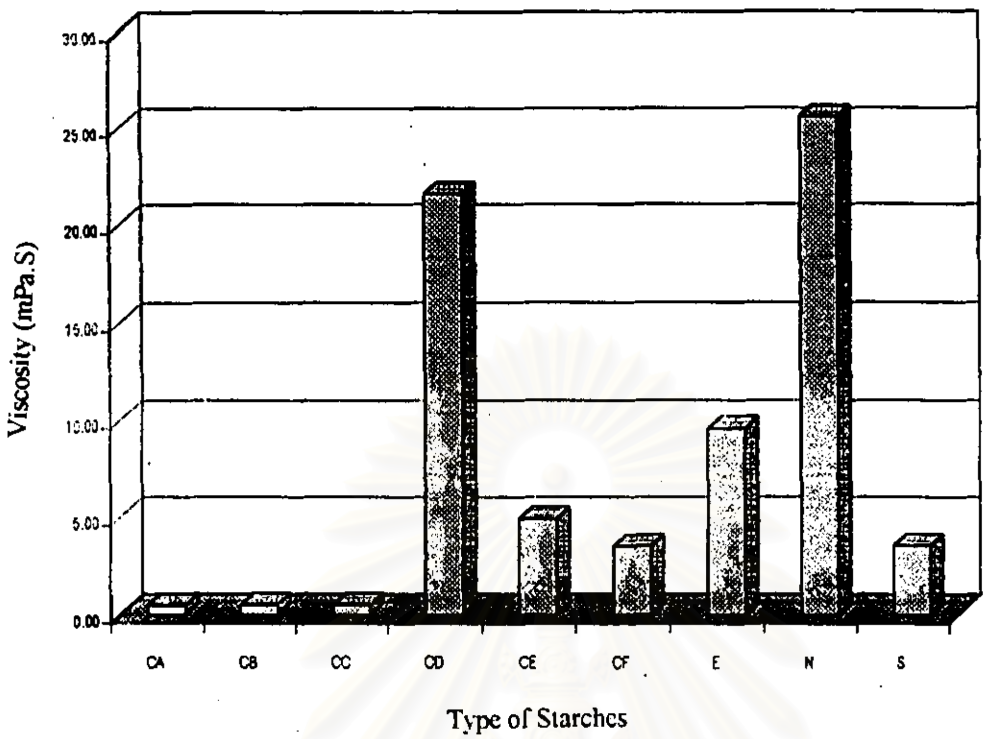


Figure 22 Viscosity (Haake viscometer) of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

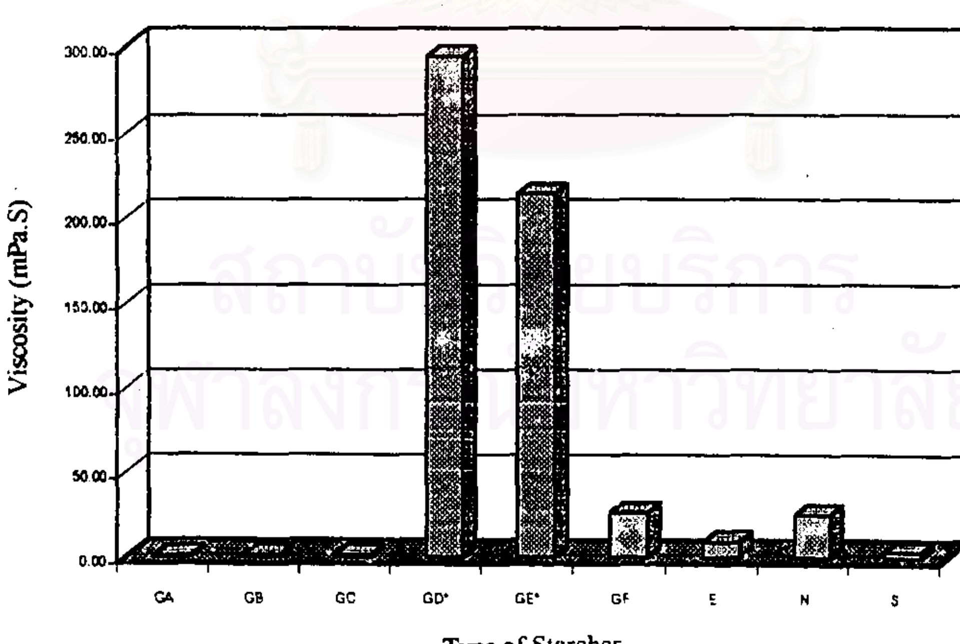


Figure 23 Viscosity (Haake viscometer) of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

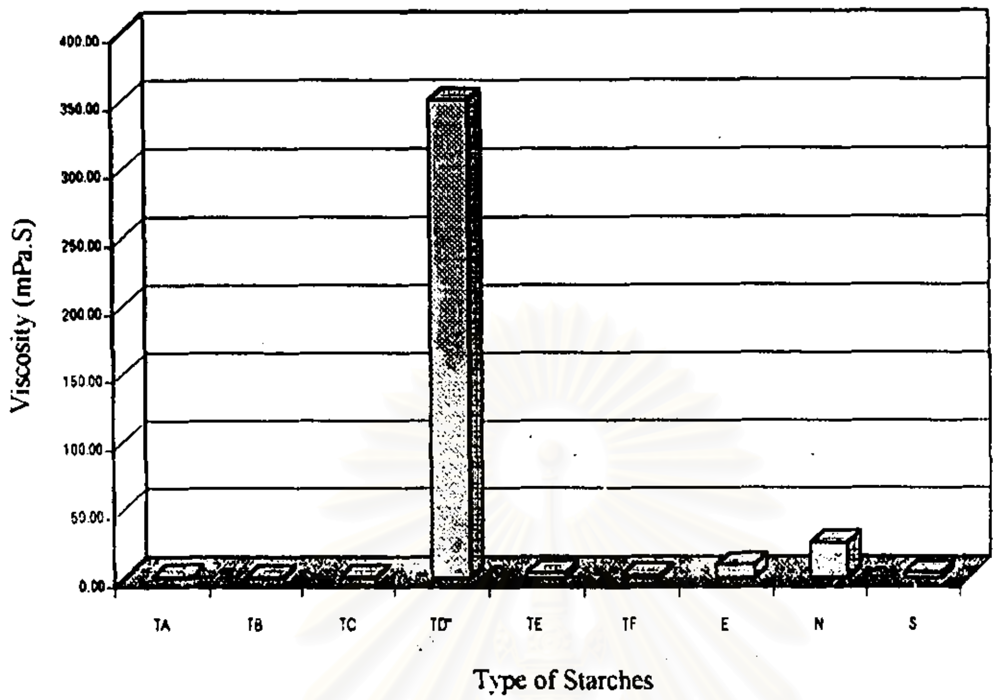


Figure 24 Viscosity (Haake viscometer) of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

The Morphology by SEM

1.1 Starch Morphology by SEM

Electron micoscopy has been used for the morphology study of starch granules. Scanning electron microscope exhibits good depth of field and gives detailed information about surface of dry granule.

The discussion will focus on granule morphology using scanning electron microscopy. The granule shape and size is the characteristic of the botanical origin of starch and can be used to identify the materials. The granules of tapioca starch tend to larger and more regular in shape than of corn starch and glutinous rice starch (**Figure 25**). Descriptive terms used for these types of granules include round, elliptical, or oval. Horny starches, such as corn and glutinous rice, are usually described as polygonal because of the angular sides caused by the close packing of the granule in the kernel.

Figure 26 shows SEM pictures of the acid treated corn starches (CB, CC) the granules appear virtually unchanged. The surface of the granules are relatively smooth and not porous. Trubiano (1985) discovered that there are pores on the surface of starch granule, these pores are openings to channels that penetrate granules, probably to activity at the hilum. The key point is that, channels which open to the outside of a granule provide a much larger surface area exposed to chemical reagents and provide easier access of reagents to the granule interior. But such size of pores insufficiently large to be resolved by SEM. The photomicrograph of acid treated glutinous rice (GB, GC) and acid treated tapioca starch (TB, TC) were also not different from their native starches as shown in **Figure 27** and **Figure 28**, respectively.

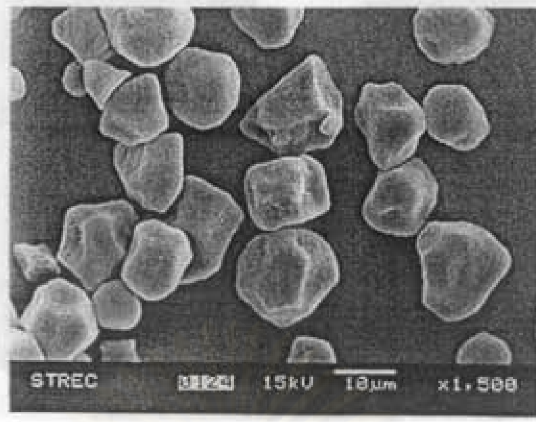
The pregelatinized starch samples exhibit an entirely different morphology, as shown in **Figure 26-29.** The particles are irregular and show large pores for the majority of particles. The pregelatinization process has ruptured the granules resulting in a new particle morphology.

The pregelatinized of native corn starch (CD) shows the smooth, unaltered starch fragments, while the pregelatinized of acid treated starches show the roughened surface and porous characteristic of acid treatment. This characteristic was clearly seen at high magnification of CF. Anyway this evident was occurred in only corn starches.

It seems very difficult to differentiate the pregelatinized starches subjected to different levels of acid treated starches by SEM.

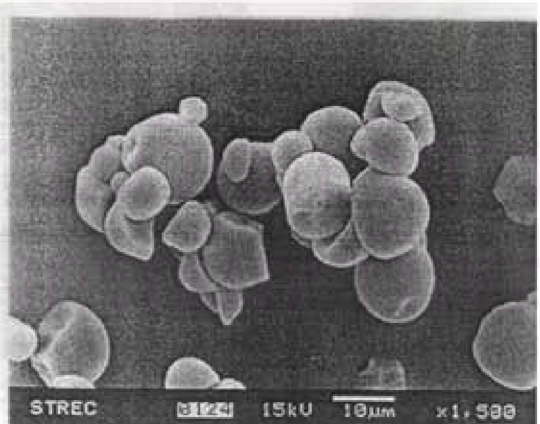
Figure 29 shows photomicrographs of individual granule of Era-gel and National 1551. Both have the similar shape and size. However the particle surface of Era-gel was rougher and appeared more porous than that of National 1551. This might be the characteristic of native starch used and the process modification.

The Starch 1500 (S) shows a variety of particle size and shapes. It consisted of the complete starch granules and granule fragments. This could be depicted that Starch 1500 is partially pregelatinized starch.



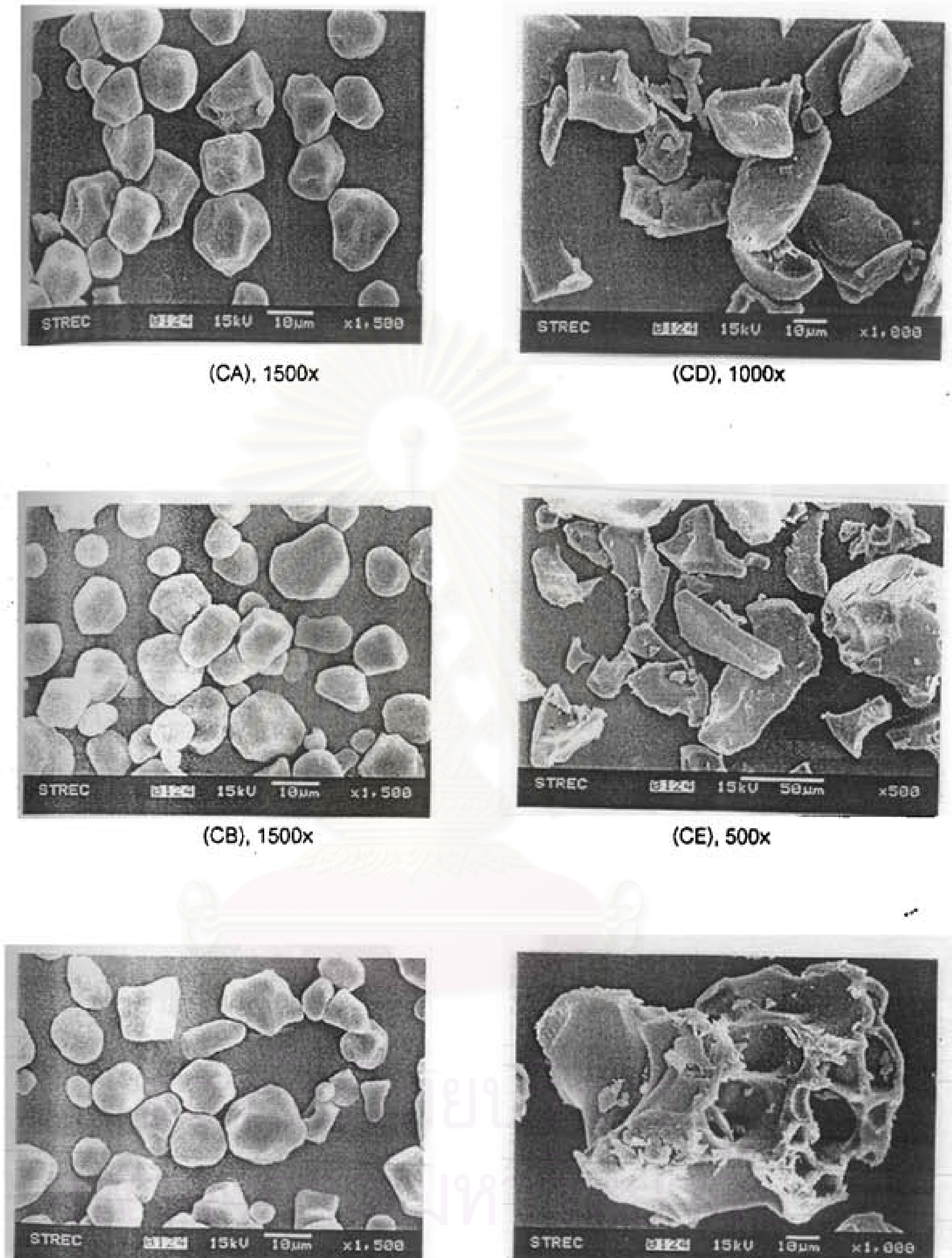
(CA), 1500x

(GA), 1500x



(TA), 1500x

Figure 25 Scanning electrom micrographs of native corn starch (CA), glutinous rice starch (GA), and tapioca starch (TA)

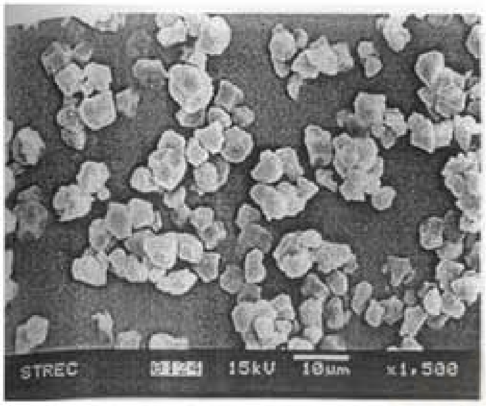


(CA), 1500x (CD), 1000x

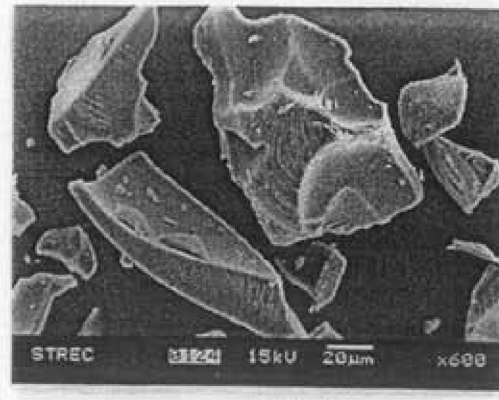
(CB), 1500x (CE), 500x

(CC), 1500x (CF), 1000x

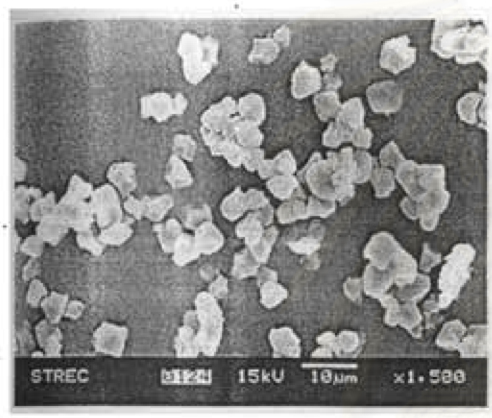
Figure 26 Scanning electron micrographs of native (CA), acid treated (CB, CC) and pregelatinized corn starches (CD, CE,CF)



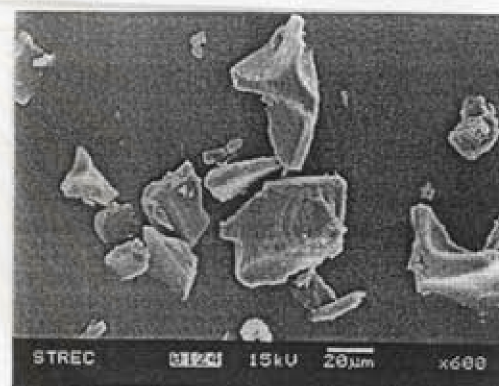
(GA), 1500x



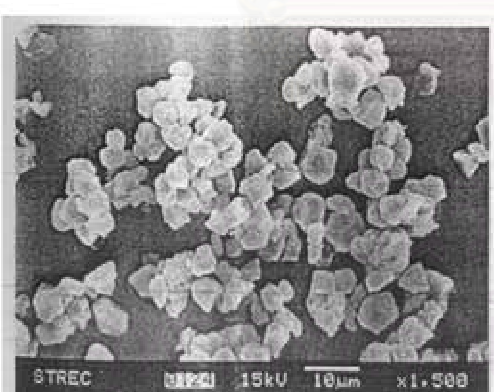
(GD), 600x



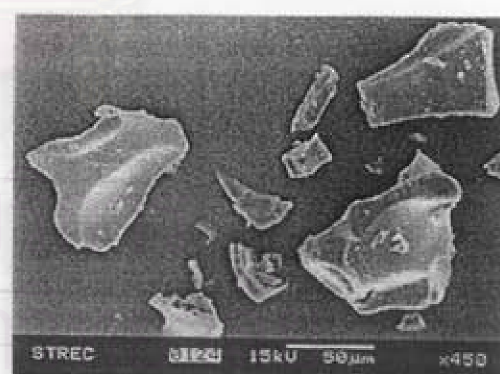
(GB), 1500x



(GE), 600x

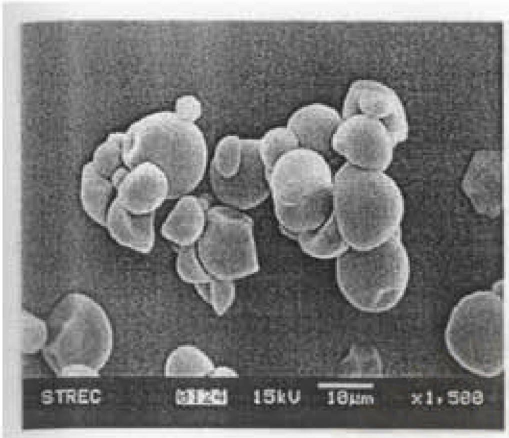


(GC), 1500x

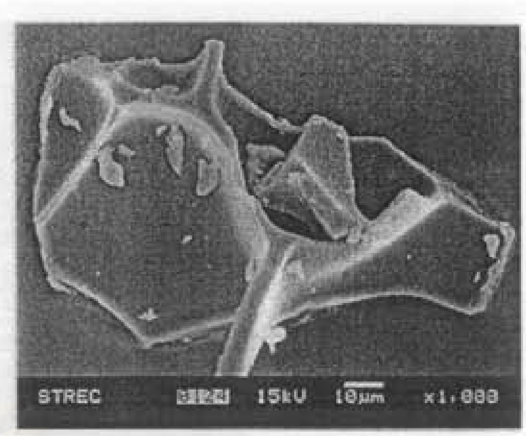


(GF), 600x

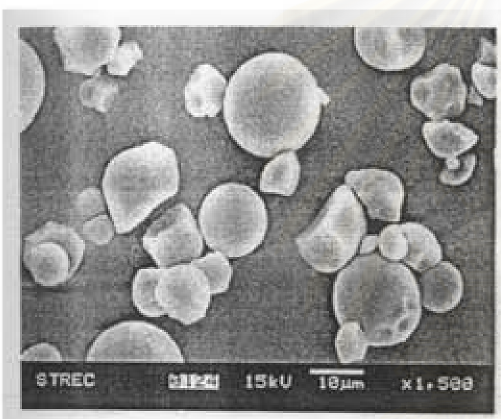
Figure 27 Scanning electron micrographs of native (GA), acid treated (GB, GC) and pregelatinized glutinous rice starches (GD, GE, GF)



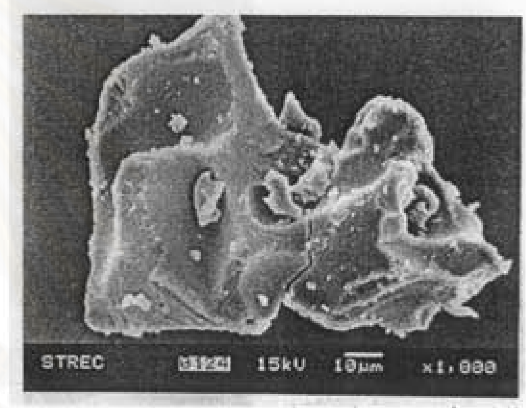
(TA), 1500x



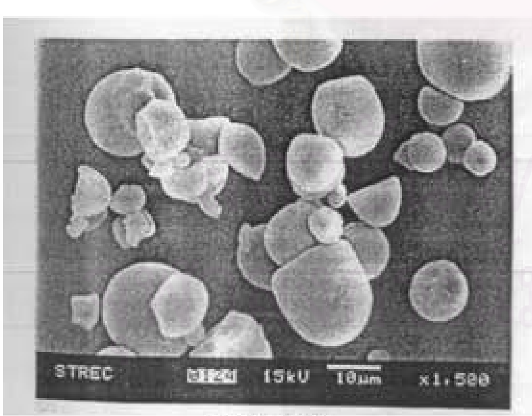
(TD), 1000x



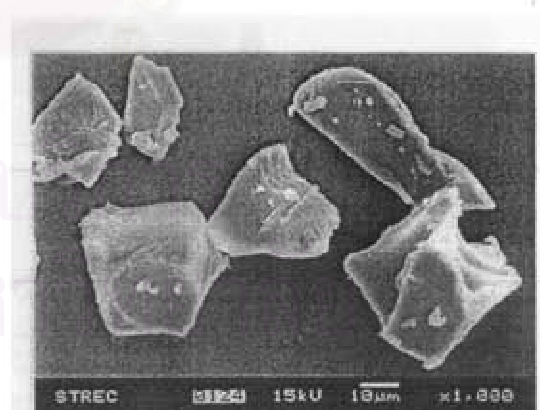
(TB), 1500x



(TE), 1000x

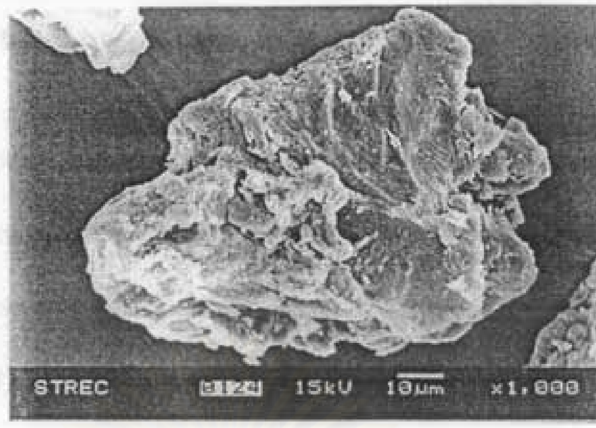


(TC), 1500x

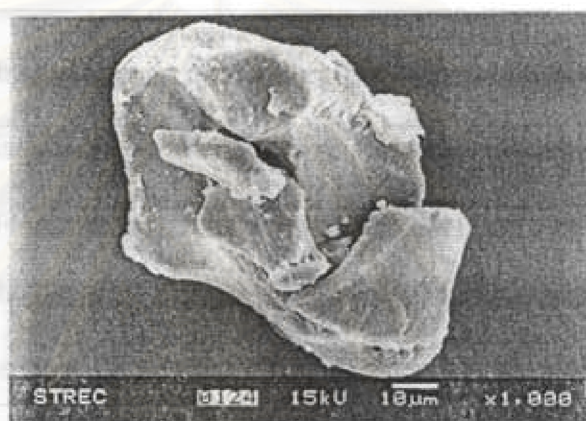


(TF), 1000x

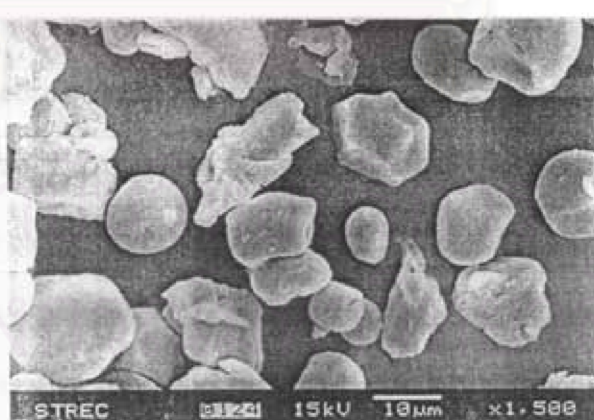
Figure 28 Scanning electron micrographs of native (TA), acid treated (TB, TC) and pregelatinized starches (TD, TE, TF)



(E), 1000x



(N), 1000x



(S), 1500x

Figure 29 Scanning electron micrographs of commercial pregelatinized starches, Era-Gel (E), National 1551 (N) and Starch 1500 (S)

1.2 The Polarizing Microscope Examination of Starch

Optical microscopy has been a powerful tool in the study of starch materials and common starches have been readily identified using this technique. A polarizing microscope also gives information about the starch granules when unmodified starch granules are observed using polarized light, two dark line intersecting at the hilum will from a cross or a V-shape. The shape of the cross can be used to help identify type of starch. One explanation for this feature suggests that the density and distribution of moisture throughout the granule are not uniform and the hilum contains more moisture than the other regions. As the granule dry, stresses are formed within the granule resulting in the bright regions observed under the polarized light. When the starch swell or gelatinized, the cross is no longer visible with the polarizing microscope. The absence of this cross is a simple and accurate determination of the presence of gelatinized granules in a starch sample (Gallant and Sterling, 1976).

The optical photomicrographs of native starches and acid treated starches at both levels of viscosity of corn starch, glutinous rice starch and tapioca starch were shown in **Figure 30-32**. The acid treated of all starches at both levels illustrated no differences in particle morphology comparing with theirs native starches. It was found that the polygonal was the evident for corn starch and glutinous rice starch while the round shape was the evident for the tapioca starch. These results were agreed with the photomicrographs from SEMs, but less detail was obtained.

The starch samples were also analyzed under crossed polarizers, and the crosses are clearly observed for the granules. These polarizing crosses of acid treated of all types of starches were also observed under polarized light. These results are the characteristic of native and ungelatinized starches. In this study, all types of acid treated starches were prepared by hydrolyzing the starch in the presence of HCl acid, at temperature below the gelatinization point of the starches. The resulting starches are degraded with cleavage of some or all the macromolecules but little change in the external form or birefringence of the granule (BeMiller, 1965).

The optical photomicrographs of the pregelatinized starches obtained were depicted in **Figure 33-35**. All of fully pregelatinized starches were observed from the ordinary light microscope that those starch particles were very irregular shape in various sizes indicating the fragmented or ruptured granules. These ruptured granules could not be seen in the dark field under the polarized light. And they exhibited no trace of ungelatinized granules showing polarization crosses.

Figure 36 shows the optical photomicrographs of commercial pregelatinized starches used. It was observed that the particle morphology if Era-Gel and National 1551 was similar to that of all types pregelatinized starches obtained in this study. While the starch 1500, the partially pregelatinized starch was presented different that there are some complete granules which showed polarizing crosses, as well as ruptured granules which could not be seen in dark light.

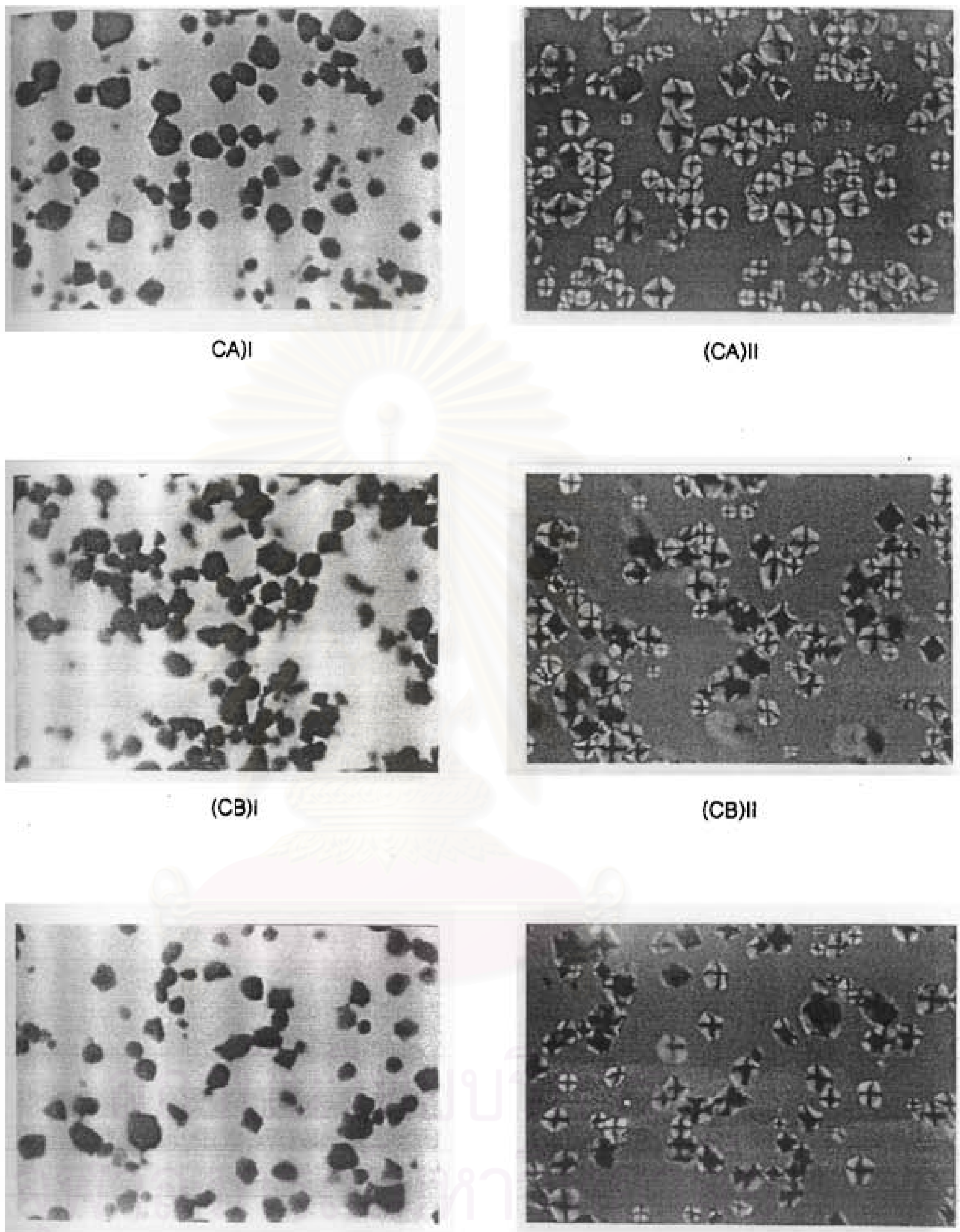


Figure 30 Microscopical appearance of native corn starch (CA) and acid treated corn starches (CB,CC) under normal light (I) and polarized light (II), 400x

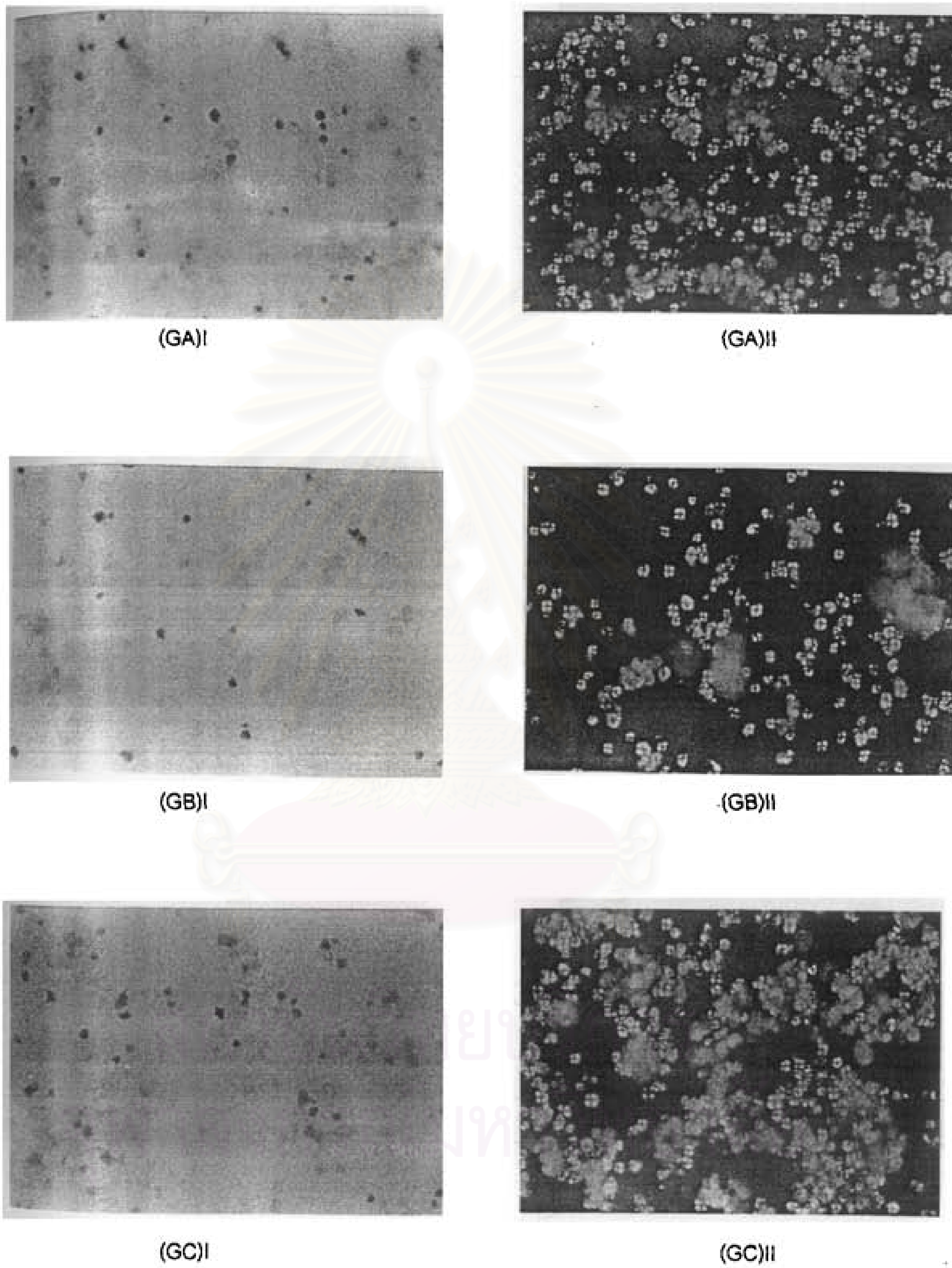
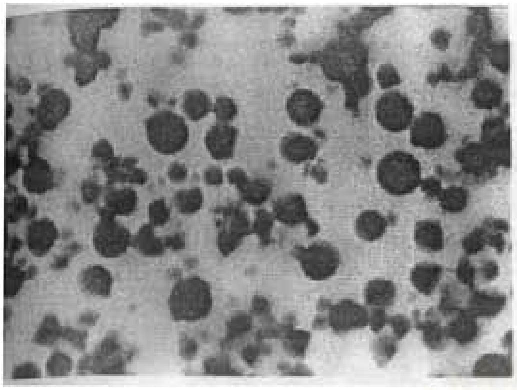
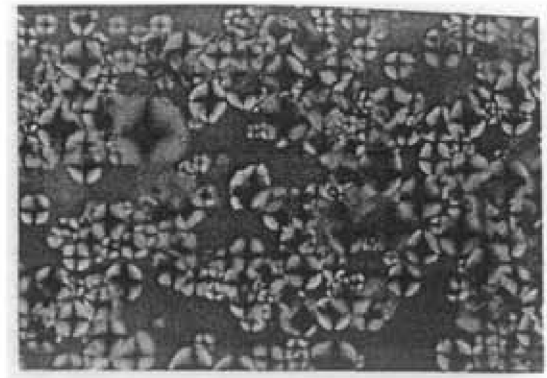


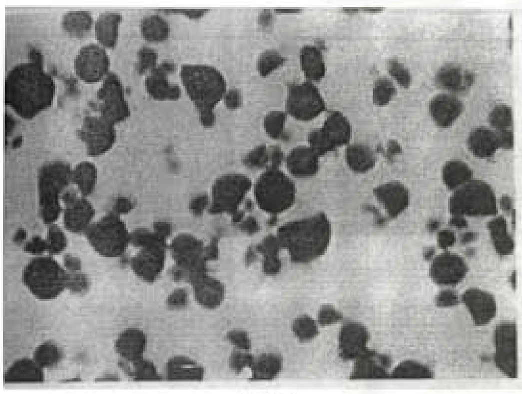
Figure 31 Microscopical appearance of native glutinous rice starch (GA) and acid treated glutinous rice starches (GB, GC) under normal light (I) and polarized light (II), 400x



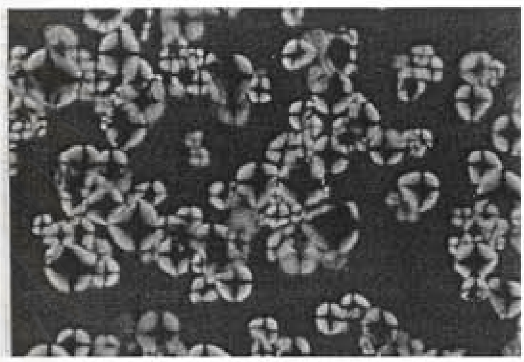
(TA)I



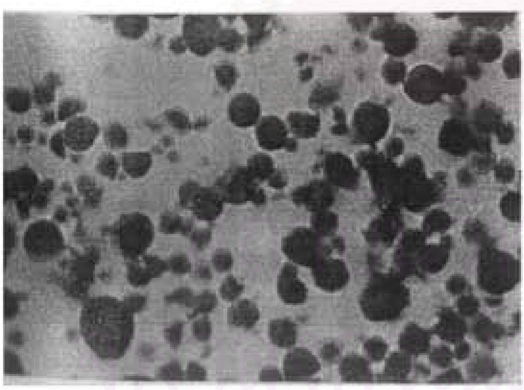
(TA)II



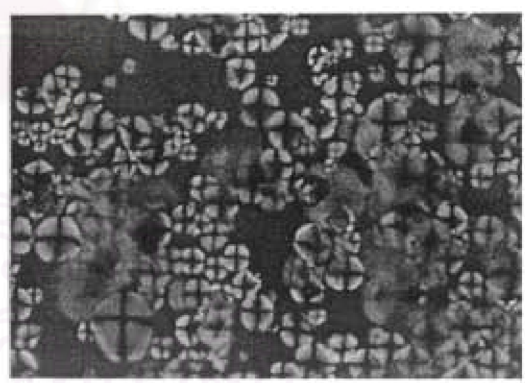
(TB)I



(TB)II



(TC)I



(TC)II

Figure 32 Microscopical appearance of native tapioca starch (TA) and acid treated tapioca starches (TB, TC) under normal light (I) and polarized light (II), 400x

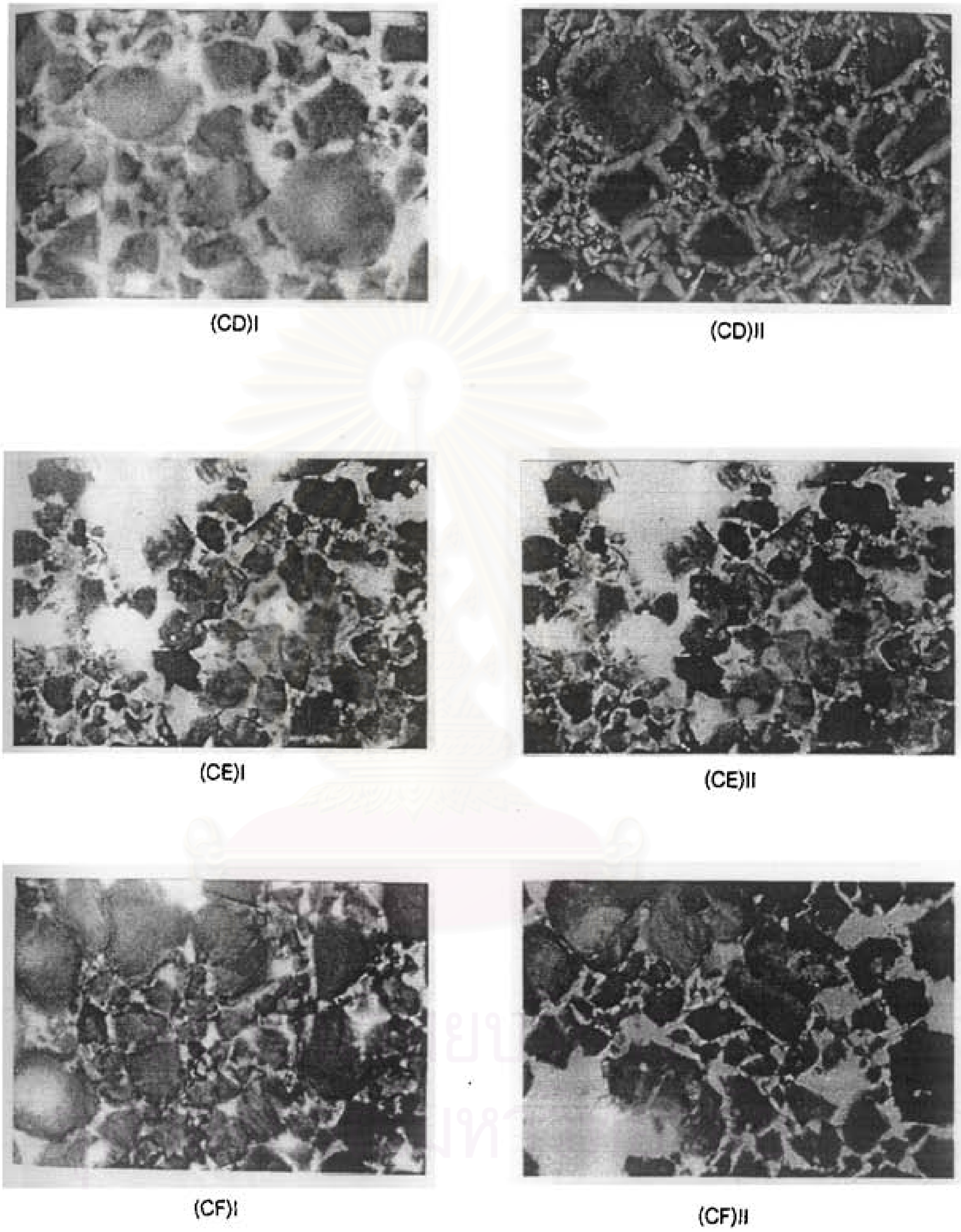
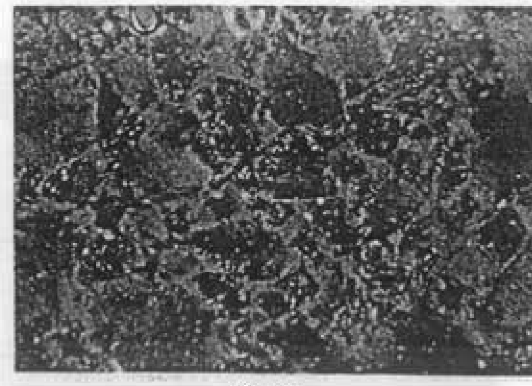
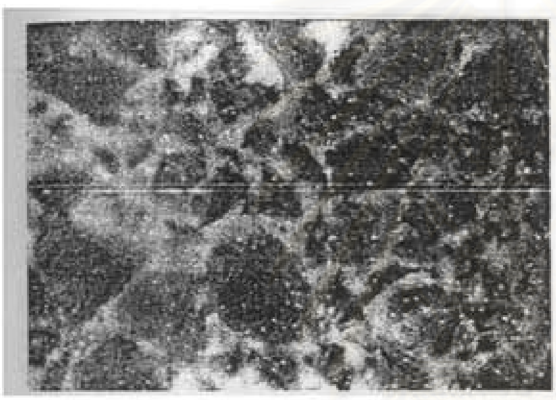


Figure 33 Microscopical appearance of pregelatinized corn starch (CD) and pregelatinized of acid treated corn starches (CE, CF) under normal light (I) and polarized light (II), 200x

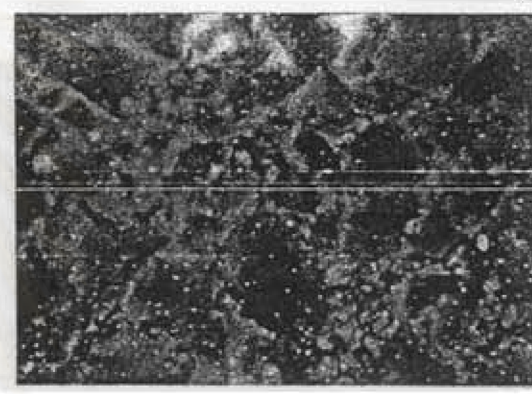
(GD)I



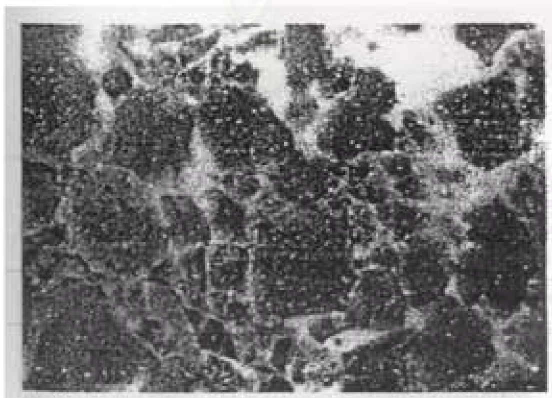
(GD)II



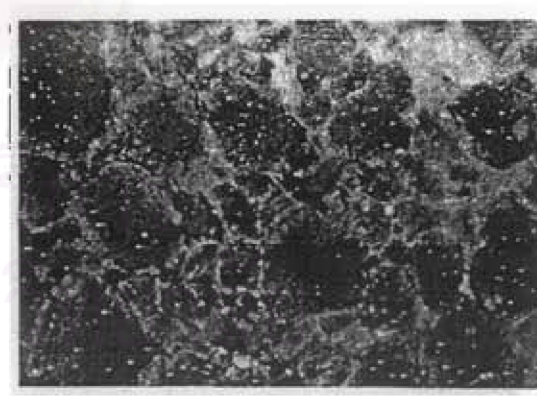
(GE)I



(GD)II



(GF)I



(GF)II

Figure 34 Microscopical appearance of pregelatinized glutinous rice starch (GD) and pregelatinized of acid treated glutinous rice starches (GE, GF) under normal light (I) and polarized light (II), 200x

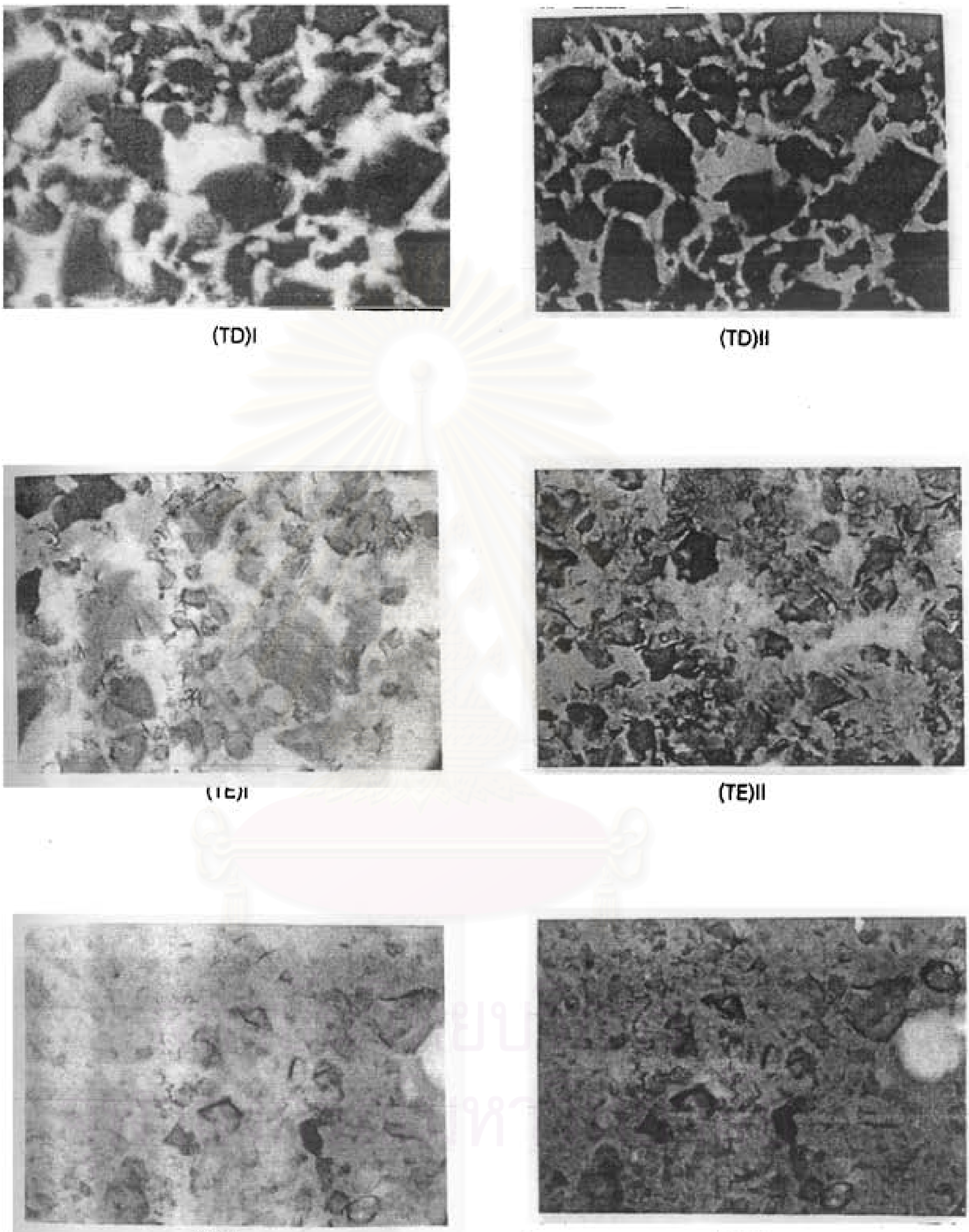


Figure 35 Microscopical appearance of pregelatinized tapioca starch (TD) and pregelatinized of acid treated tapioca starches (TE, TF) under normal light (I) and polarized light (II), 200x

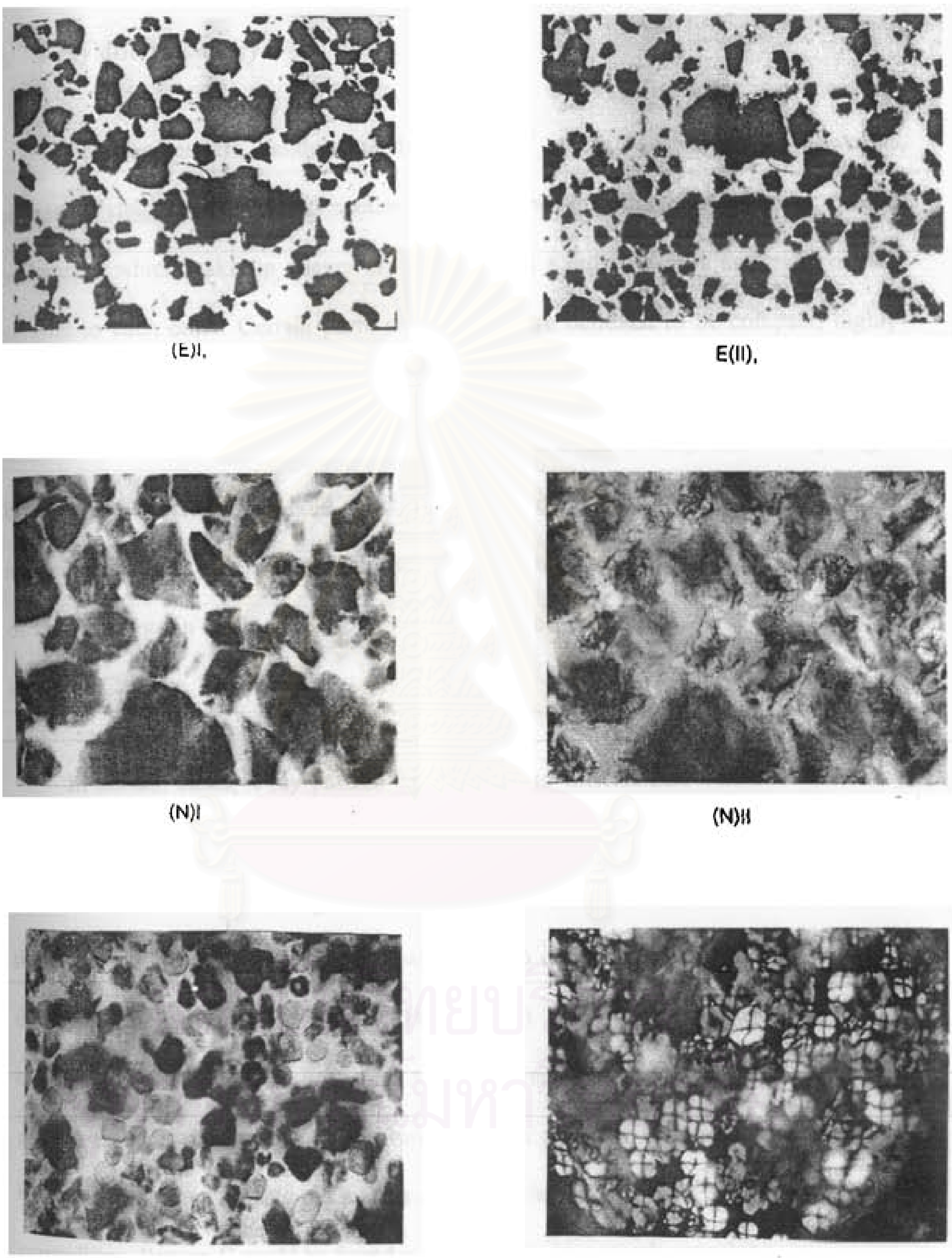


Figure 36 Microscopical appearance of commercial pregelatinized starches, Era-Gel (E, 200x), National 1551 (N, 200x) and Starch 1500 (S, 400x) under normal light (I) and polarized light (II)

2. X-ray diffractometry

The granules are believed to be made of starch molecules laid down in concentric rings, which in cross section look like the rings in a slice of onion. Starch molecules, which make up a layer are deposited in a radial fashion and more or less parallel to each other. Certain parts of each ring are believed to be compact, highly order crystalline state. These radially arranged crystallines are linked by amorphous areas in which the starch molecules are deposited in a less orderly fashion. Hydrogen bonds are the force, which hold starch molecules together in the less ordered regions as well as in the crystalline areas. In formation about the submicroscopic organization of the starch grain is obtained from x-ray diffraction techniques, differ for individual starches (Charley, 1982).

In certain cases, x-ray pattern can be used to differentiate between cereal and root starches and to defect changes in crystallinity brought about by physical or chemical treatment of starch granule. The method has been used as a tool to measure the extent of gelatinization. Newman et al.(1996) described that starch exits in three crystal forms designated A, B and C (**Figure 37**). These forms are dependent on the botanical source of the starch. Pattern A is observed for cereal grain starches, whereas pattern B is charateristic of tuber, fruit and stem granules. Pattern C is intermediate between the A and B patterns and has been attributed to mixtures of A and B type crystallites. Pattern C could be found in several rhizome starch granules.

Hizukuri, 1996. recognized that there are x-ray diffraction patterns of starch granules from various botanical sources which are called A, B and C types as shown in **Figure 37**. Most cereal starches exhibited the A type, root and tuber starches showed the B type while several rhizome and bean starches showed the C type.

In this study, the x-ray patterns of all types of native starches and theirs acid treated starches at both levels were similar to the A type pattern. It is commonly that corn starch (**Figure 38**). and glutinous rice starch (**Figure 39**), the cereal starches showed the A type pattern. The another one tapioca is root starch which should be belonged to the B type but it is the exception, showing the A-type (**Figure 40**). This result was in agreement with the study of Hizukori (1996).

Since the x-ray patterns showed no differences between the native starches and theirs acid treated starches, and the two levels of acid modification could not change the x-ray patterns of the starch granules. These could be explained that the granules of acid treated starches resemble those of unmodified starches. By the action of hydrochloric acid at temperature below gelatinized point, the starch granules were degraded with cleavage of some or all the macromolecules but little changed in the external form. Since the initial attack is in the gel or amorphous region. This degradation leads to a reduction only in the viscosity of starch paste but the main crystalline granule structure may remain intact (Rohwer and Klem, 1984).

The fully pregelatinized of all types of glutinous rice, tapioca starches and Era-Gel exhibited no crystallized patterns indicating that completely amorphous material was obtained.It was considered that these starches were completely gelatinized because of their complete loss of crystallinity (Eliasson and Gudmundsson, 1996).

The patterns of all types of pregelatinized corn starches (CD, CE, CF) and National 1551 (fully pregelatinized corn starch) showed weak diffraction lines at 4.5 A° spacing (20° 2θ), which was typical of the V pattern. This event is the characteristic of cereal starches which the A pattern was lost during gelatinization, only the V pattern was obtained cause of the formation of amylose-lipid complex and the occur of recrystallization process. Gelatinized lipid-containing starches normally exhibited this pattern.

Varriano-Marston, et. al (1980) and Hizukuri (1996) indicated that the amorphous-lipid in cereal starch granules could not be obtained by x-ray diffraction, so these complexes were not organized into the crystalline state but they were only be burried in the amorphous region. So we can conclude that all types of drum dried corn starches obtained and also National 1551 were completely gelatinized. Anyway the patterns of CD, CF and National 1551 have some other weak diffraction lines indicating that the minimal portions of ungelatinized granule still remained. Since these were too small amounts and no other diffraction lines were observed indicating that these starches were completely gelatinized.

The pattern of Starch 1500, partially pregelatinized starch can be observed in **Figure 41**. This starch exhibited the A type pattern obtained from some complete starch granules and V pattern which occurred due to the gelatinized lipid containing starch granules.

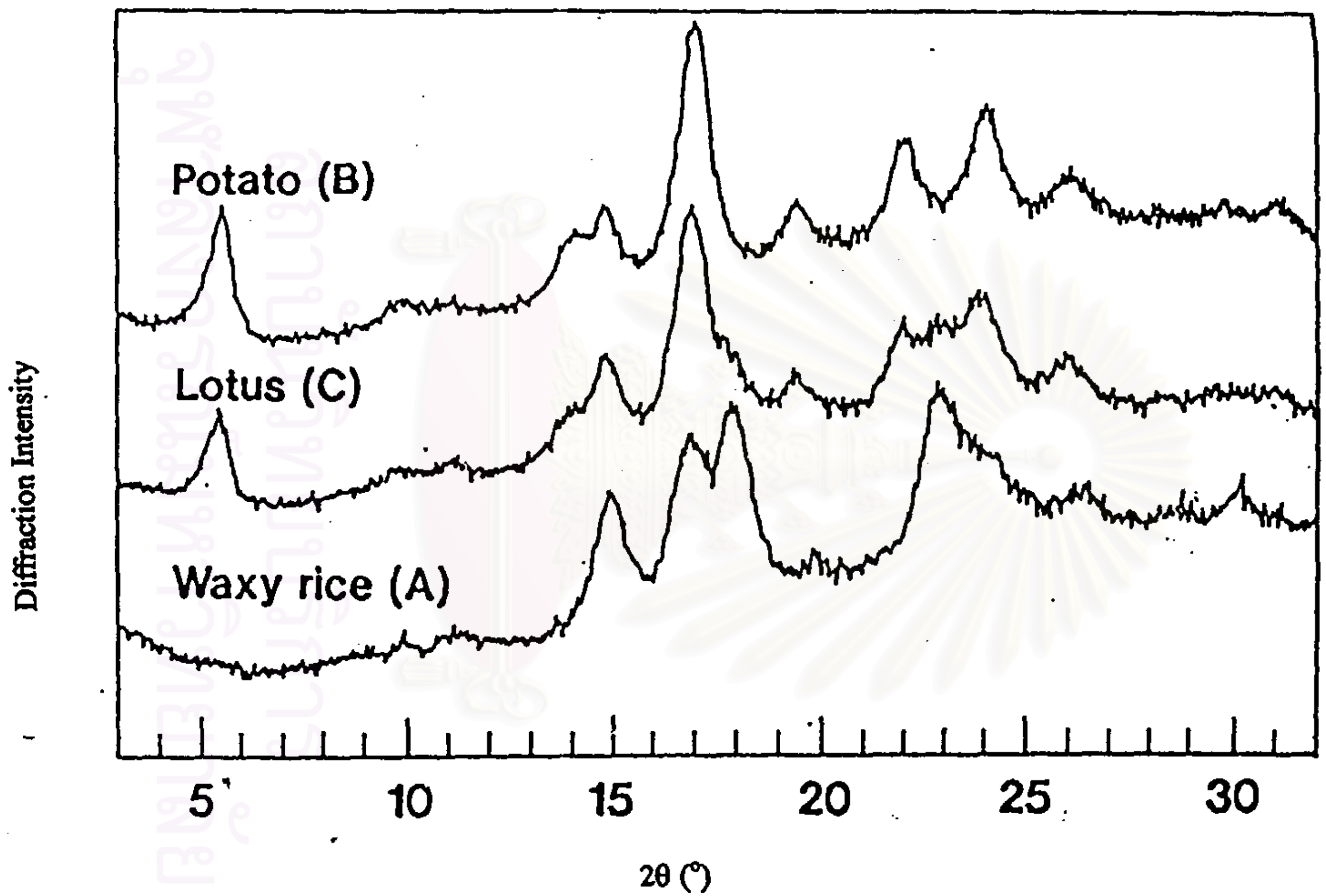


Figure 37 X-ray diffraction patterns of A, B and C type (Hizukuri, 1996)

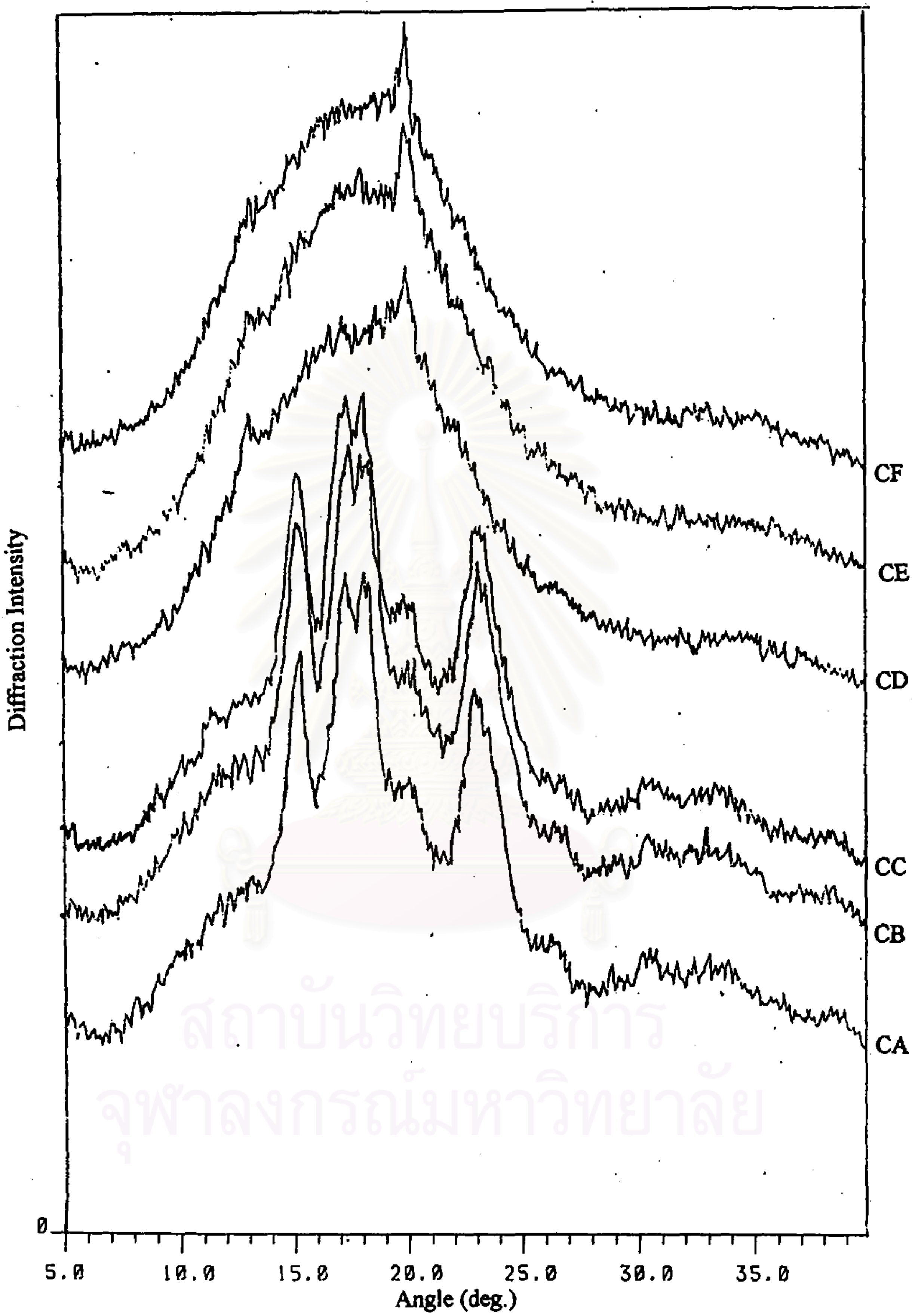


Figure 38 Comparison of X-ray diffraction patterns of corn starches

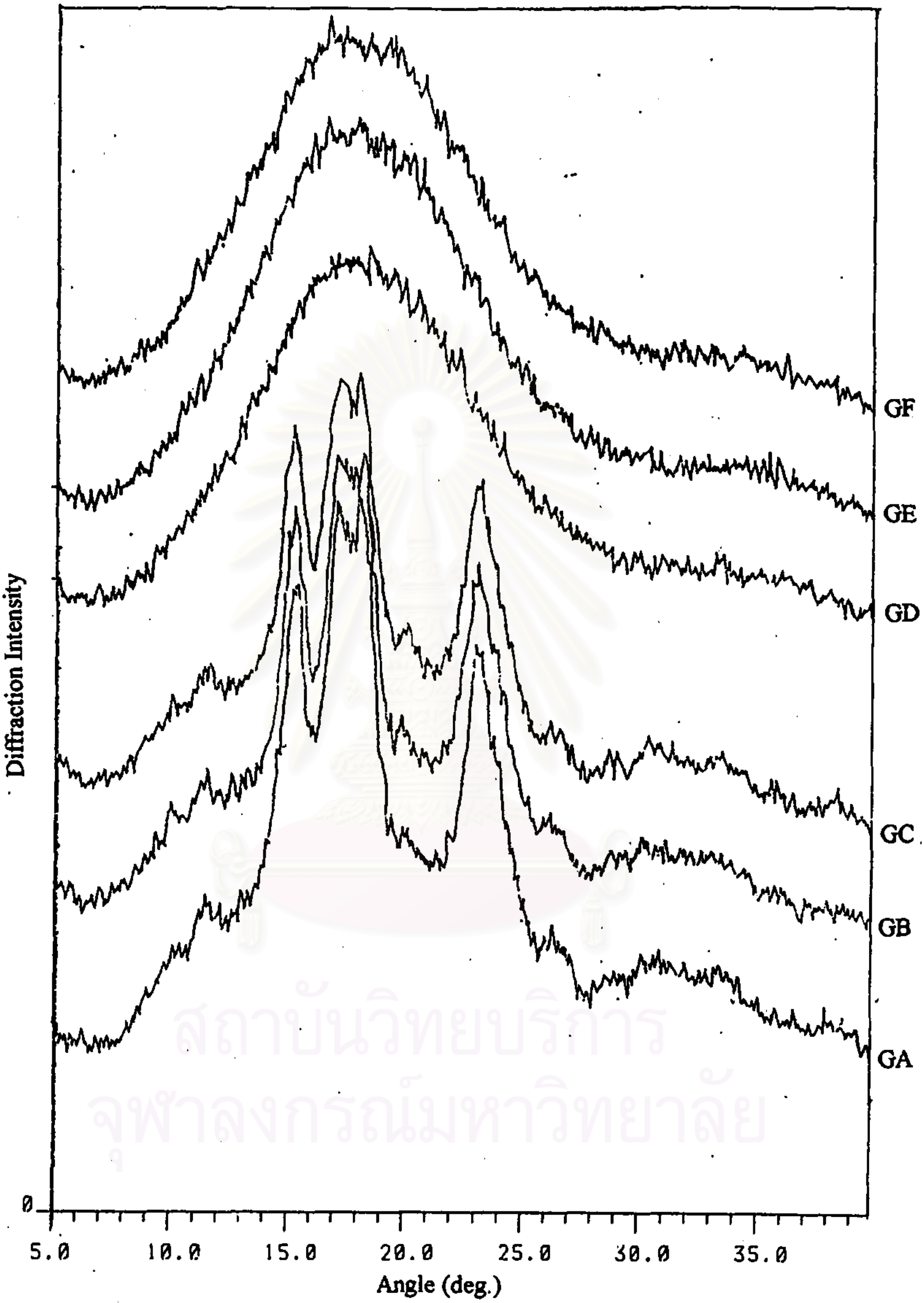


Figure 39 Comparison of X-ray diffraction patterns of glutinous rice starches

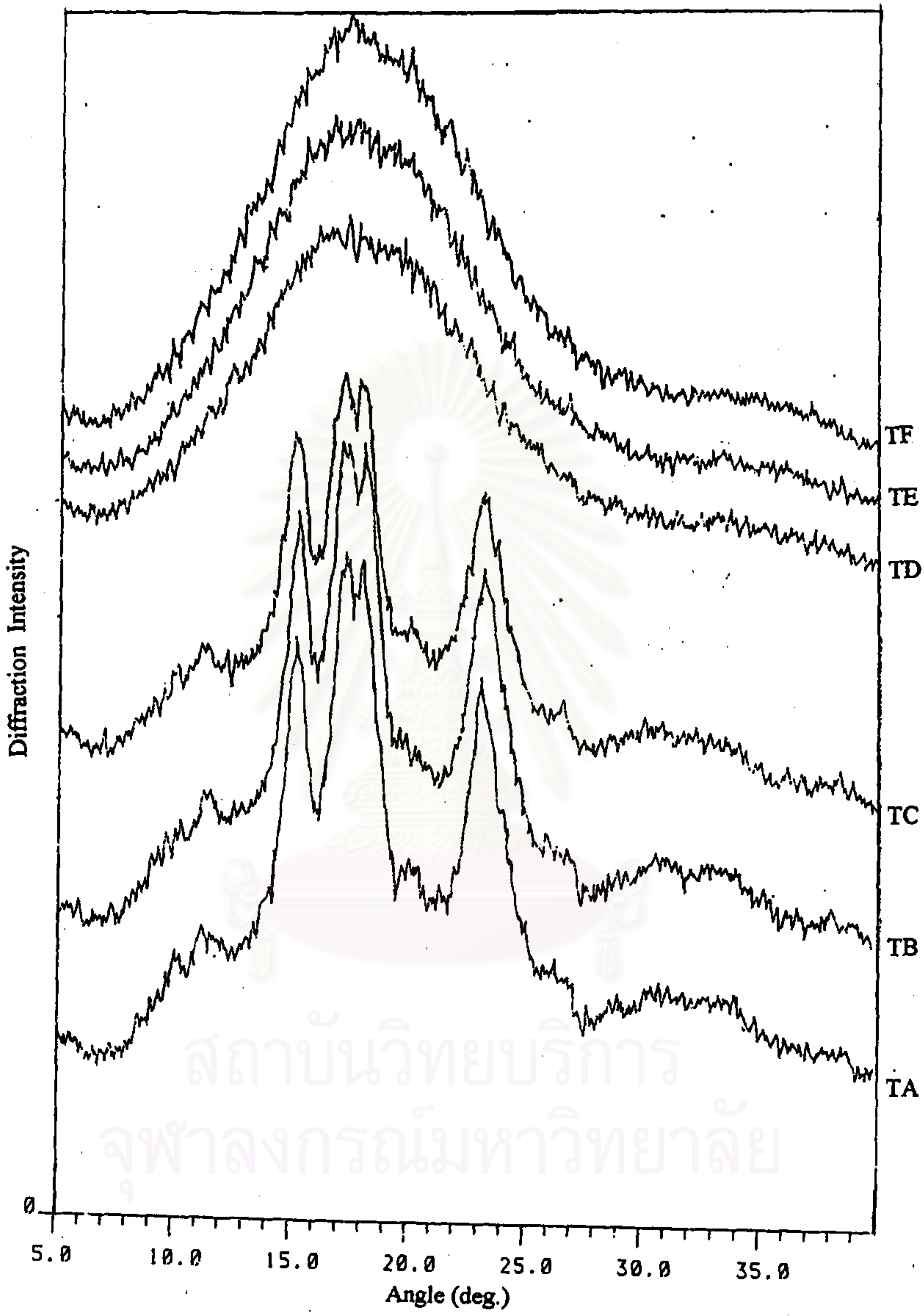


Figure 40 Comparison of X-ray diffraction patterns of tapioca starches

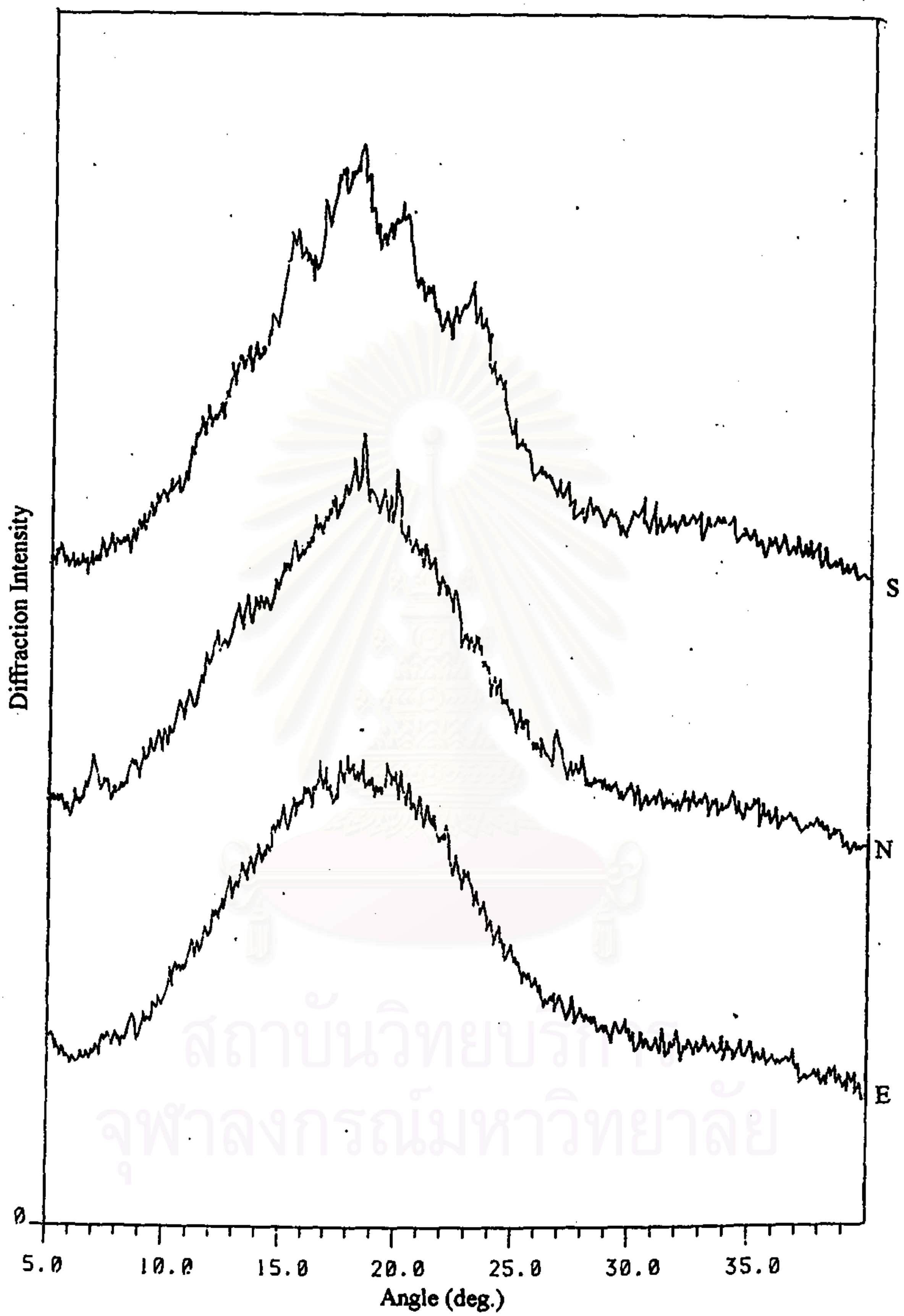


Figure 41 Comparison of X-ray diffraction patterns of commercial pregelatinized starches

3. Differential Scanning Calorimeter

Gelatinization studies of starch have been performed using DSC. There were several studies using this method for determination starch gelatinization (Wooten and Bamunuarachchi, 1979; Gomez and Aguilera, 1984; Herman, Remon and DeVilder, 1989). The purpose of differential thermal system is to record the difference between an enthalpy change, which occurs in a sample and that in some inert reference material when both are heated. Starches are different in their gelatinization charateristics. Thus the different cooking characteristics of the starches depend on starch source.

Since enthalpy of gelatinization (ΔH) is a linear function of degree of gelatinization, ΔH can be utilized directly as a measure of the amount of ungelatinized starch for calculations of rate constants. It can be seen that the final degree of gelatinization (ΔH value) is dependent on temperature of heating and furthermore, that a significant degree of gelatinization has been accomplished at the end of lag time. The process of gelatinization is complex and not readily described by pseudo first-order kinetics. This makes sense when one considers that there is a population of starch granules, each with its unique degree of crystallinity.

The degree of gelatinization is determined as the change of enthalpy during heating of the sample using differential scanning calorimetry (DSC). The gelatinization point (onset temperature of the endothermal peak) as well as the thermal energy may be due to variations in the origin of the starch and a different scanning rate.

The data of gelatinization characteristics has been shown in **Table 8** The DSC thermogarms of corn starch, glutinous rice starch and tapioca starch comparing with those of commercial pregelatinized starches were presented in **Figure 42, 43** and **44** respectively.

The DSC thermograms of native and acid treated starches showed a single endotherm. The gelatinization temperature of native and acid treated of individual starches are in ordering, corn starches (70.8-71.6°C) > tapioca starches (65.2-68.3°C) ≅ glutinous rice starches (65.3-65.8°C). While the enthalpy of native and acid treated corn starches are lower than that of tapioca starch and glutinous rice starches. The results indicated that corn starch had a more thermo-stable granular structure, probably due to the more compact structures, and the formation of amylose-lipid complex during gelatinization. The higher enthalpy of tapioca starch was probably due to the higher proportion of amylopectin, which is similar to that of glutinous rice starch.

There were no endothermic peak of all types of fully pregelatinizes starches indicating that all were completely gelatinized (degree of gelatinized = 100%). This can be attributed to the fact that all granulations were disrupted in the crystalline area. These were confirmed by the results from x-ray patterns described earlier.

Since the Starch 1500 was depicted as partially pregelatinized starch. The DSC thermogram could be seen in the broad shallow endotherm.

Table 8 Gelatinization characteristics of starch dispersion in water determined by DSC

Type of starches (CODE)	Endothermic properties			% UG	% degree of gelatinization
	To (°C)	Tp (°C)	ΔH (J/g)		
Corn starches					
CA	67.2	71.6	14.27	100.00	0.00
CB	67.0	71.2	13.76	96.38	3.62
CC	66.7	70.8	13.33	93.38	6.62
CD	*	*	*	0.00	100.00
CE	*	*	*	0.00	100.00
CF	*	*	*	0.00	100.00
Glutinous rice starches					
GA	58.7	65.8	15.37	100.00	0.00
GB	57.1	64.8	13.32	86.65	13.35
GC	58.4	65.3	13.18	85.70	14.30
GD	*	*	*	0.00	100.00
GE	*	*	*	0.00	100.00
GF	*	*	*	0.00	100.00
Tapioca starches					
TA	62.1	68.3	15.37	100.00	0.00
TB	56.7	65.1	14.70	95.64	4.36
TC	57.6	65.3	14.35	93.16	6.84
TD	*	*	*	0.00	100.00
TE	*	*	*	0.00	100.00
TF	*	*	*	0.00	100.00
Commercial Pregelatinized starches					
E	*	*	*	0.00	100.00
N	*	*	*	0.00	100.00
S	66.4	72.4	1.50	10.51	89.49

* No observation endothermic peak

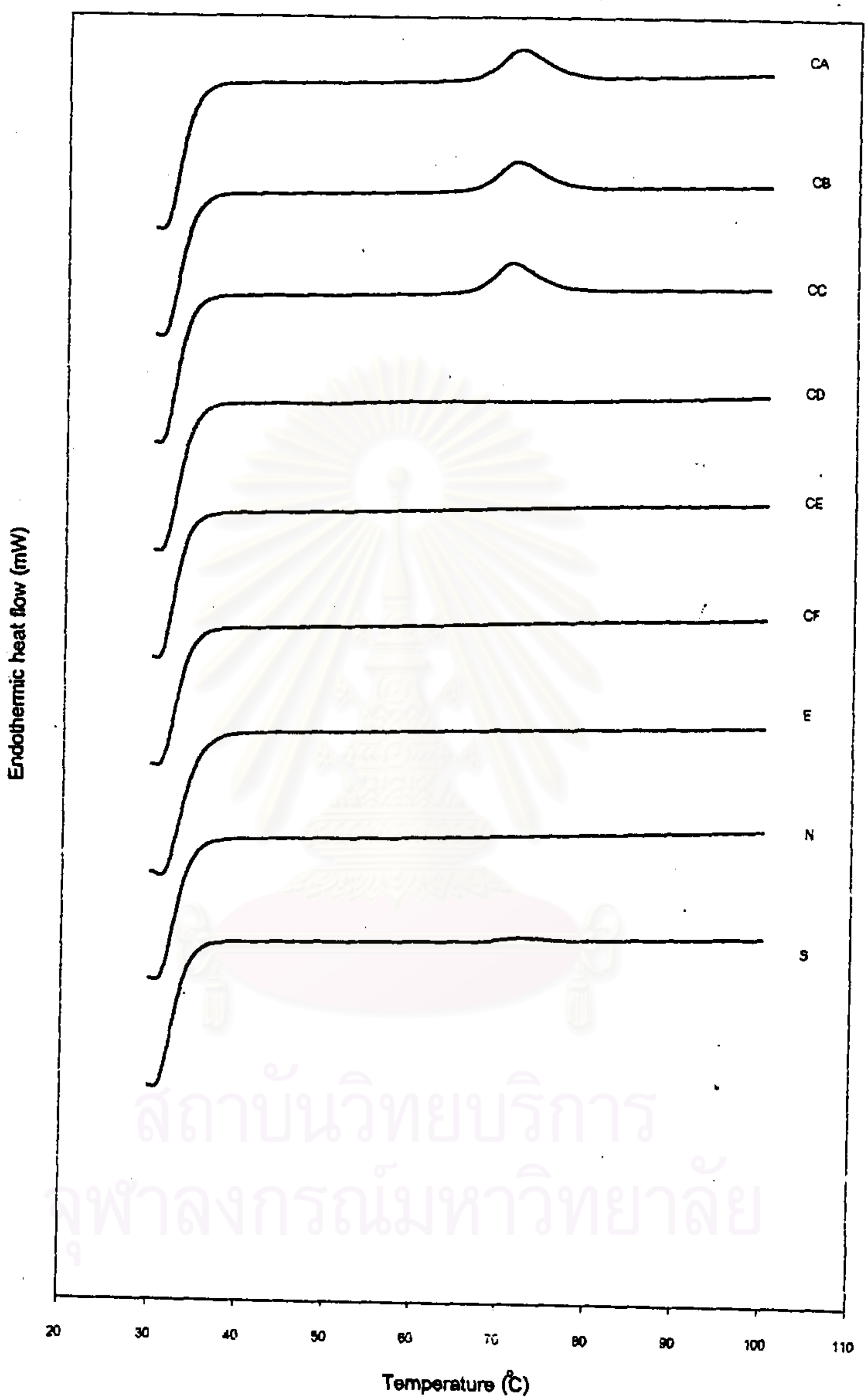


Figure 42 The DSC thermograms of native, acid treated and pregelatinized corn starches compared with commercial pregelatinized starches

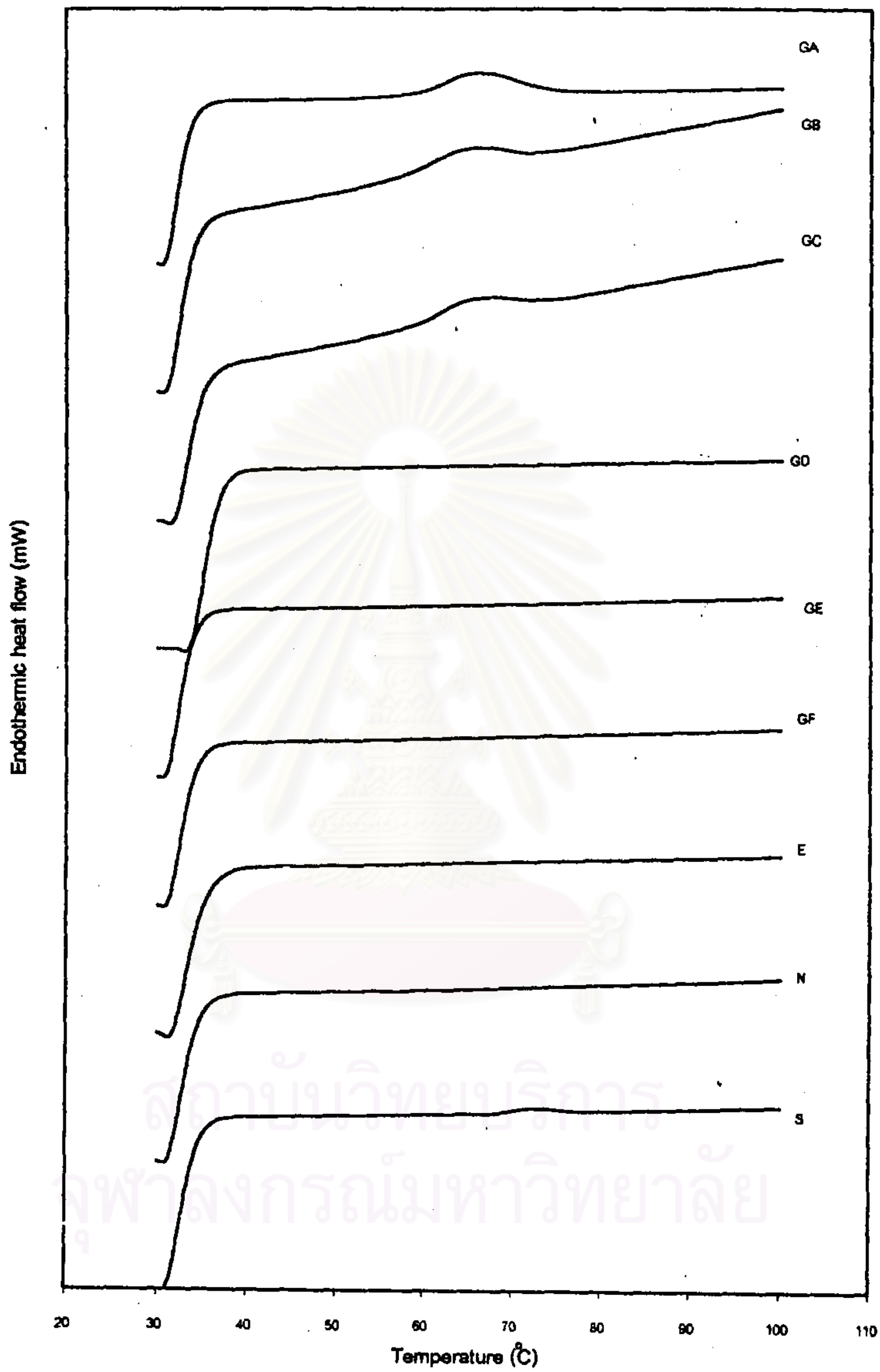


Figure 43 The DSC thermograms of native, acid treated and pregelatinized glutinous rice starches compared with commercial pregelatinized starches

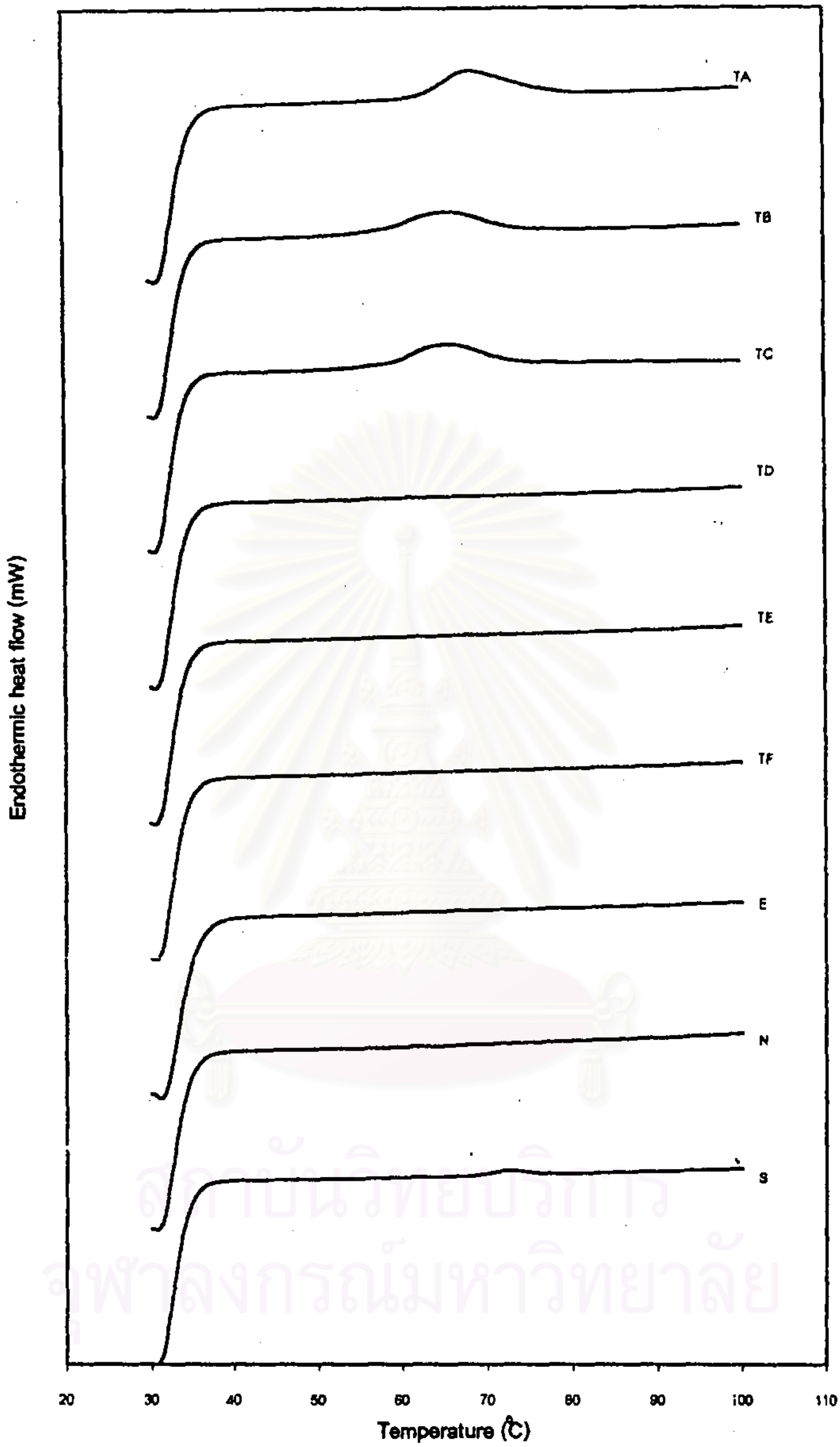


Figure 44 The DSC thermograms of native, acid treated and pregelatinized tapioca starches compared with commercial pregelatinized starches

4. Infrared Spectrophotometer

The IR spectrum of native, acid treated and pregelatinized of all types starches were presented in **Figure 45-48**.

The peaks of starch appeared at 3400 cm^{-1}, resulted from OH-stretching, Peaks at 2900 cm^{-1} resulted from CH-stretching. Peaks between 1160-1100 cm^{-1} result from CO-streching of COH and COC groups.

There were the important zones used to characterize carbohydrate types which were the peaks between 960-730 cm^{-1}. In this study all peaks appeared at 844 ± 8 cm^{-1} indicating that all the absorbance bands are consistent with the structured of starch (Colthup, Daly and wiberly, 1975; New man, et al.,1996).

The infrared spectrum of all type of starches showed that there were no chemical function groups in all starches during acid modification and pregelatinization process.

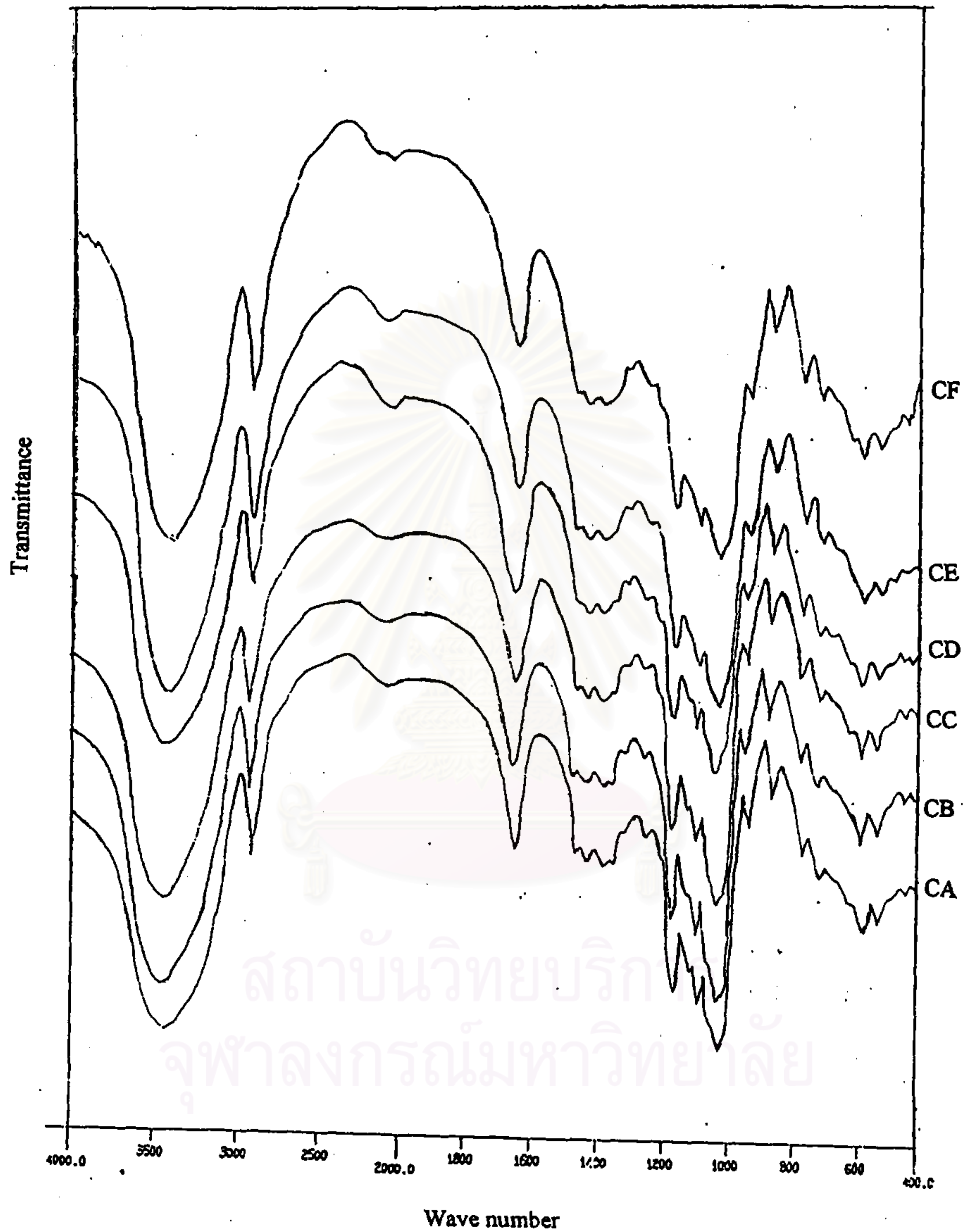


Figure 45 Comparison of FTIR spectrums of corn starches

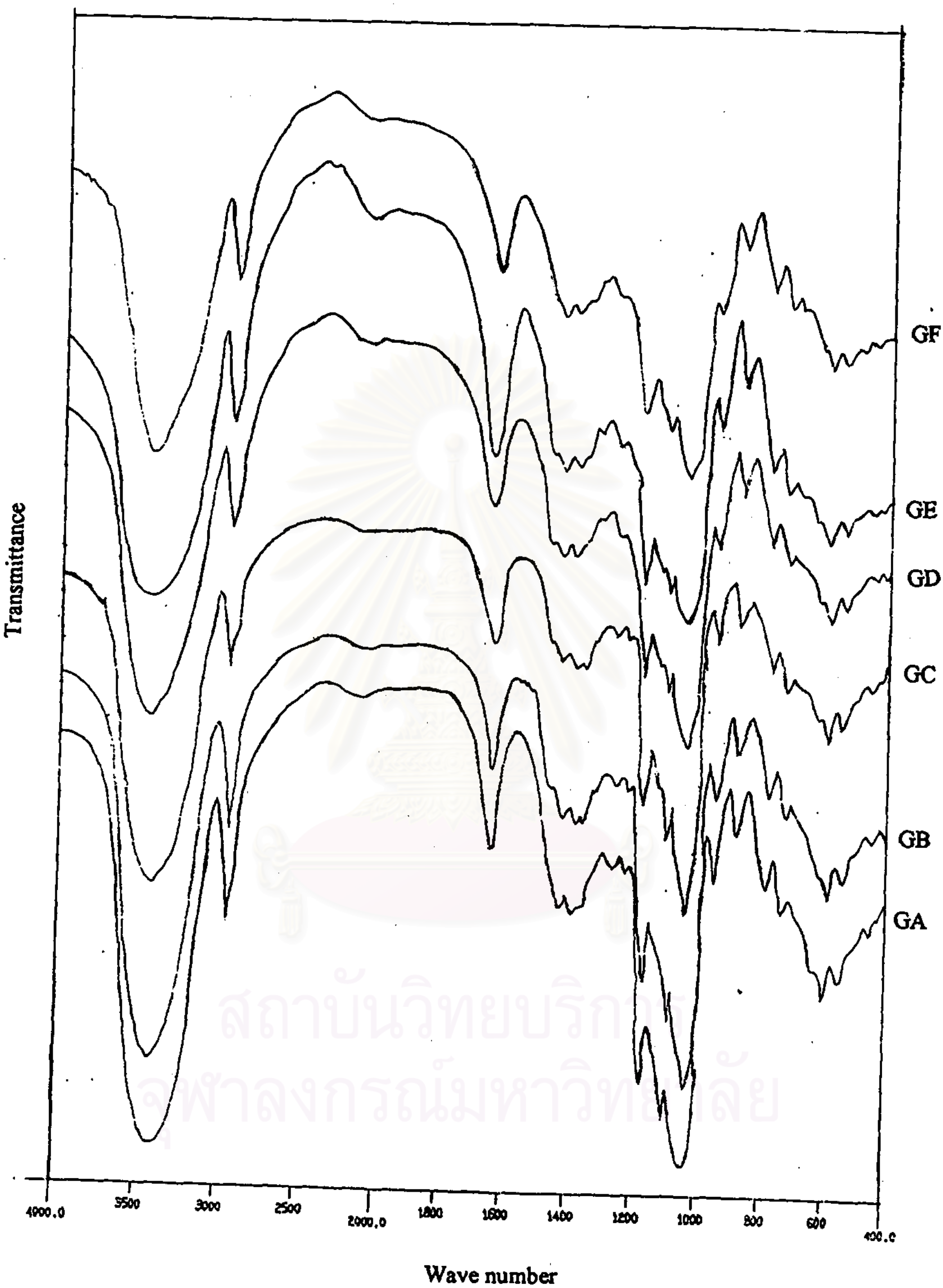


Figure 46 Comparison of FTIR spectrums of glutinous rice starches

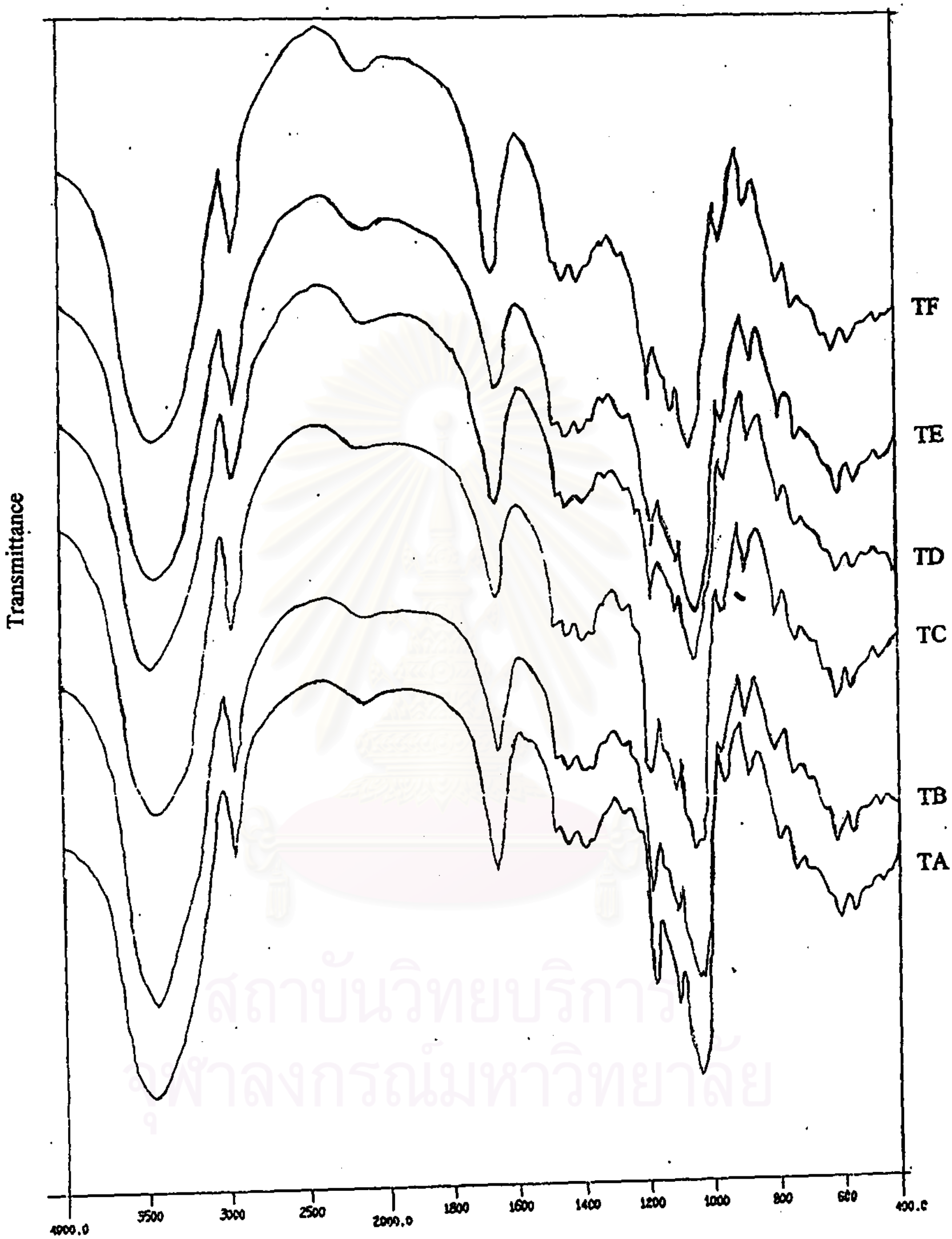


Figure 47 Comparison of FTIR spectrums of tapioca starches

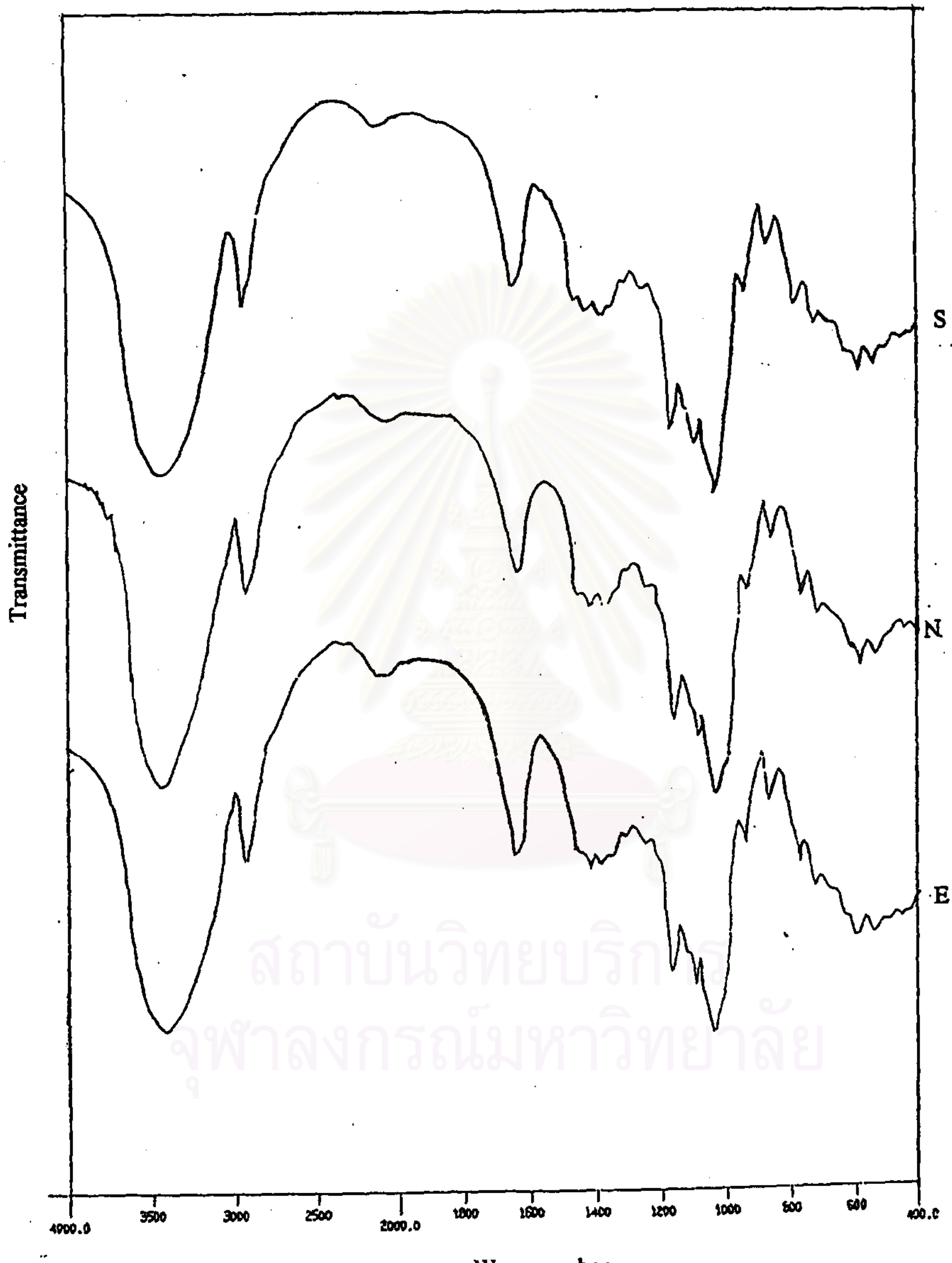


Figure 48 Comparison of FTIR spectrums of commercial pregelatinized starches

5. Swelling Capacity

The starch from the commercial sources consists of starch grains from which most of the moisture has been removed. As the grain dried, molecule of starch pack more closely and the grain shrink. When uncooked and undamaged starch grains are put into cold water, they absorb water and swell. However, the amount of water absorbed and the swell are limited. Crystallinity and birefringence of the granules are unchanged. The uptake water is exothermic (Charley, 1982).

The granule swelling power is defined as the extent of swelling. The swelling characteristics of the different starches are described in **Table 9**. For pregelatinized starches the swelling capacity and amount of soluble are all related to the amylopectin content. A low swelling capacity is seen for pregelatinized starch containing a high amount of amylose because amylose tends to precipitate in water in contradiction to amylopectin which is said to be partially water soluble (Young, 1984) resulting in a high amount of water solubles for amylose free starches.

This was in agreement with the results in this study that the swelling capacity of tapioca starch and glutinous rice starch are higher than that of corn starches. Non pregelatinized starches show low values for all tests carried because the amylopectin enclosed in the undisrupted starch grains is not able to come into action (Herman, et al., 1989).

The granule swelling power is defined as the extent of swelling. The swelling characteristics of the different starches are described in **Table 9**. For pregelatinized

The Figure 49-51 are the histograms of swelling capacity of all starches used comparing with commercial pregelatinized starches, On the other hand, the **Figure 52-55** presented the clearly results of swelling capacity by the photographs when it was kept in cylinder.

Table 9 Swelling capacity of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Swelling capacity* (times) (SD)
Corn starches	
CA	0.78 (0.01)
CB	0.83 (0.01)
CC	0.84 (0.05)
CD	4.82 (0.12)
CE	5.44 (0.28)
CF	5.62 (0.31)
Glutinous rice starches	
GA	1.40 (0.06)
GB	1.01 (0.05)
GC	0.99 (0.04)
GD	5.11 (0.25)
GE	5.48 (0.19)
GF	5.66 (0.19)
Tapioca starches	
TA	0.67 (0.05)
TB	0.74 (0.04)
TC	0.77 (0.06)
TD	5.52 (0.22)
TE	6.15 (0.24)
TF	6.39 (0.24)
Commercial pregelatinized starches	
E	4.32 (0.17)
N	4.48 (0.29)
S	3.33 (0.50)

* Average and standard deviation were calculated from three determinations.

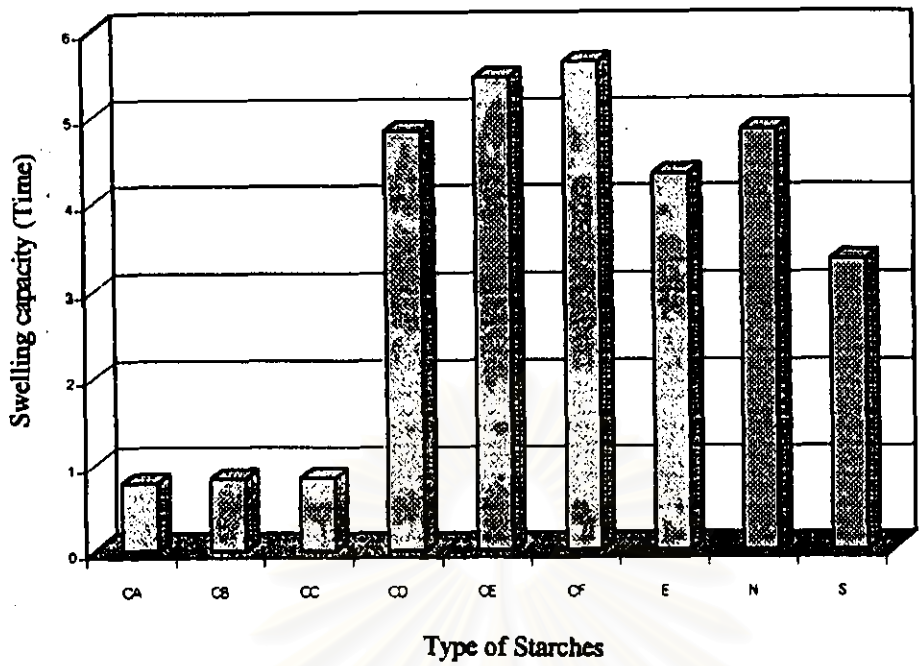


Figure 49 The histogram of swelling capacity (times) of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

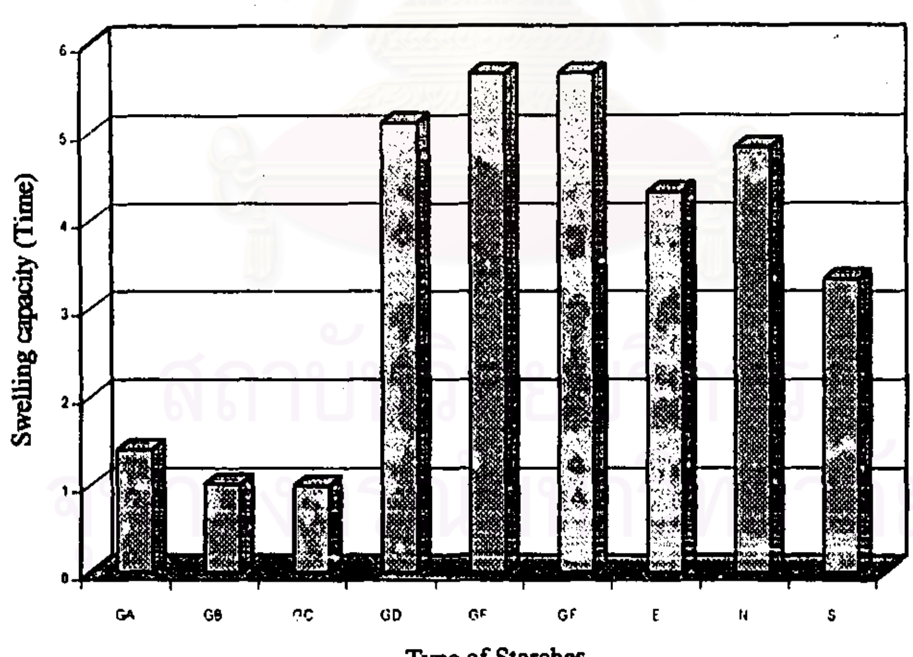


Figure 50 The histogram of swelling capacity (times) of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

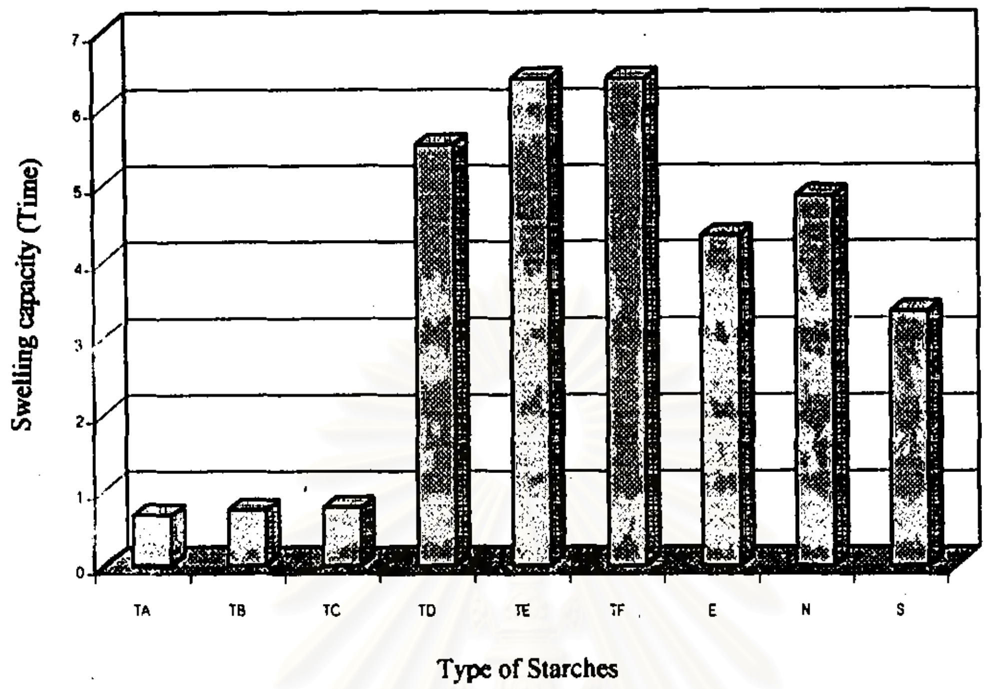


Figure 51 The histogram of swelling capacity (times) of native, acid treated, pregelatinized tapioca rice starches and commercial pregelatinized starches

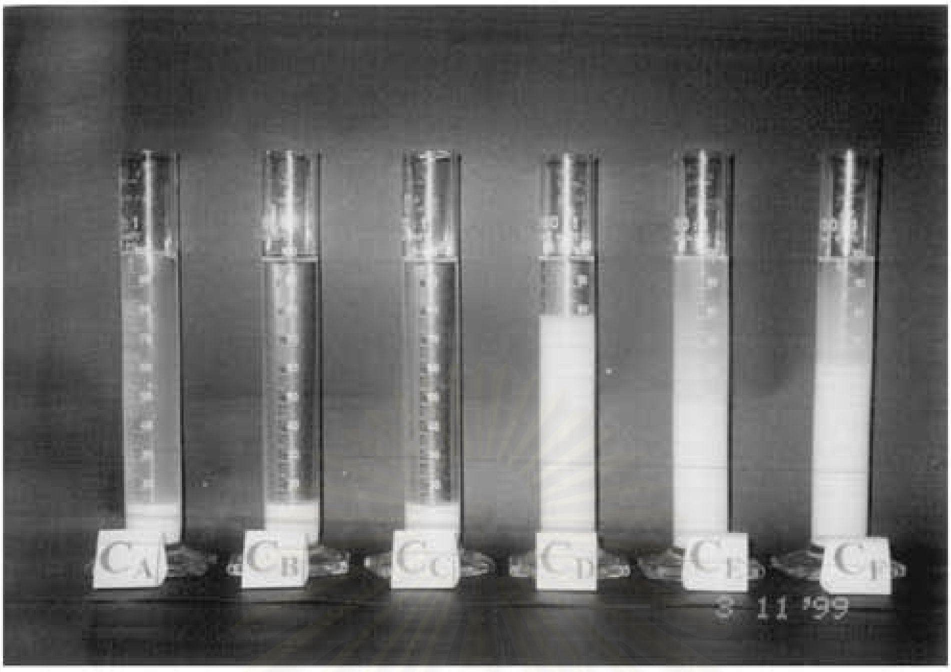


Figure 52 The swelling capacity of corn starches in cylinder method studying

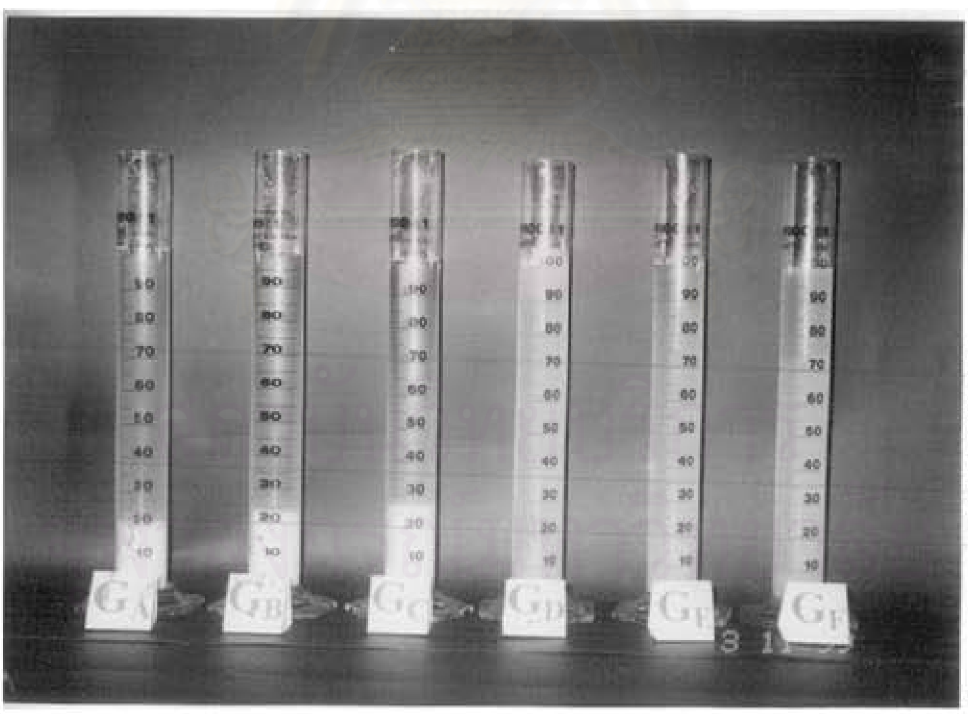


Figure 53 The swelling capacity of glutinous rice starches in cylinder method studying

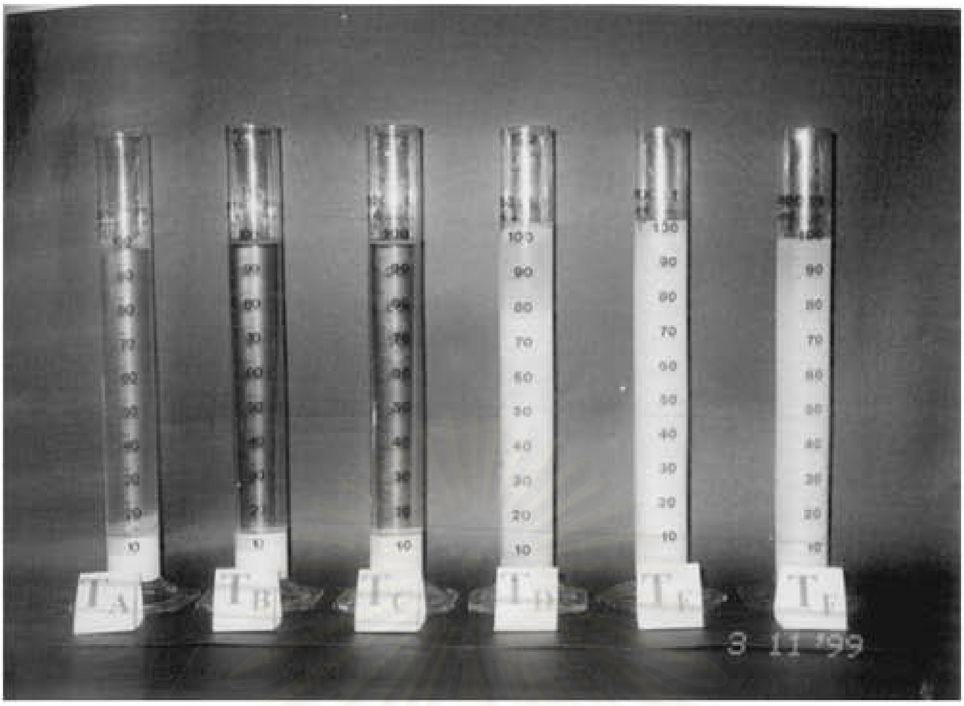


Figure 54 The swelling capacity of tapioca starches in cylinder method studying

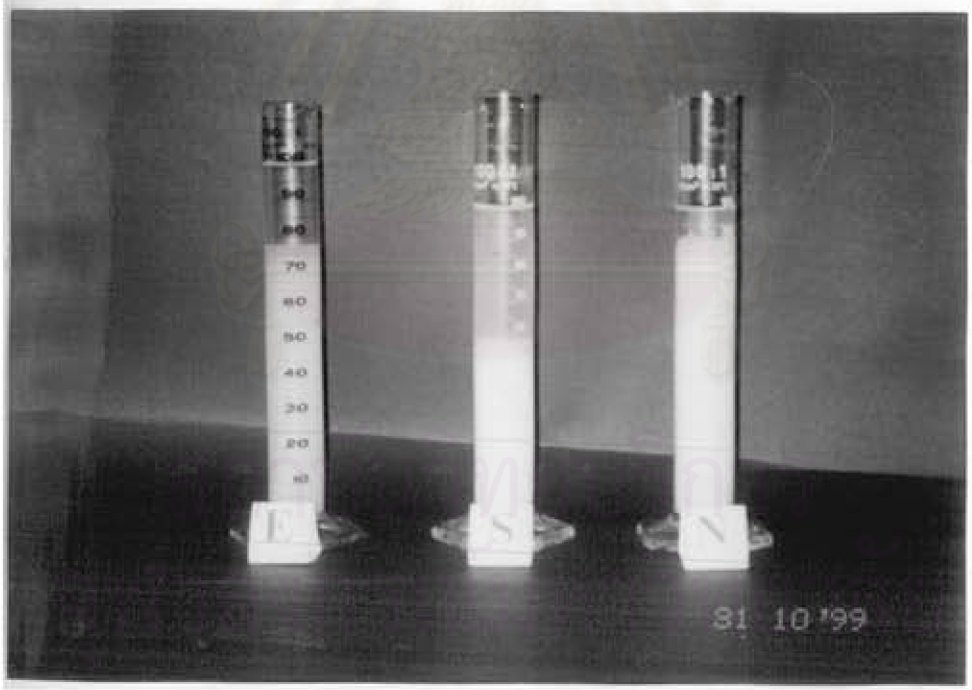


Figure 55 The swelling capacity of commercial pregelatinized starches in cylinder method studying

6. Amount of Solubles

The results of amount of soluble substances are shown in **Table 10** and **Figure 56-58** . The relatively low swelling capacity demonstrated the poor amount of soluble. The native and acid treated starches exhibited the lowest amount of soluble while that of all pregelatinized starches seemed to be higher. From the data, the pregelatinized of acid treated in both levels of tapioca starches gave the highest in amount of solubles. It is interested to display that most of the pregelatinized acid treated starches have higher in amount of solubles than that of preglatinized of unmodified starches. These results were in agreement with the explanation of pregelatinized starch, which could be defined in the term of soluble starch.

Table 10 Amount of soluble substances of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Amount of soluble* (%w/w) (SD)
Corn starches	
CA	0.42 (0.00)
CB	0.12 (0.00)
CC	0.16 (0.00)
CD	22.21 (0.01)
CE	18.47 (0.01)
CF	25.13 (0.00)
Glutinous rice starches	
GA	3.20 (0.00)
GB	2.76 (0.00)
GC	1.92 (0.00)
GD	55.53 (0.02)
GE	32.22 (0.03)
GF	31.15 (0.01)
Tapioca starches	
TA	0.04 (0.00)
TB	0.22 (0.00)
TC	0.19 (0.00)
TD	20.65 (0.01)
TE	49.79 (0.00)
TF	47.15 (0.00)
Commercial pregelatinized starches	
E	31.86 (0.00)
N	34.95 (0.00)
S	6.02 (0.01)

* Average and standard deviation were calculated from three determinations.

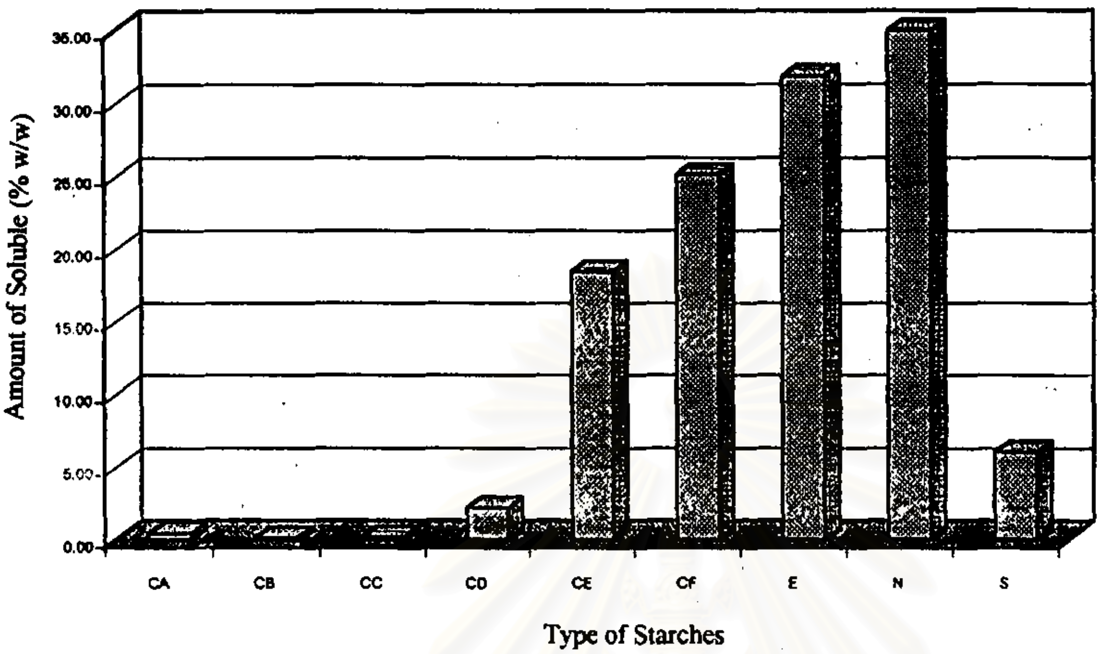


Figure 56 The histogram of soluble substance (%w/w) of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

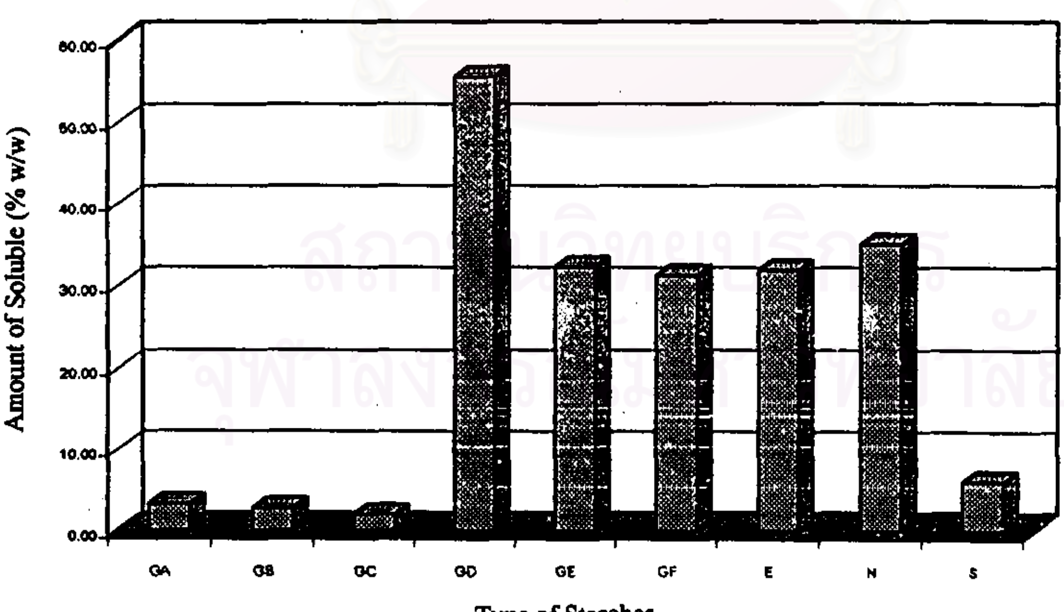


Figure 57 The histogram of soluble substance (%w/w) of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

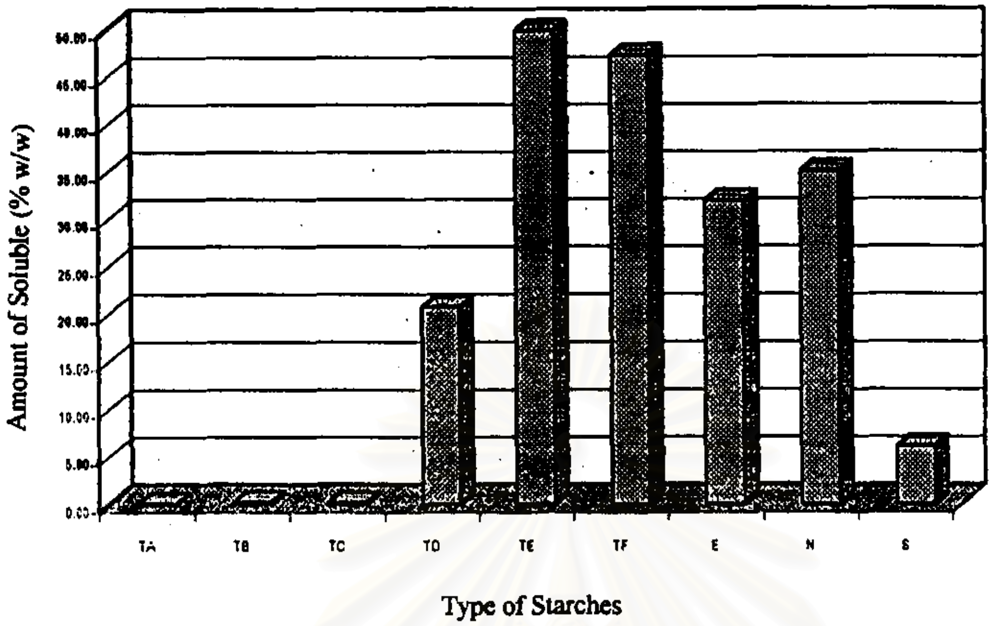


Figure 58 The histogram of soluble substance (%w/w) of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

7. Moisture determination

There was no difference in moisture content **(Table 11, Figure 59-61)** among all native and acid treated starch granules. The moisture content was about nearly 10%. All freshly prepared pregelatinized starches have much lower moisture content. Anyway the moisture content of commercial pregelatinized starches studied were appeared nearly to 10%. It is common for the starch to absorb the moisture to its equilibrium under storage. It was found that the more disrupted the granular structure, the more easily the water could be absorbed, especially in high humidity conditions (Herman et al., 1989).

Table 11 Moisture content of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Moisture* (%) (SD)
Corn starches	
CA	10.56 (0.29)
CB	8.37 (0.15)
CC	9.44 (0.16)
CD	5.14 (0.19)
CE	4.91 (0.09)
CF	4.35 (0.92)
Glutinous rice starches	
GA	9.64 (0.08)
GB	12.56 (0.32)
GC	10.58 (0.34)
GD	4.34 (0.27)
GE	2.93 (0.09)
GF	2.54 (0.11)
Tapioca starches	
TA	10.55 (0.10)
TB	10.34 (0.21)
TC	12.61 (0.33)
TD	4.42 (0.28)
TE	3.67 (0.17)
TF	4.28 (0.06)
Commercial pregelatinized starches	
E	9.33 (0.10)
N	10.36 (0.13)
S	9.64 (0.31)

* Average and standard deviation were calculated from three determinations.

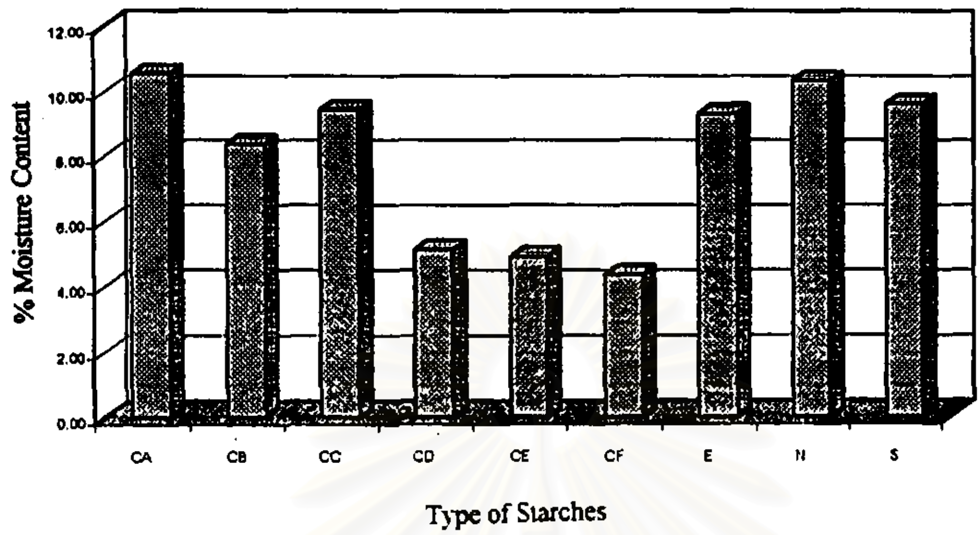


Figure 59 The histograms of percent moisture content of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

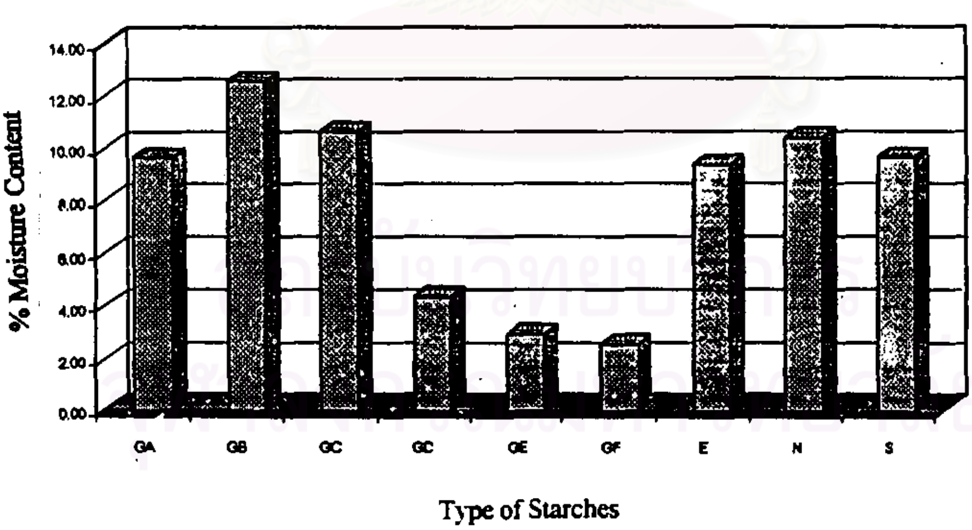


Figure 60 The histograms of percent moisture content of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

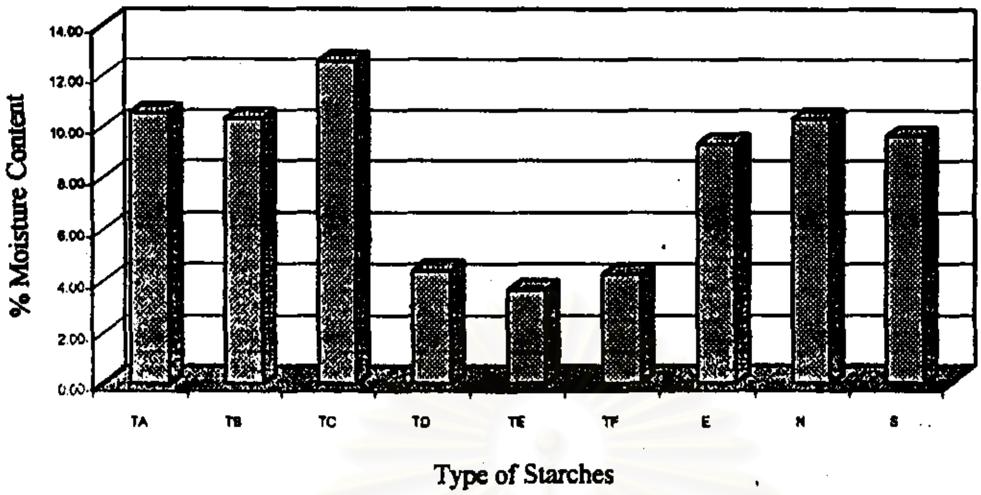


Figure 61 The histograms of percent moisture content of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

8. Particle Size Analysis

The laser light scattering analysis was dependent on the model used to fit the data and better reproducibility was obtained with samples suspended in liquid.

Results of the particle size analysis are shown in **Table 12**. The fine particle can be explained by the fact that these starches were milled in desired particle size after drying during the modification process in both acid modification and/or pregelatinization.

The particle size distribution of all type of starches were similar to be log-normal distribution except Starch 1500, the only pattern that showed bimodal distribution (see **Figure 62-82**). This could be explained that Starch 1500 is the partially pregelatinized starch. It was consisted of both ruptured gelatinized starch particles resulting in larger particle size fraction as well as the intact granules produced a mode towards the lowest particle size mode.

The results show that all types of pregelatinized starches seemed to have higher average particle sizes when compare with ungelatinized starch (native and acid treated starches) indicating that acid treated starches could not be changed in particle sized of starch granules while the pregelatinization produced larger particle size due to agglomeration formation after pregelatinization process and became the flaky shape even if the grinding was performed after pregelatinization by drum dryer. This was confirmed by SEMs (see "**Starch Morphology by SEM**").

The particle sized analysis were clearly presented in histograms **(Figure 83-85)**

Table 12 Particle size distribution of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Volumetric diameter (um)* D (V, 0.1) (SD)		D (V, 0.5) (SD)		D (V, 0.9) (SD)	
CA	4.48	(0.06)	14.50	(0.09)	23.50	(0.14)
CB	5.87	(0.03)	15.43	(0.04)	25.12	(0.12)
CC	6.16	(0.06)	15.76	(0.08)	26.09	(0.39)
CD	34.44	(0.13)	104.25	(0.56)	209.40	(0.90)
CE	30.53	(0.09)	89.85	(0.34)	179.10	(1.30)
CF	23.76	(0.09)	82.20	(0.51)	166.75	(0.55)
GA	1.25	(0.03)	8.30	(0.28)	26.60	(3.05)
GB	1.24	(0.06)	8.32	(0.59)	23.31	(4.34)
GC	1.49	(0.07)	10.08	(0.62)	29.77	(4.47)
GD	22.72	(0.16)	73.39	(0.32)	152.92	(0.61)
GE	25.88	(0.17)	86.05	(0.21)	172.24	(1.39)
GF	25.32	(0.27)	86.19	(0.20)	179.21	(0.48)
TA	3.59	(0.19)	13.53	(0.08)	23.34	(0.55)
TB	4.40	(0.12)	14.50	(0.18)	24.72	(0.48)
TC	5.74	(0.09)	15.38	(0.15)	25.80	(0.40)
TD	33.94	(0.24)	100.50	(0.53)	202.32	(1.58)
TE	23.72	(0.34)	92.23	(0.32)	199.46	(0.97)
TF	27.20	(0.35)	92.36	(0.32)	192.04	(2.29)
E	41.48	(0.49)	129.78	0.92	278.06	(3.46)
N	12.38	(0.14)	49.24	0.43	116.10	(1.75)
S	13.69	(0.06)	75.29	0.85	178.42	(1.77)

*Average and standard deviation were calculated from three determinations.

D(V, 0.1) : volume diameter of 10% undersize

D(V, 0.5) : volume diameter of 50% undersize

D(V, 0.9) : volume diameter of 90% undersize

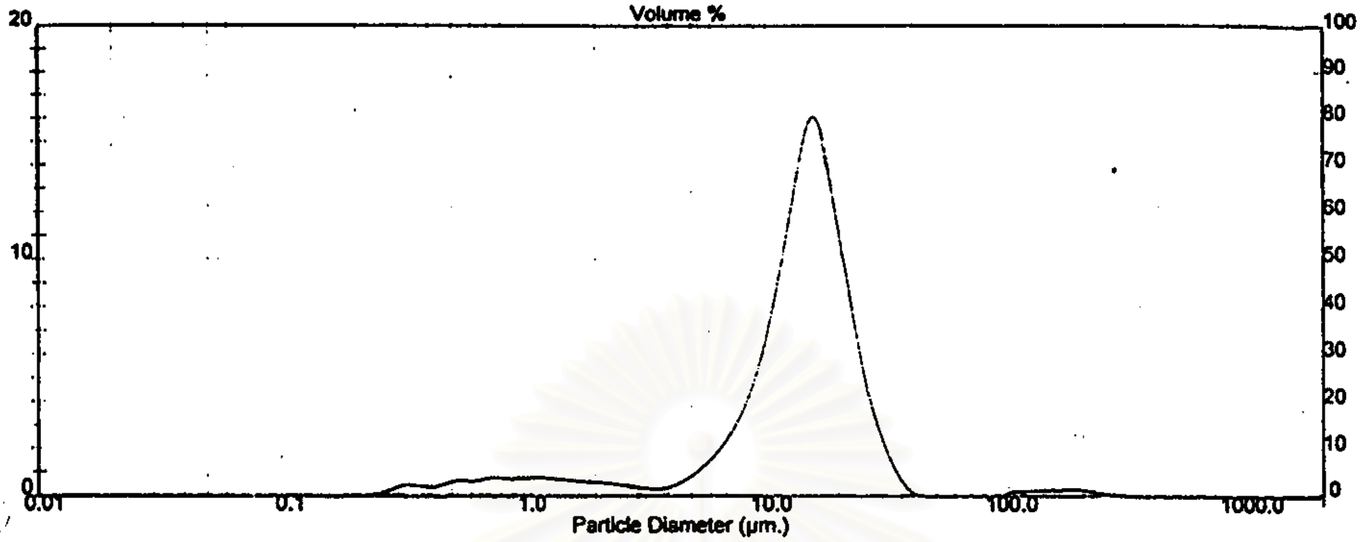


Figure 62 Particle size distribution of native corn starch (CA)

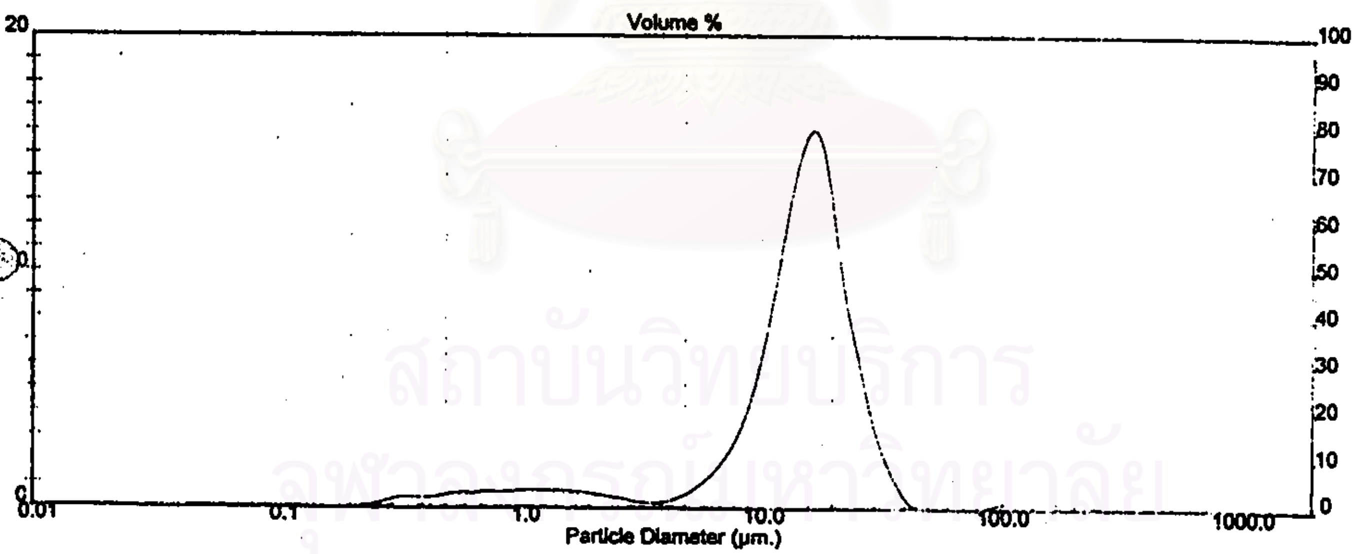


Figure 63 Particle size distribution of acid-treated corn starch (CB)

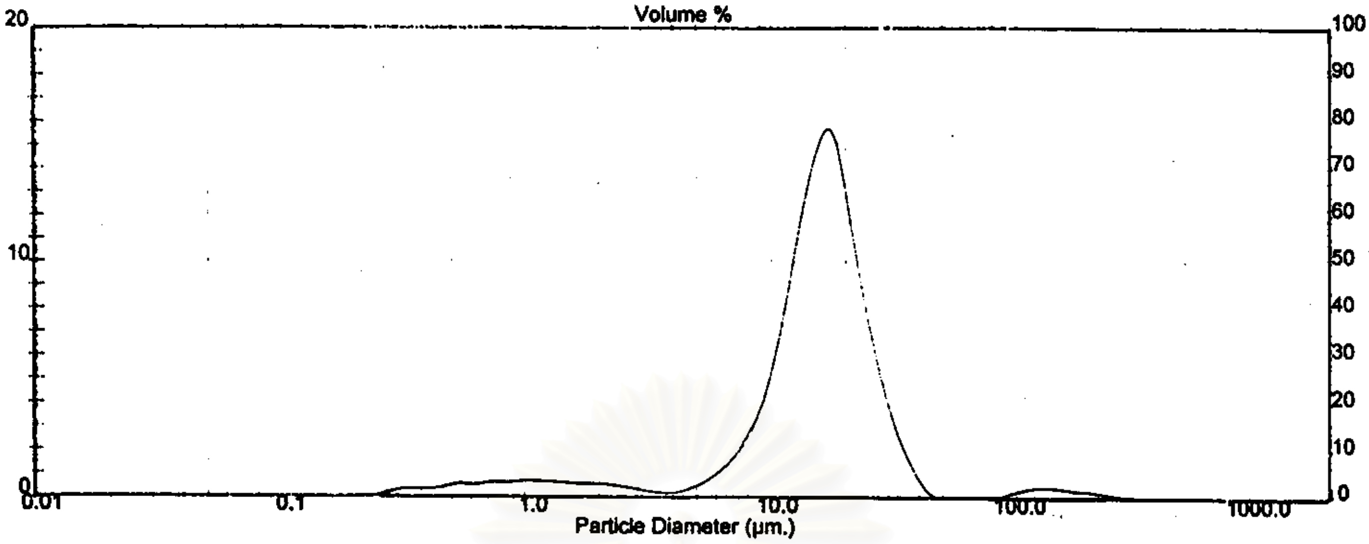


Figure 64 Particle size distribution of acid-treated corn starch (CC)

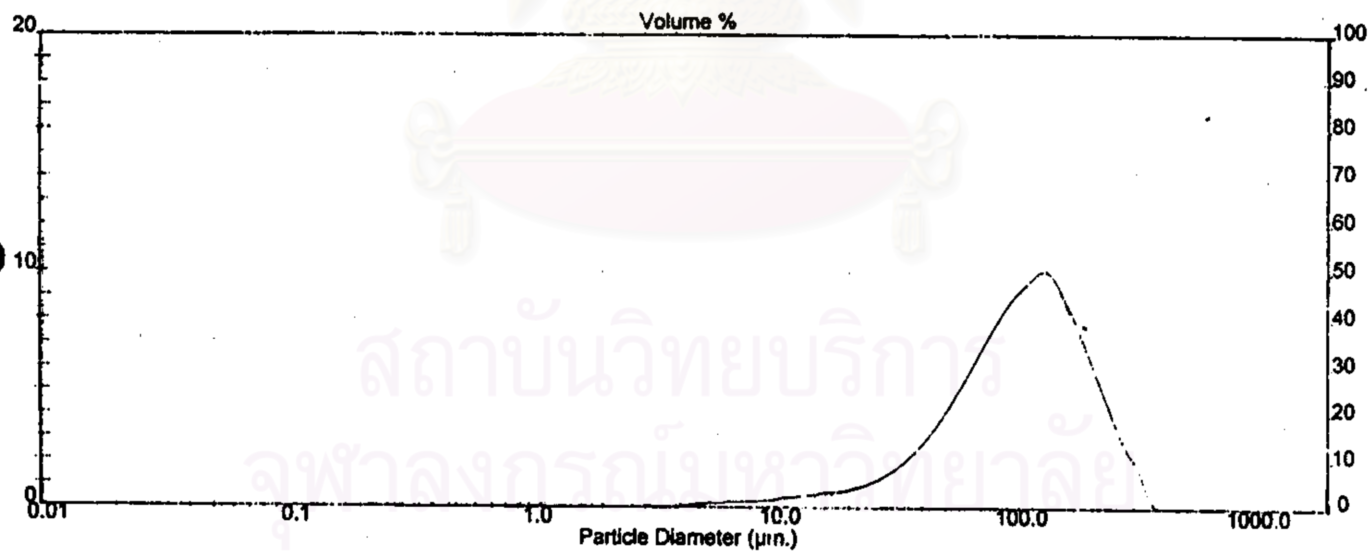


Figure 65 Particle size distribution of pregelatinized corn starch (CD)

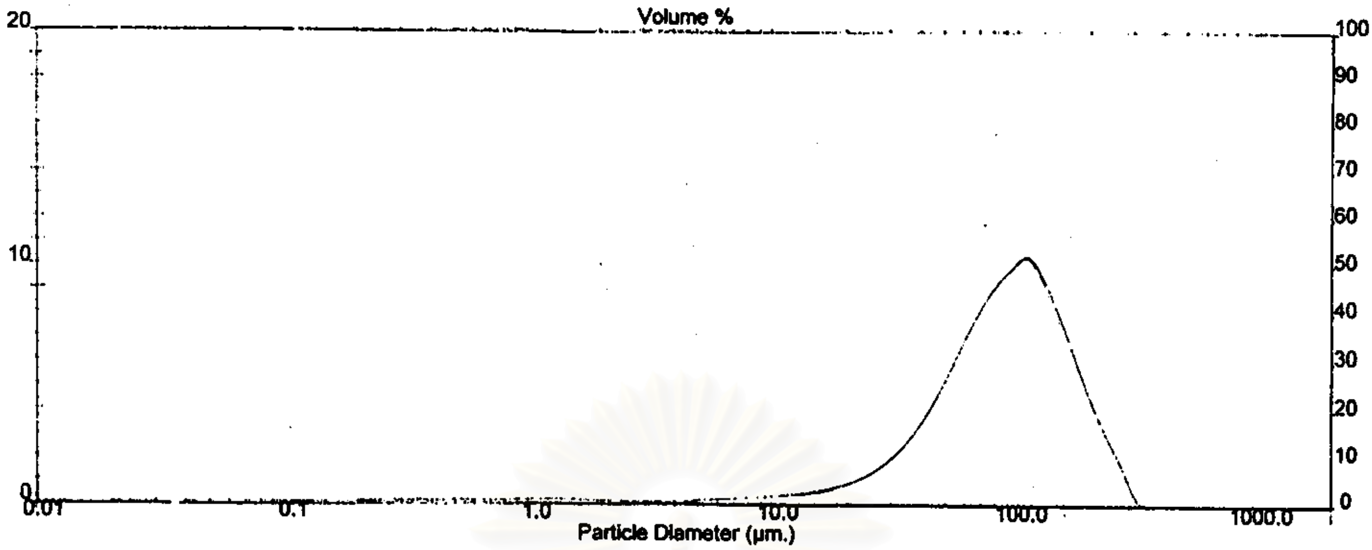


Figure 66 Particle size distribution of pregelatinized-acid treated corn starch (CE)

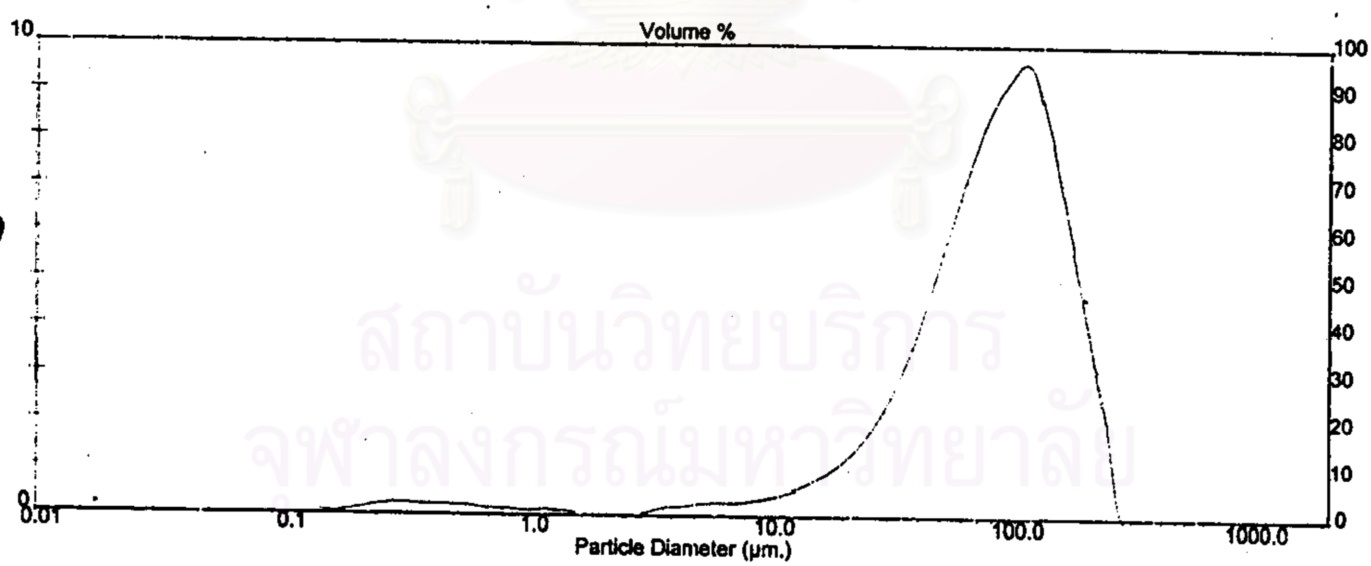


Figure 67 Particle size distribution of pregelatinized-acid treated corn starch (CF)

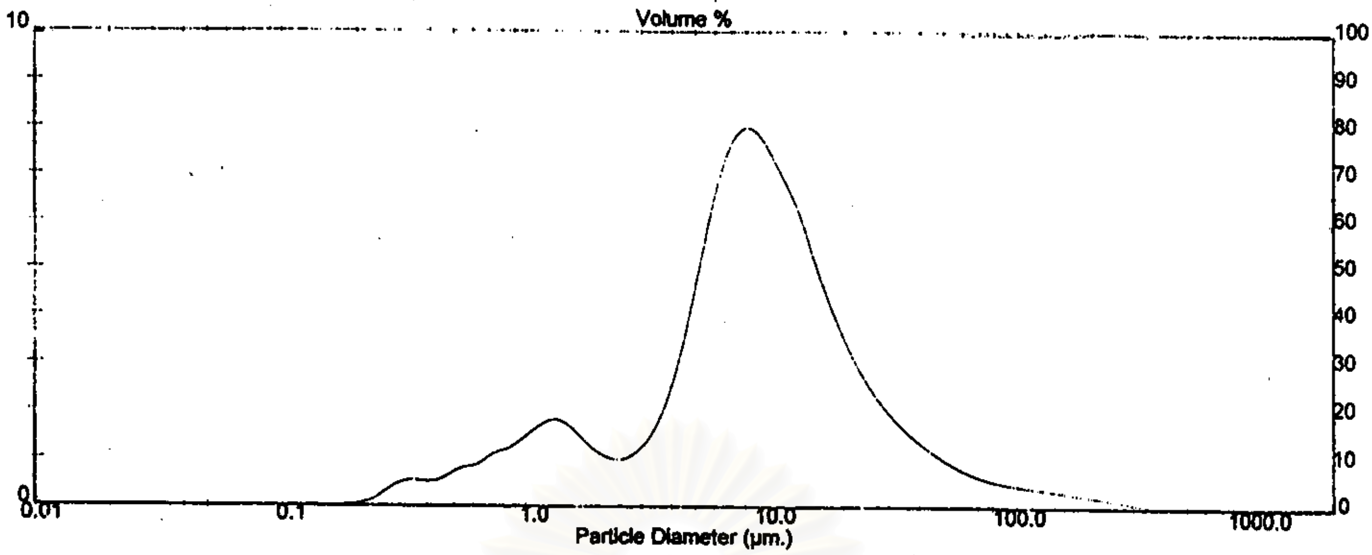


Figure 68 Particle size distribution of native glutinous rice starch (GA)

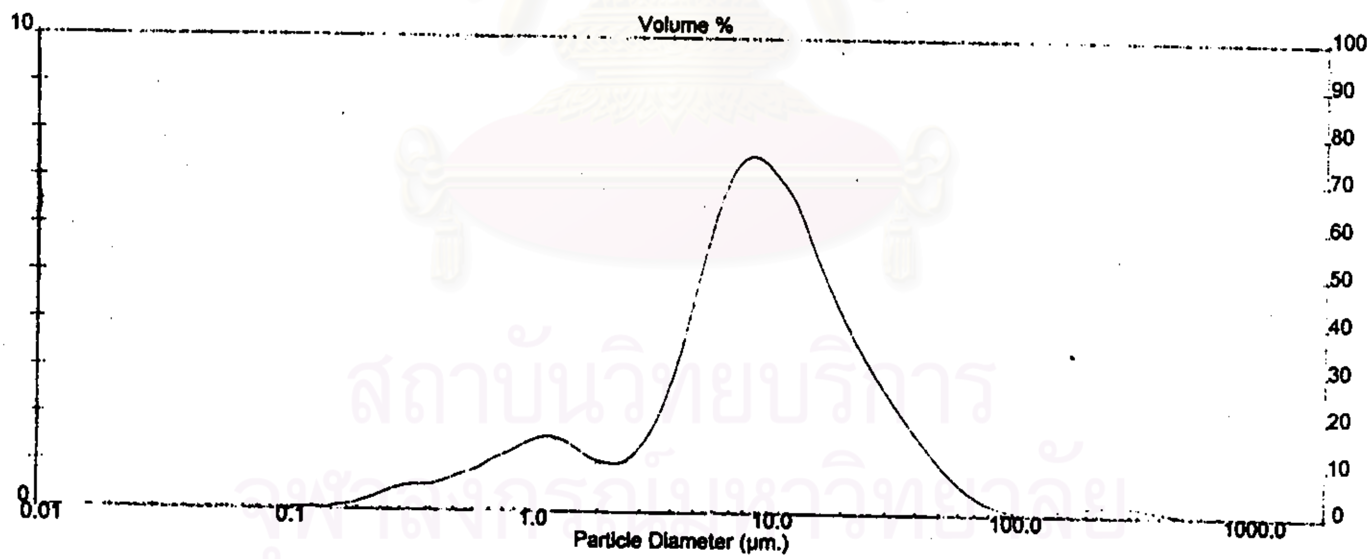


Figure 69 Particle size distribution of acid-treated glutinous rice starch (GB)

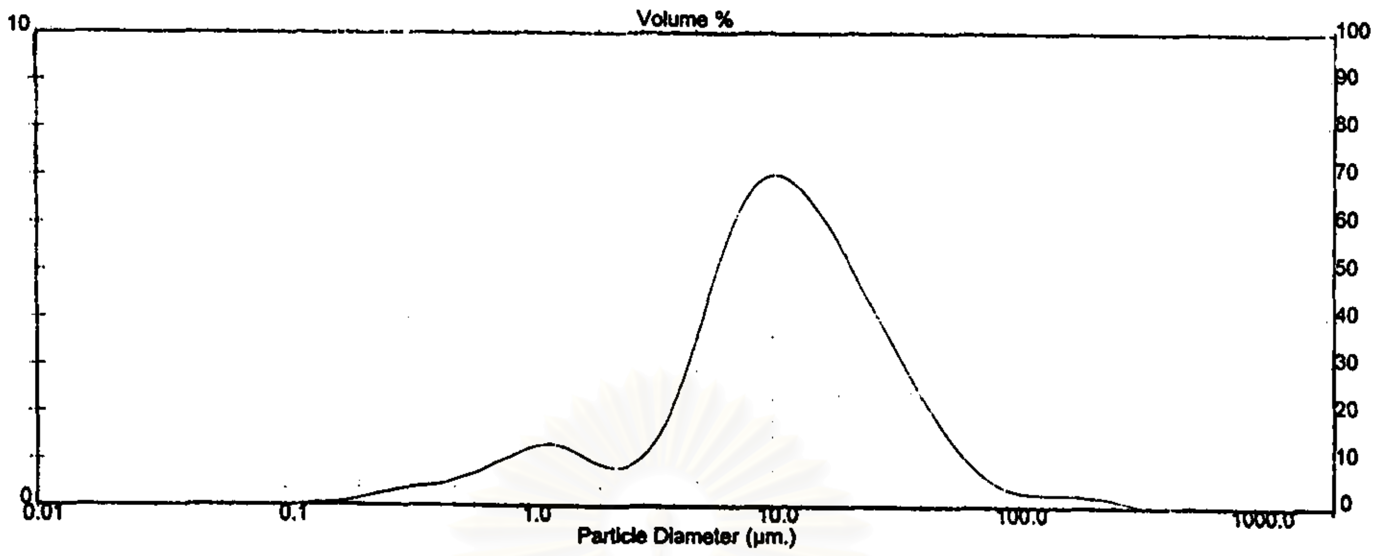


Figure 70 Particle size distribution of acid-treated glutinous rice starch (GC)

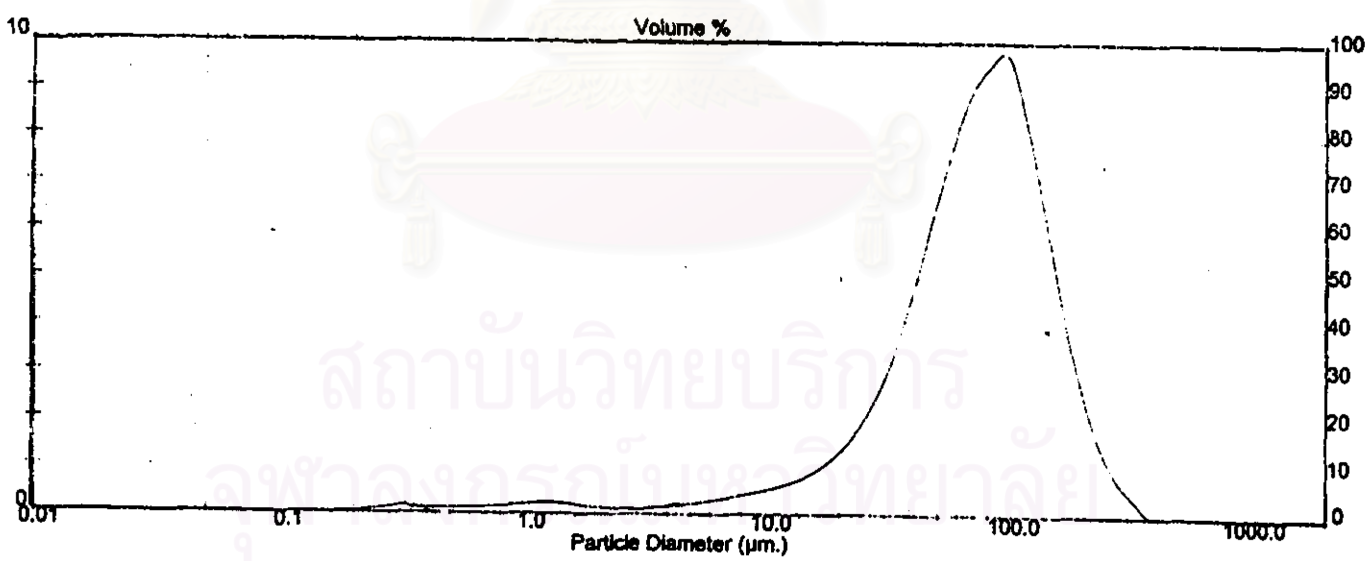


Figure 71 Particle size distribution of pregelatinized glutinous rice starch (GD)

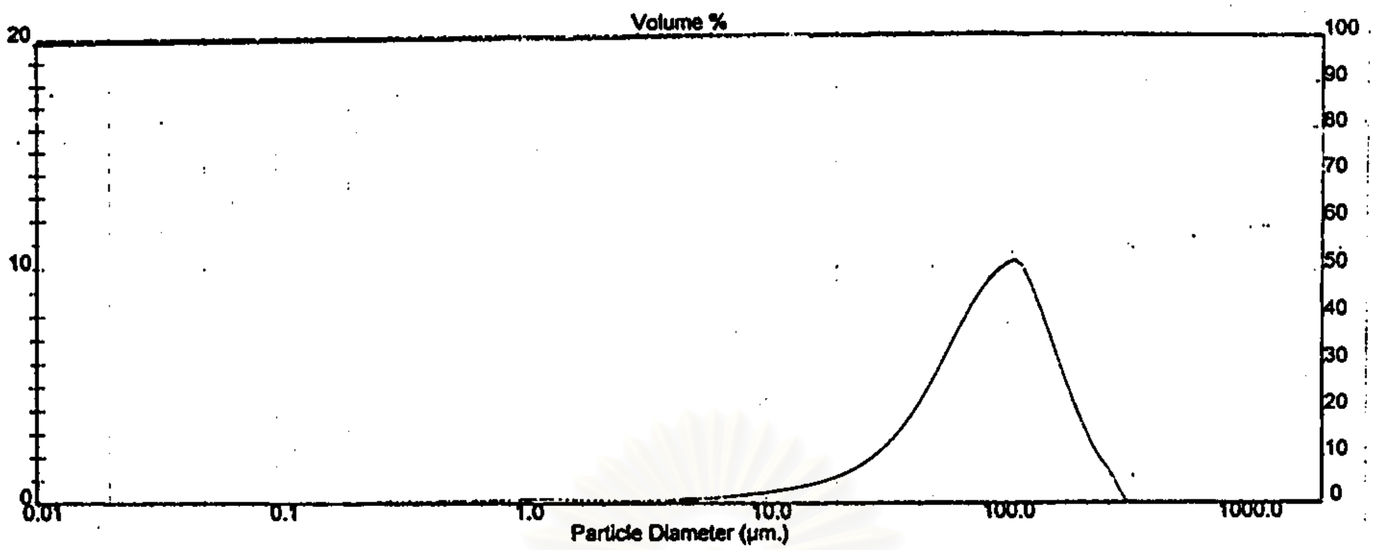


Figure 72 Particle size distribution of pregelatinized-acid treated corn starch (GE)

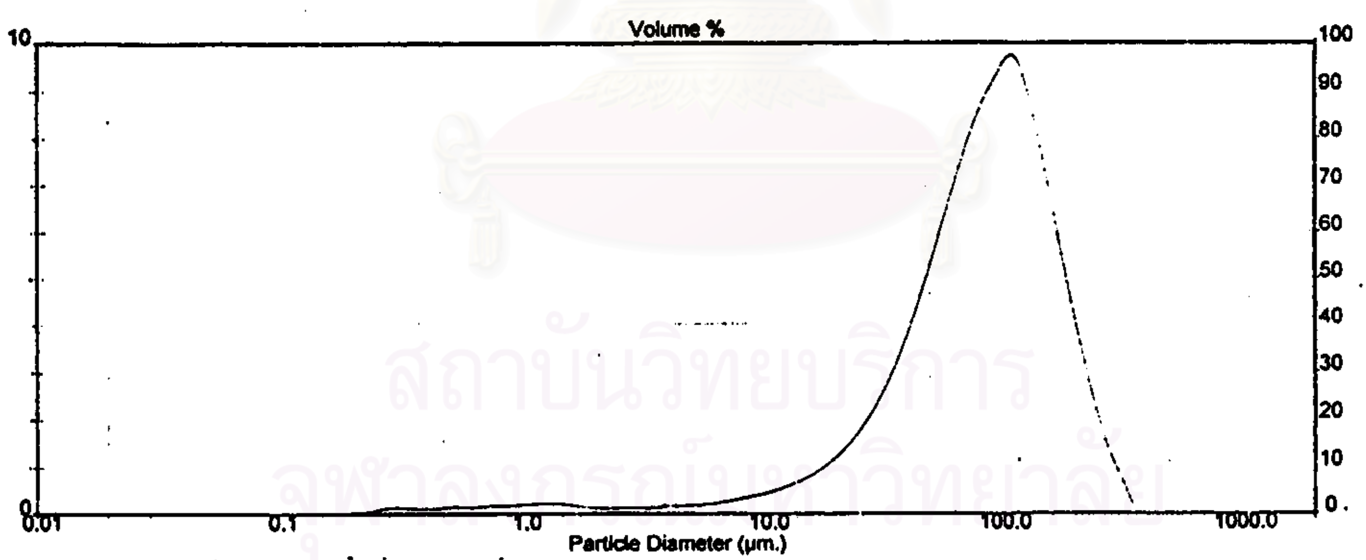


Figure 73 Particle size distribution of pregelatinized-acid treated corn starch (GF)

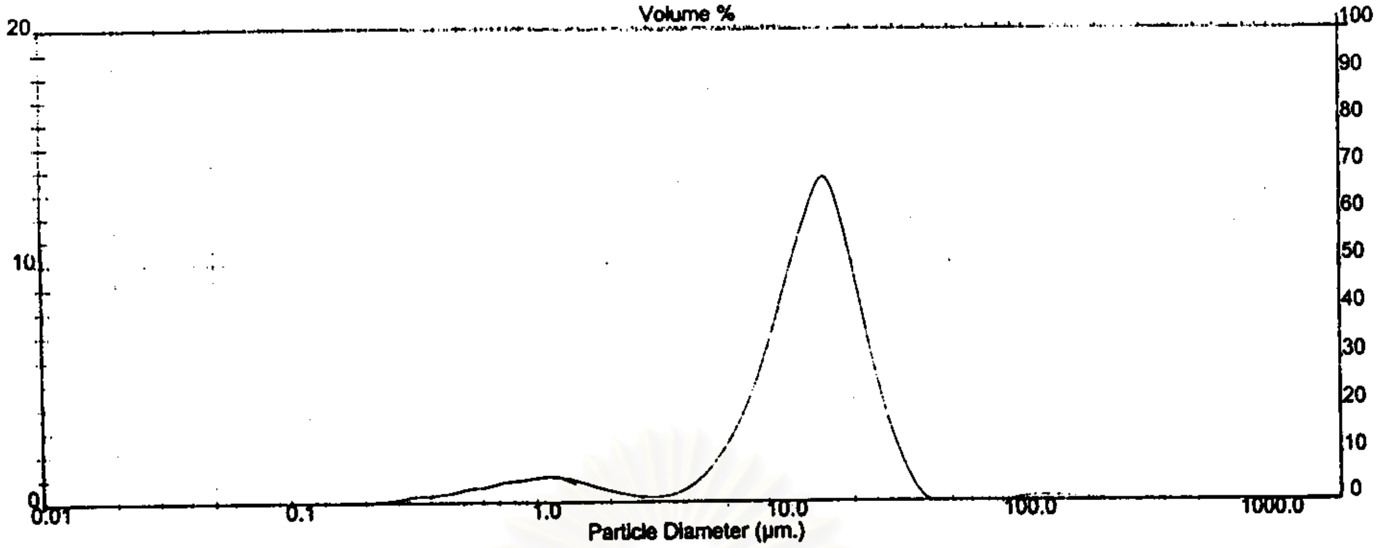


Figure 74 Particle size distribution of native tapioca starch (TA)

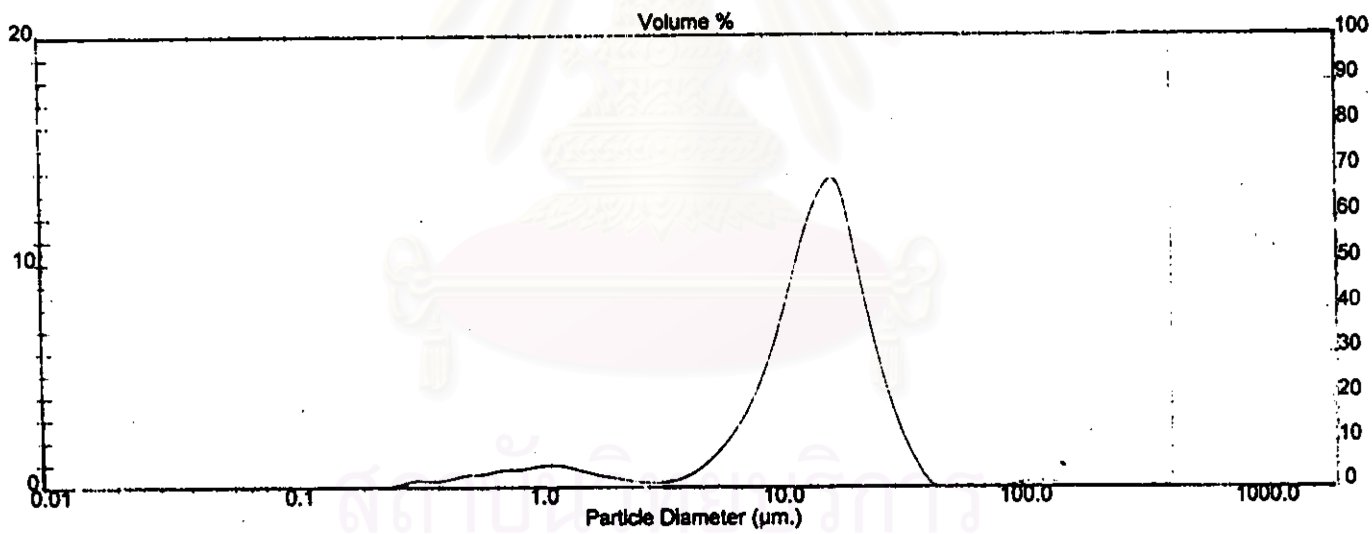


Figure 75 Particle size distribution of acid-treated tapioca starch (TB)

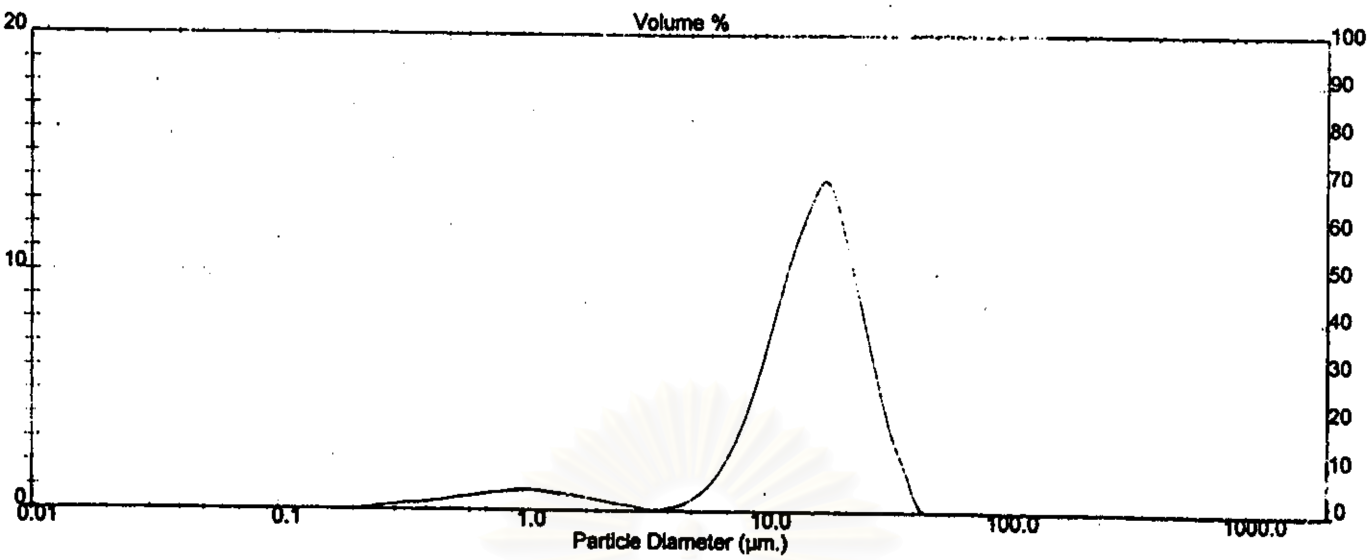


Figure 76 Particle size distribution of acid-treated tapioca starch (TC)

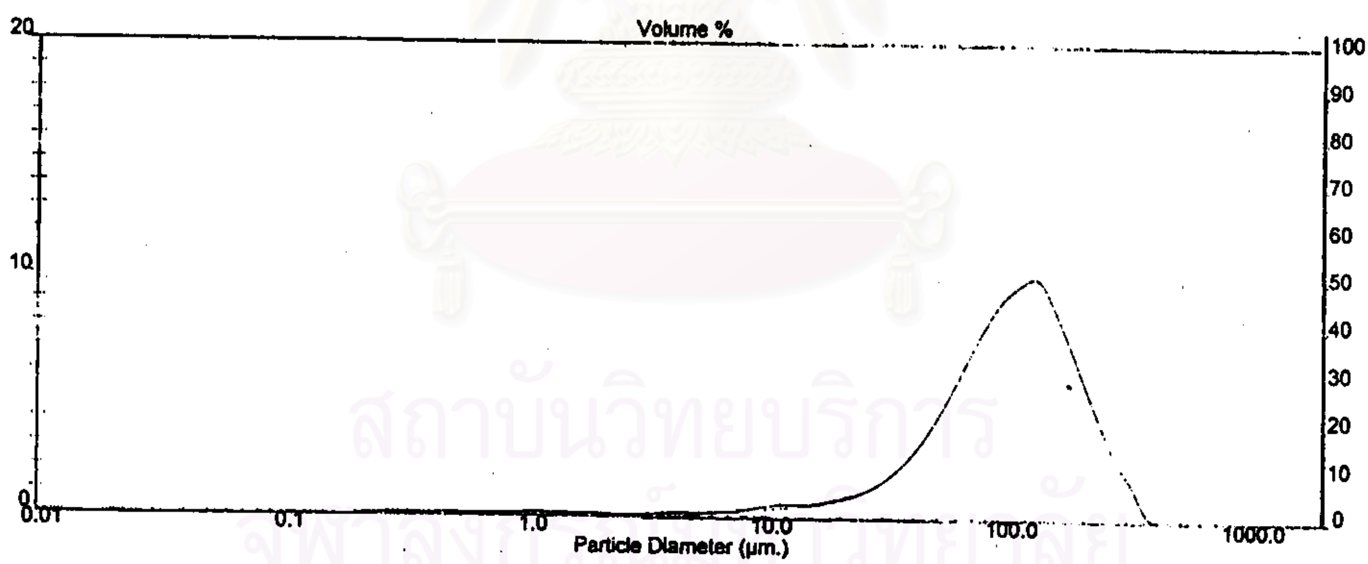


Figure 77 Particle size distribution of pregelatinized tapioca starch (TD)

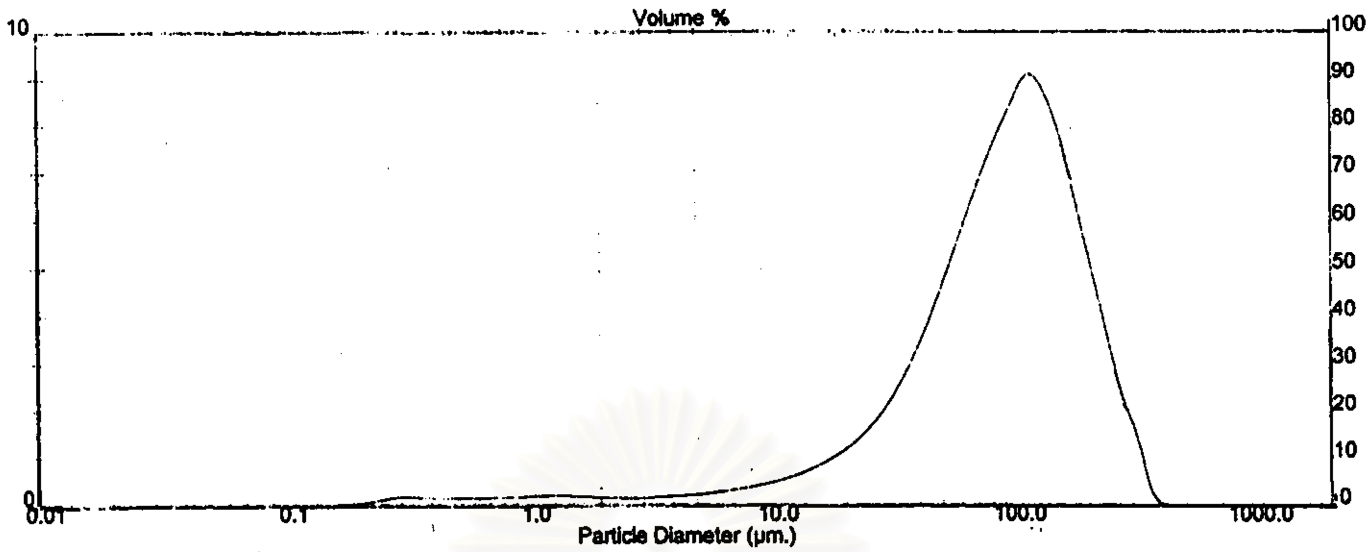


Figure 78 Particle size distribution of pregelatinized-acid treated tapioca starch (TE)

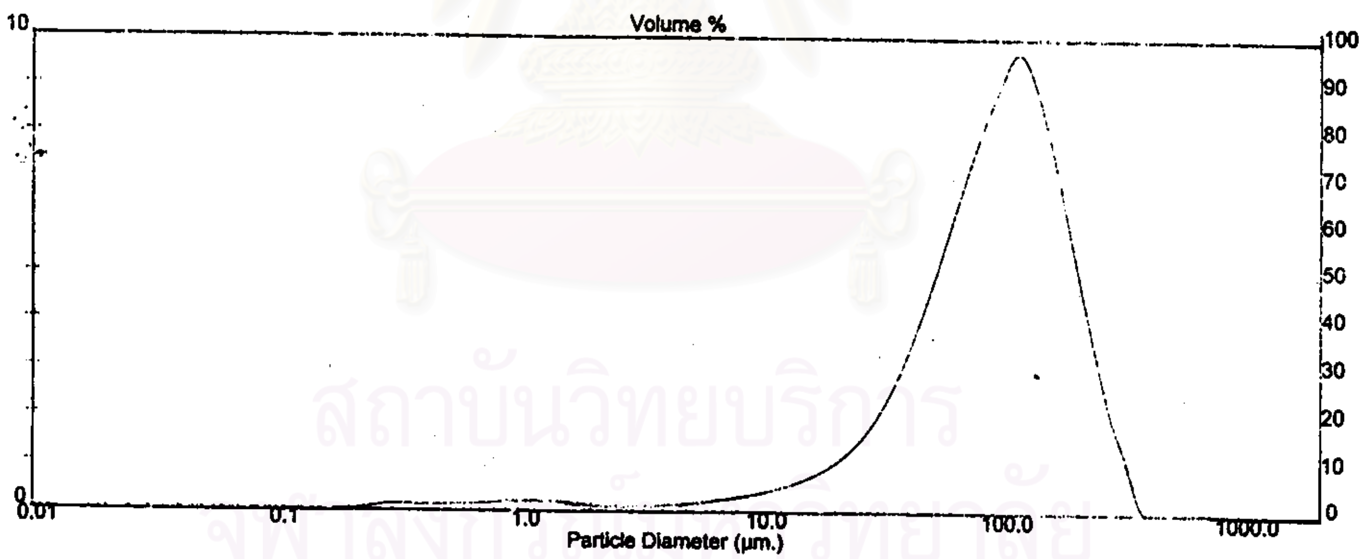


Figure 79 Particle size distribution of pregelatinized-acid treated tapioca starch (TF)

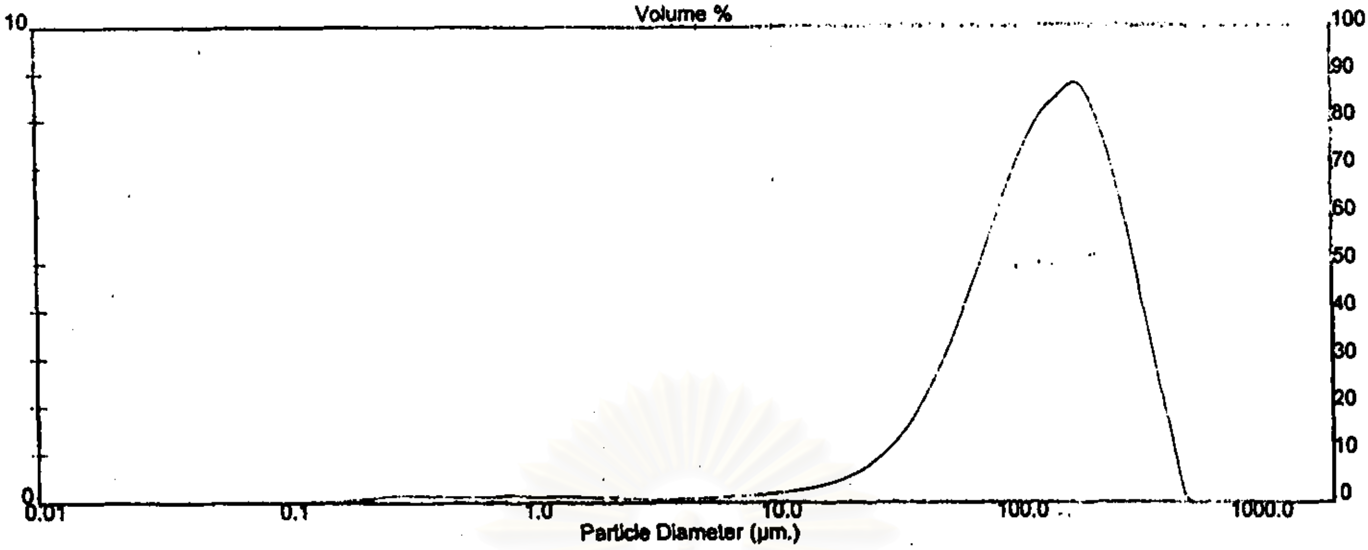


Figure 80 Particle size distribution of Era-Gel (E)

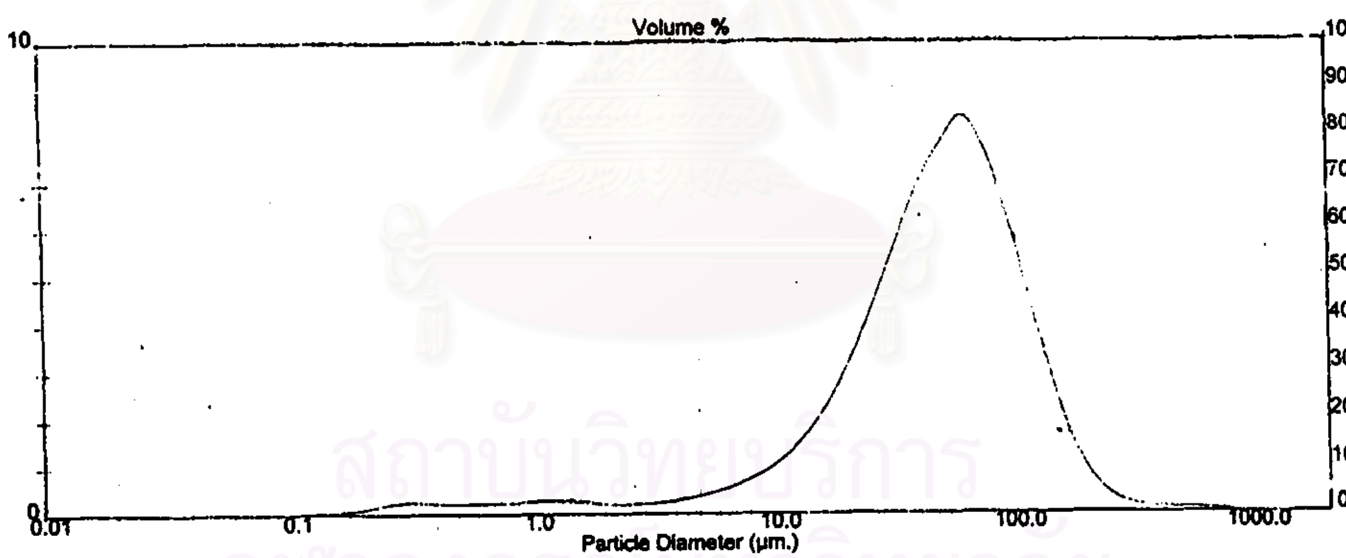


Figure 81 Particle size distribution of National 1551 (N)

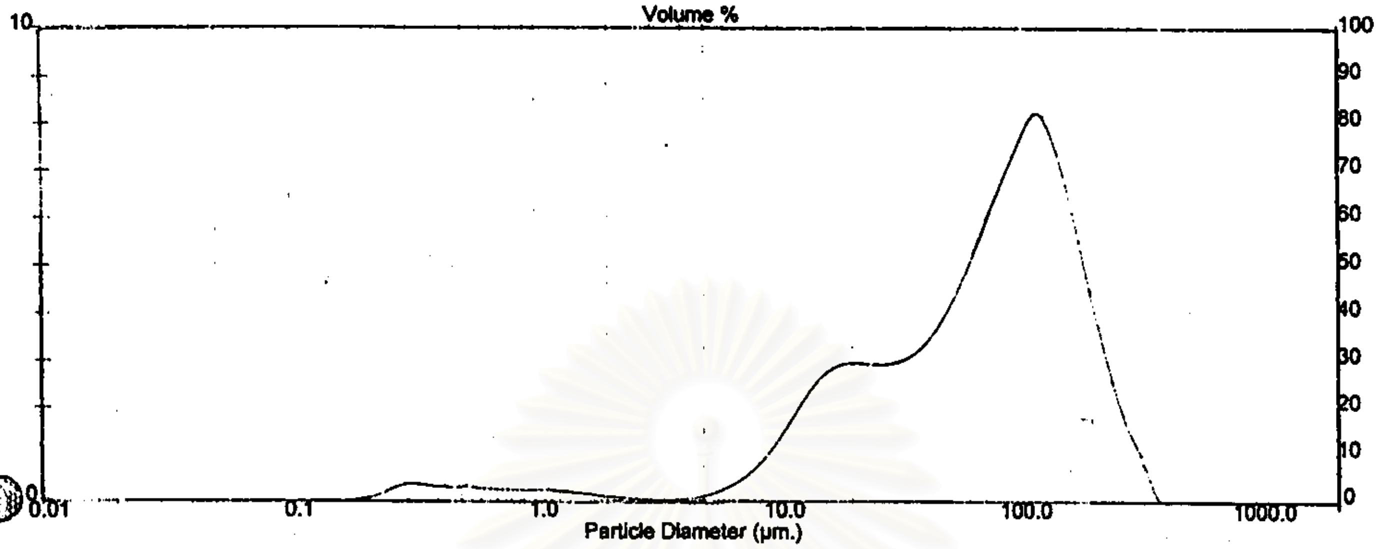


Figure 82 **Particle size distribution of Starch 1500 (S)**

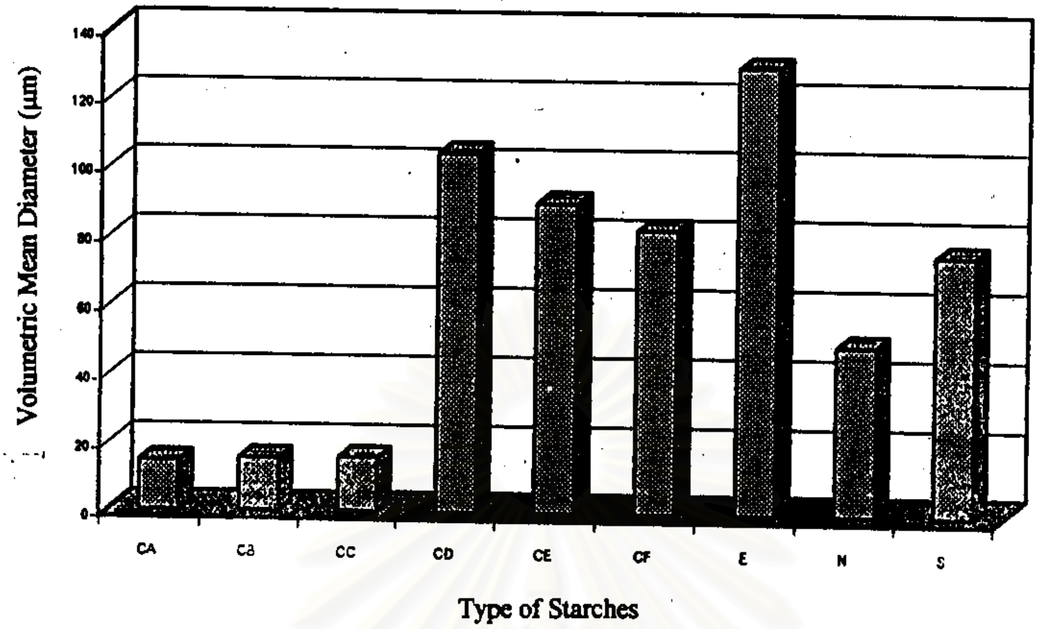


Figure 83 The histograms of volumetric diameter (um) of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

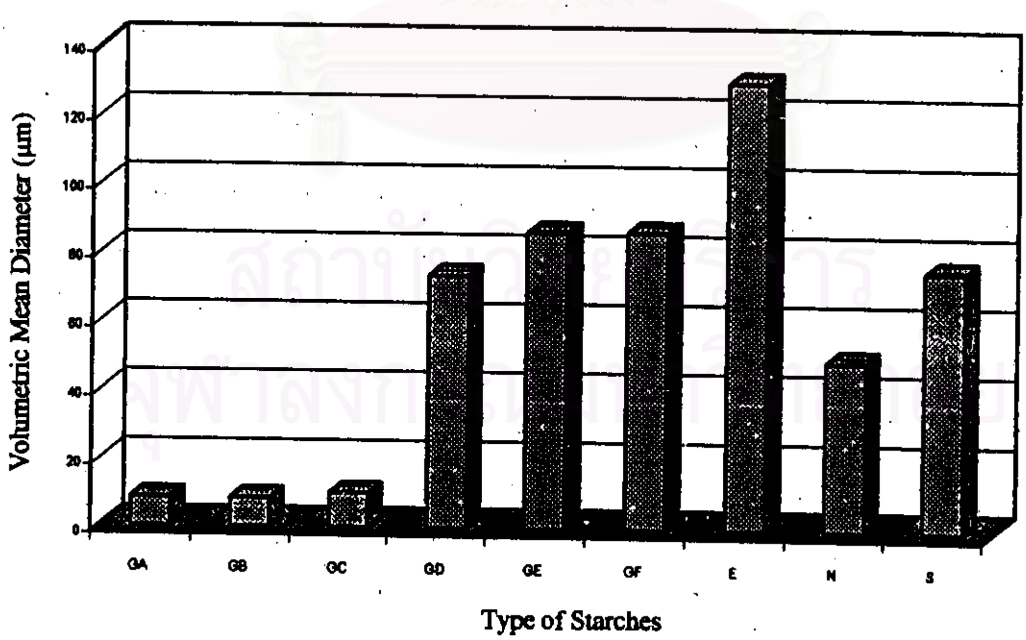


Figure 84 The histograms of volumetric diameter (um) of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

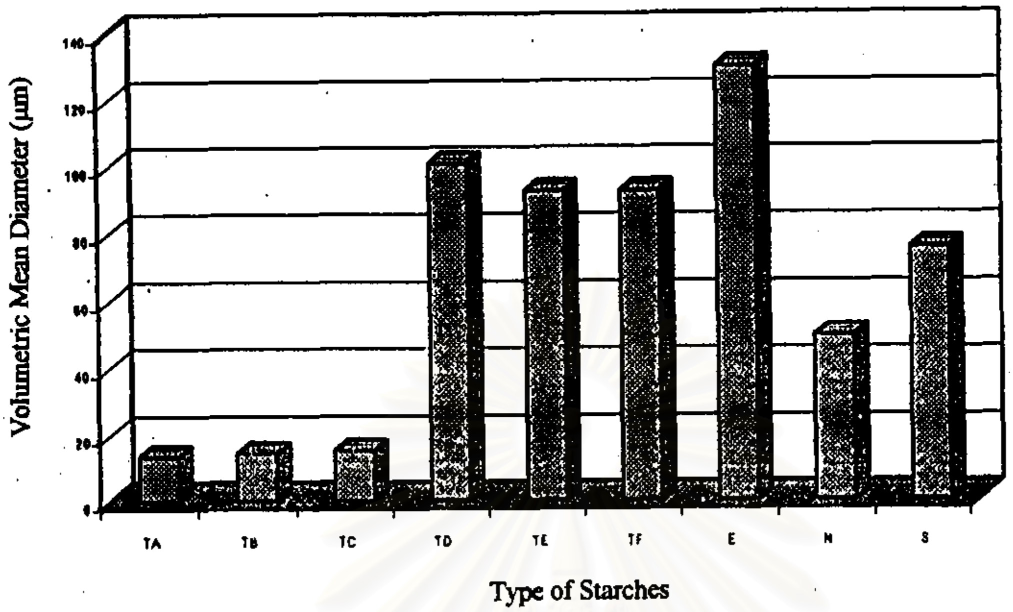


Figure 85 The histograms of volumetric diameter (μm) of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

9. Bulk, Tapped Density and Percent Compressibility

Bulk density and tapped density were determined using powder characteristic tester as described in **Chapter III**. The result was presented in **Table 13 and Figure 86-91**.

All fully pregelatinized starches exhibited high bulk density and lower in percent compressibility when compared with native and acid treated starches. The result is related to the particle size determination, the higher particle size is, the higher will be the bulk density. Anyway this different was not found between two levels of acid treated in individual starches. The result represented the better flowability of pregelatinized starches obtained from all native starches.

Comparing among the pregelatinized corn starches, it was observed that the bulk density and tapped density of CD, CE and CF were not clearly different while that of pregelatinized glutinous rice starches and pregelatinized tapioca starches had some differences and could be ranked as follows: GD < GE < GF and TD < TE < TF. The percent compressibility of all pregelatinized starches were in the narrow range of 23.31-25.99%.

The lowest percent compressibility was seen in commercial fully pregelatinized corn starch (National 1551) which lower than that of Era-gel, the fully pregelatinized rice starch. The starch 1500 exhibited the highest both bulk density and tapped density and also percent compressibility among those of commercial pregelatinized starches used.

Table 13 Bulk density, tapped density and percent compressibility of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Bulk density (g/cc)* (SD)	Tapped density (g/cc)* (SD)	Compressibility (%)* (SD)
CA	0.444 (0.009)	0.774 (0.001)	42.68 (1.26)
CB	0.485 (0.006)	0.795 (0.004)	39.04 (0.66)
CC	0.478 (0.009)	0.787 (0.004)	39.22 (0.81)
CD	0.567 (0.004)	0.758 (0.002)	25.27 (0.39)
CE	0.546 (0.004)	0.737 (0.006)	25.99 (1.05)
CF	0.555 (0.002)	0.747 (0.005)	25.78 (0.37)
GA	0.370 (0.004)	0.688 (0.001)	46.15 (0.65)
GB	0.311 (0.003)	0.595 (0.004)	47.78 (0.74)
GC	0.335 (0.005)	0.607 (0.002)	44.86 (0.86)
GD	0.494 (0.001)	0.659 (0.015)	25.01 (1.79)
GE	0.548 (0.004)	0.737 (0.005)	25.61 (0.88)
GF	0.563 (0.004)	0.741 (0.002)	24.10 (0.68)
TA	0.417 (0.007)	0.648 (0.002)	35.67 (1.13)
TB	0.449 (0.007)	0.761 (0.002)	41.00 (0.85)
TC	0.384 (0.003)	0.712 (0.007)	46.04 (0.73)
TD	0.502 (0.003)	0.658 (0.004)	23.67 (0.51)
TE	0.526 (0.001)	0.713 (0.007)	26.23 (0.85)
TF	0.576 (0.010)	0.752 (0.007)	23.36 (1.95)
E	0.570 (0.001)	0.723 (0.001)	21.24 (0.14)
N	0.524 (0.103)	0.654 (0.003)	19.93 (0.67)
S	0.585 (0.009)	0.845 (0.002)	30.70 (1.01)

*Average and standard deviation were calculated from three determinations.

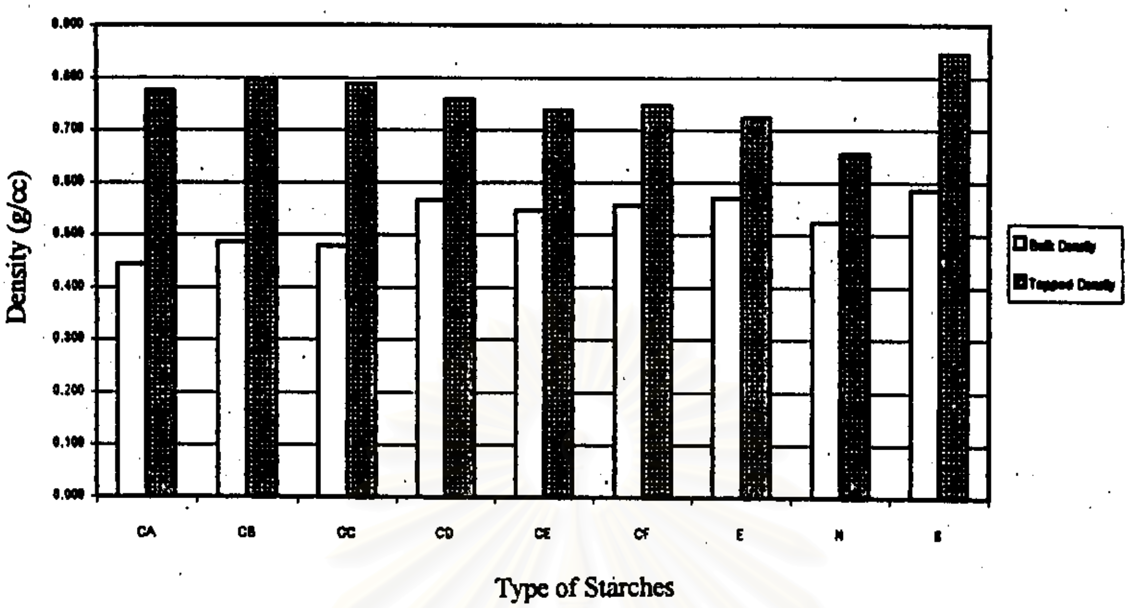


Figure 86 The histograms of bulk density and tapped density of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

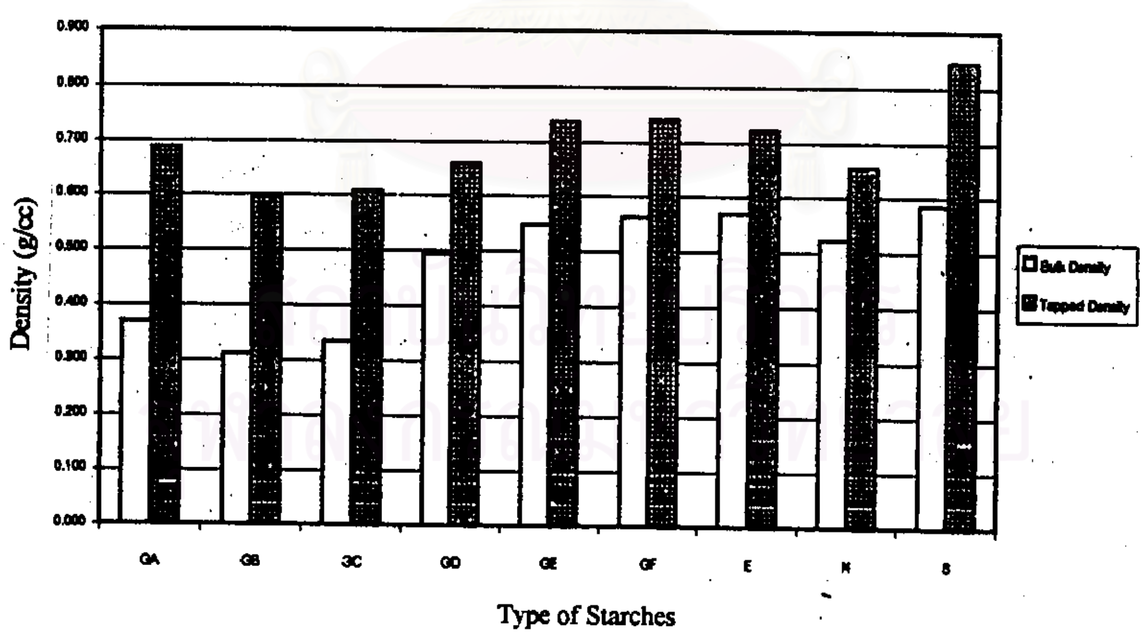


Figure 87 The histograms of bulk density and tapped density of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

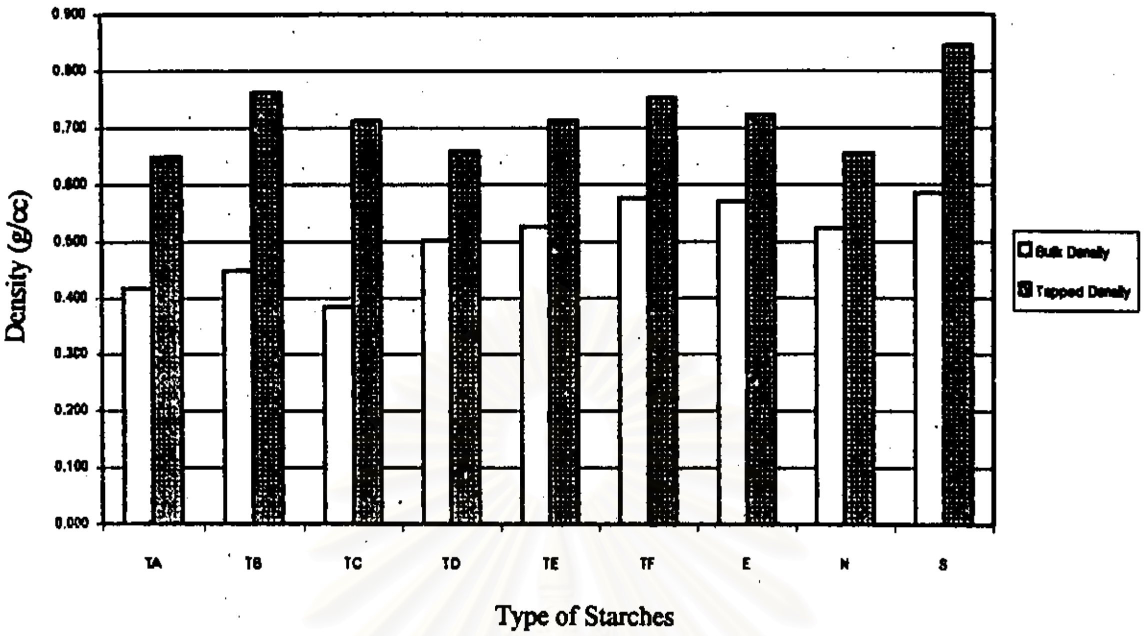


Figure 88 The histograms of bulk density and tapped density of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

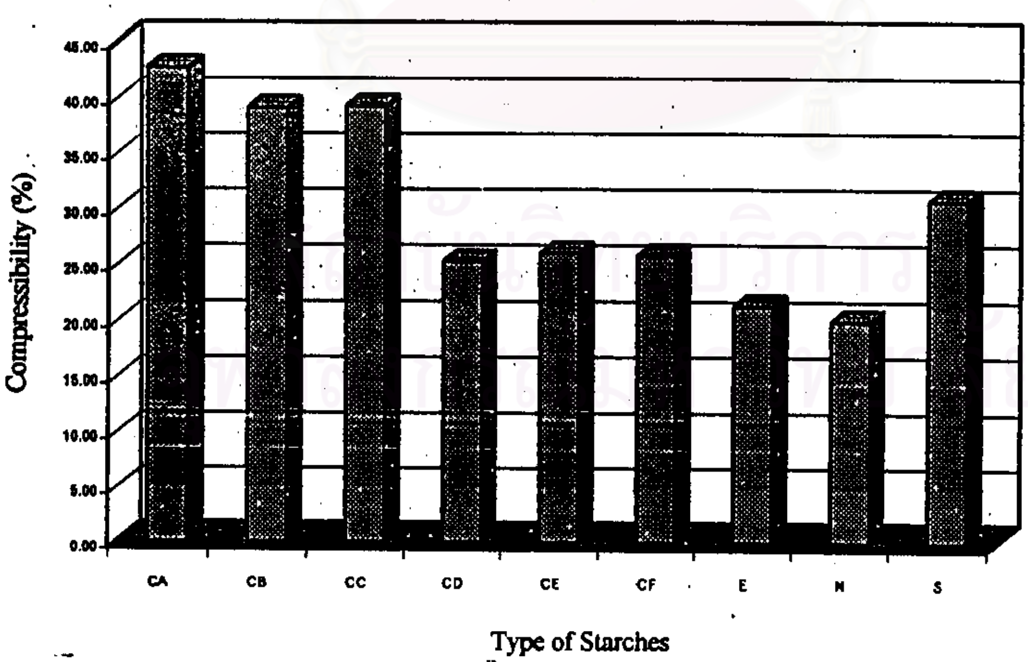


Figure 89 The histograms of percent compressibility of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches

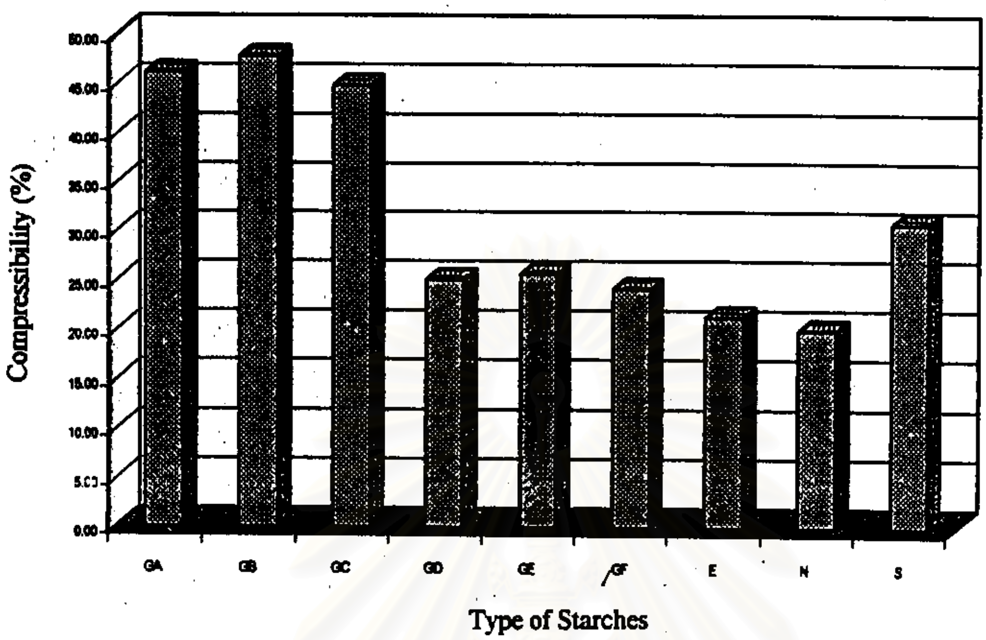


Figure 90 The histograms of percent compressibility of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches

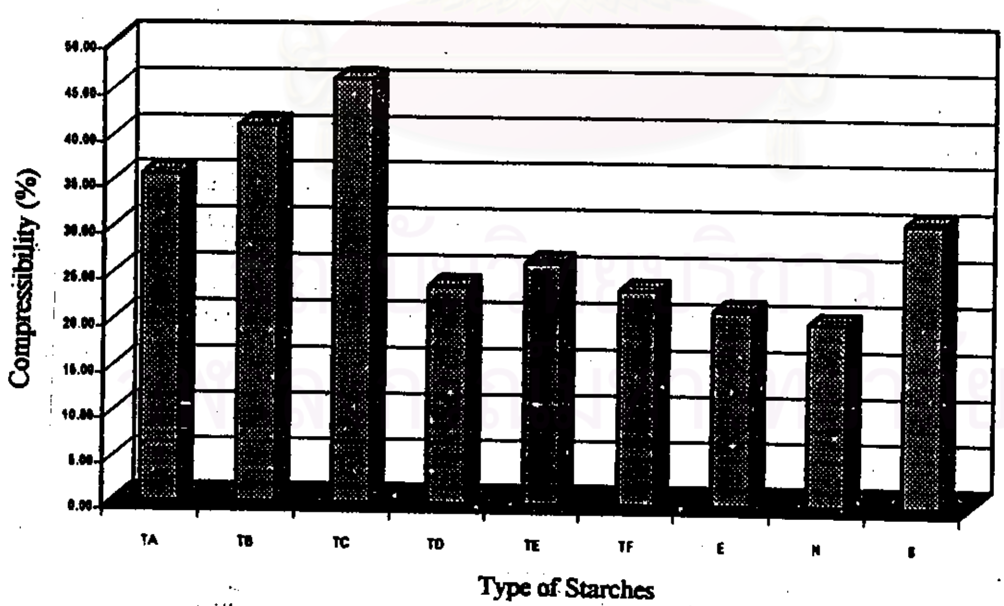


Figure 91 The histograms of percent compressibility of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches

10. Angle of Repose and Flowrate

Angle of repose and flow rate are the parameter used to obtain the flowability index. The value obtained for these tests were presented in **Table 14**. The flowability of native and acid treated of all types of starches have poor flowing powders. This were determined by the highest angle of repose and the lowest of flowrate. These were confirmed by the percent compressibility reported earlier.

The pregelatinized starches, which exhibited flowability indices in high range indicating that these materials had excellent flow properties.

The powder flow characteristics of the pregelatinized starches obtained indicated in **Table 14** are compared to some widely used commercial pregelatinized starches (Era-gel, National 1551 and Starch 1500). The flow rate is expressed as g/sec. The relatively high mass flow rate of all pregelatinized starches ranging from 1.5 to 2 g/sec demonstrated the good flow properties of these materials.

The differences in angle of repose and flow rate properties of all starches were clearly comparing by histogram as seen in **Figure 92-97**.

Table 14 Angle of repose and flow rate of various native, acid treated, pregelatinized and commercial pregelatinized starches

Type of starches (CODE)	Angle of repose (degree)* (SD)	Flow rate (g/sec)* (SD)
Corn starches		
CA	51.80 (0.66)	0.61 (0.01)
CB	47.47 (0.25)	1.30 (0.00)
CC	47.30 (0.20)	1.10 (0.07)
CD	35.20 (0.44)	2.16 (0.10)
CE	28.70 (0.70)	1.99 (0.01)
CF	29.43 (0.25)	2.11 (0.01)
Glutinous rice starches		
GA	45.90 (0.10)	0.52 (0.02)
GB	50.03 (0.50)	0.37 (0.00)
GC	48.57 (0.21)	0.38 (0.00)
GD	28.67 (0.15)	1.58 (0.08)
GE	26.87 (0.60)	1.94 (0.04)
GF	27.73 (0.32)	1.97 (0.04)
Tapioca starches		
TA	46 23 (0.25)	1.03 (0.09)
TB	46.83 (0.31)	0.88 (0.00)
TC	48.13 (0.21)	0.68 (0.01)
TD	30.57 (0.40)	1.93 (0.04)
TE	29.80 (0.20)	1.63 (0.03)
TF	28.10 (0.36)	2.07 (0.00)
Commercial pregelatinized starches		
E	27.03 (1.76)	2.80 (0.05)
N	32.87 (2.23)	1.52 (0.02)
S	30.73 (2.58)	2.02 (0.03)

* Average and standard deviation were calculated from three determinations.

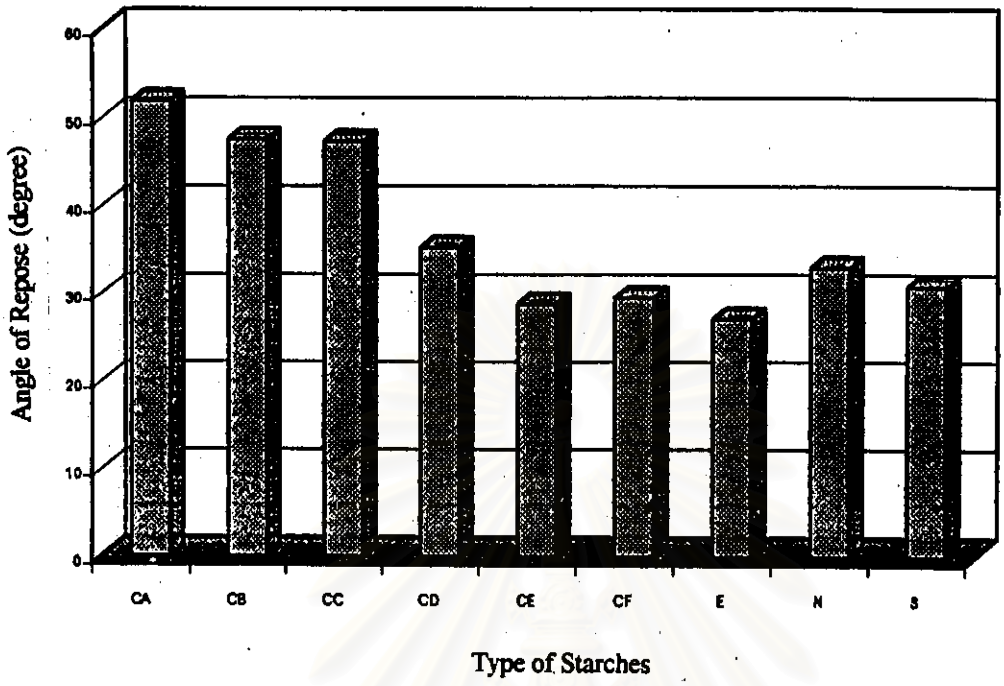


Figure 92 The histograms of angle of repose of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches.

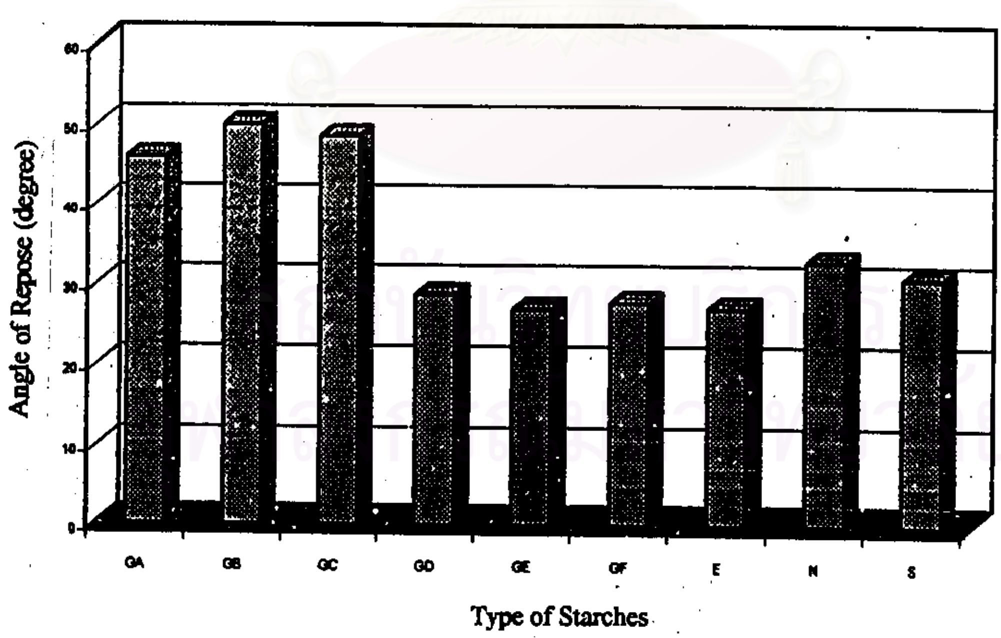


Figure 93 The histograms of angle of repose of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches.

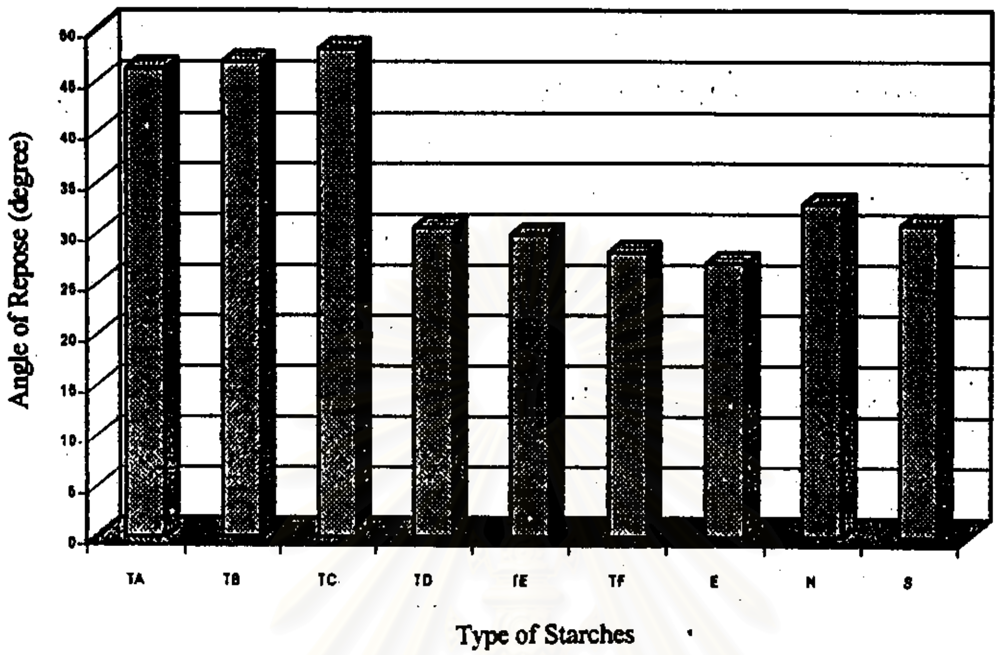


Figure 94 The histograms of angle of repose of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches.

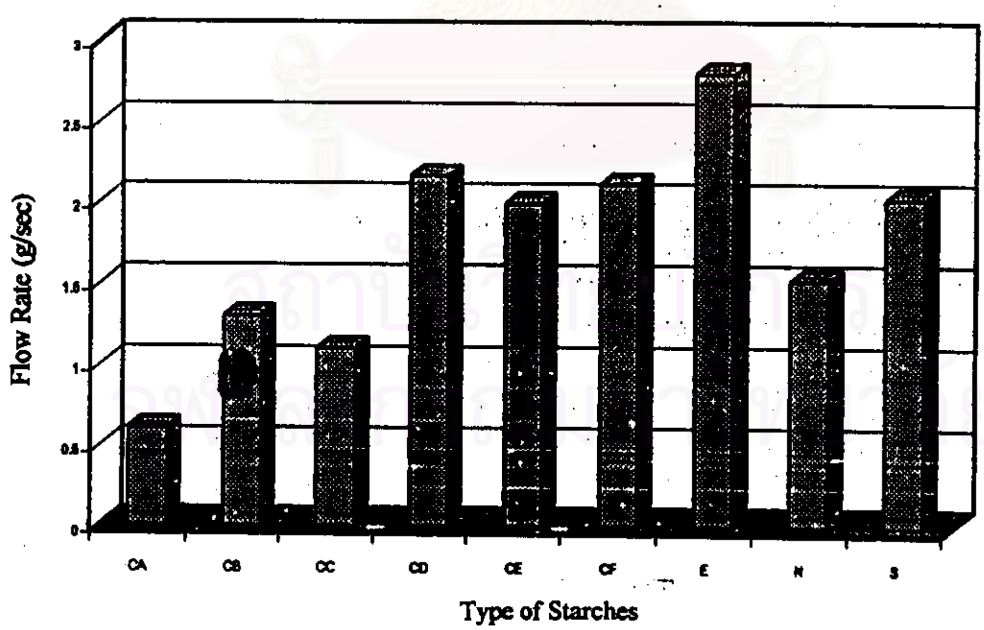


Figure 95 The histograms of flow rate of native, acid treated, pregelatinized corn starches and commercial pregelatinized starches.

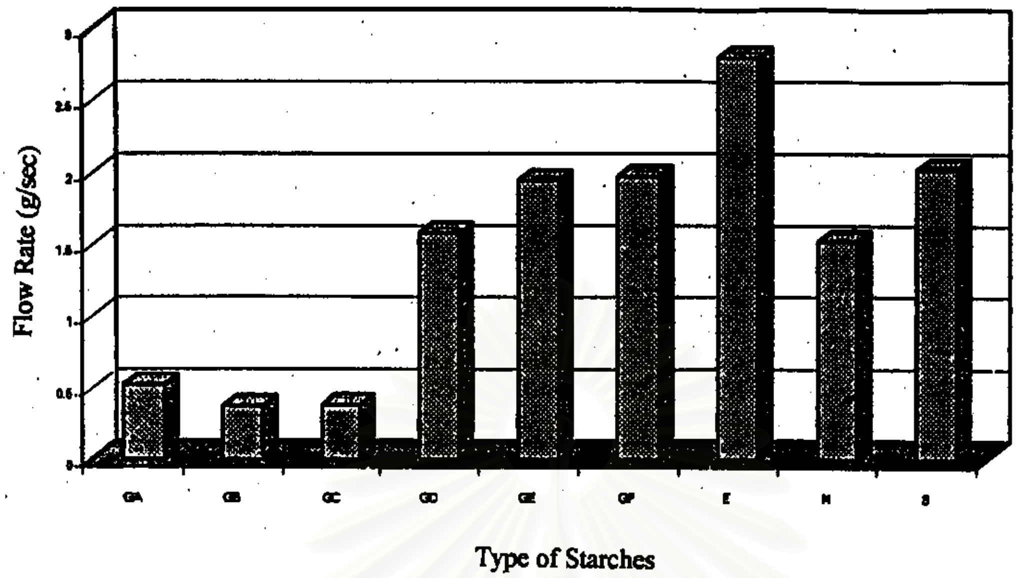


Figure 96 The histograms of flow rate of native, acid treated, pregelatinized glutinous rice starches and commercial pregelatinized starches.

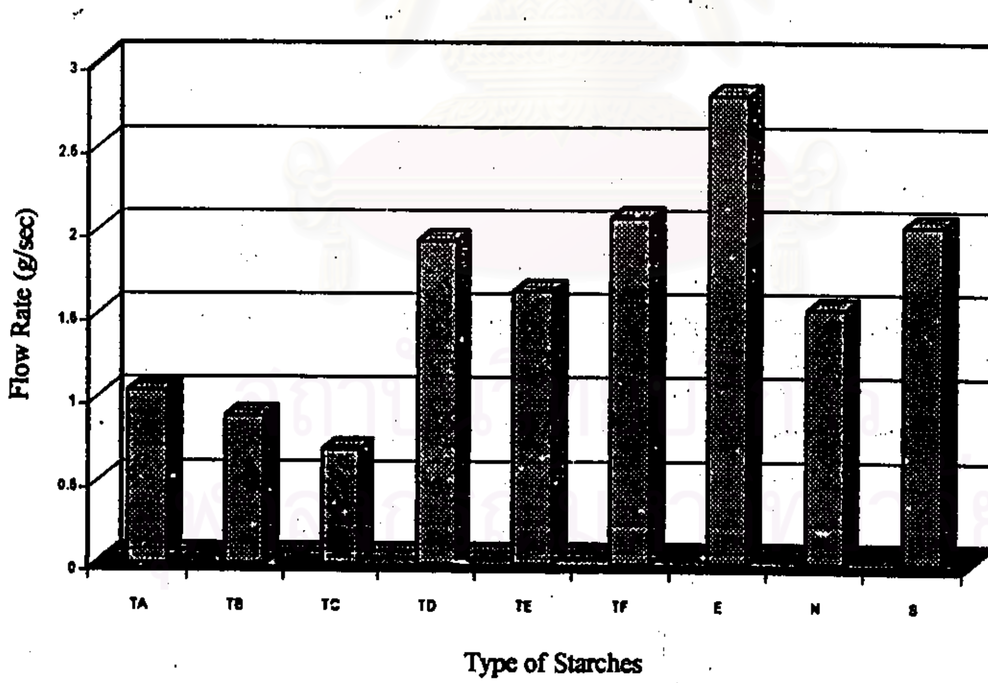


Figure 97 The histograms of flow rate of native, acid treated, pregelatinized tapioca starches and commercial pregelatinized starches.

Preparation of Tablet Formulations and Granules

Preparation of Acetaminophen Granules

Acetaminophen is a compound that might be difficult to compact into suitable tablets when incorporated into tablet formulations at high percentage. Its elastic nature provides for a good model to illustrate fillers/binders properties of the excipient employed for tablet formation(Symecko and Rhodes, 1997). So the pregelatinized starches obtained were evaluated as filler/binder using acetaminophen as a model tablet formulation.

During the process of granulation, the preparation containing pregelatinized of all types of glutinous rice starch and pregelatinized of unmodified tapioca starch seemed to be very difficult to pass their damped mass through the selected sieve. This might be the cause of the high viscosity of such starches in water at room temperature, according the result earlier.

1. Granule Evaluation

1.1 Scanning Electron Microscope

For a more complete understanding of the nature of acetaminophen granules, scanning electron photomicrographs were taken at 50x and 500x magnification in order to examine surface characteristics of each granulations.

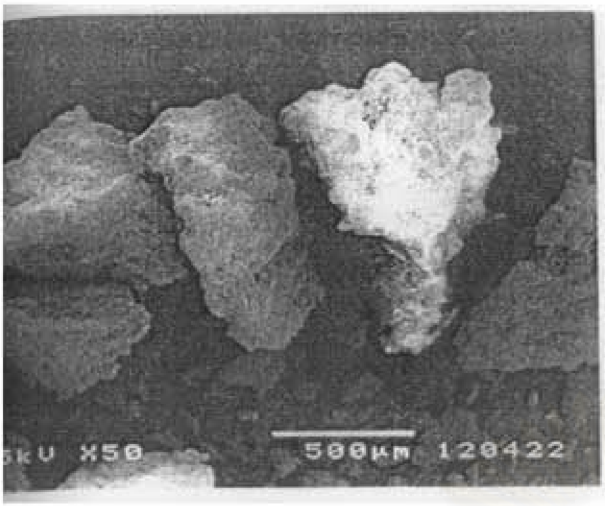
Figure 98 are the photomicrographs of acetaminophen granules containing pregelatinized corn starches (CD, CE, CF). No significant differences in surface and shape characteristics of these granules appear to exist.

The acetaminophen granules containing pregelatinized glutinous rice starches (GD, GE, GF) were illustrated in **Figure 99**. The photomicrographs taken at 50x magnification showed that they had similar in size and shape. However at the 500x magnification level, the surface of the granules were presented in form of agglomerate but they had somewhat dense surface compared to the others.

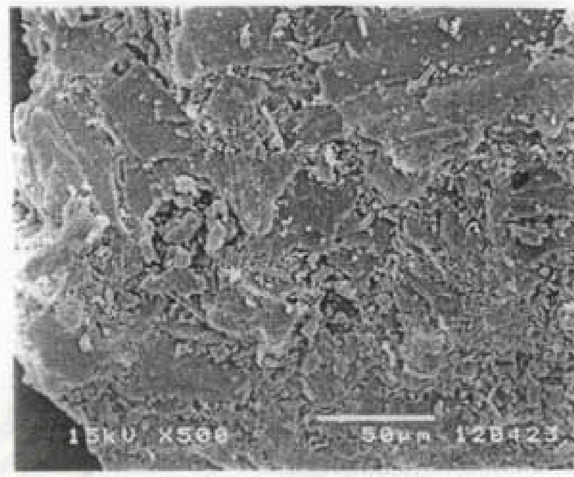
Figure 100 shows the photomicrographs of acetaminophen granules containing tapioca starches (TD,TE, TF). It was clearly seen as irregular shape particles with vary sizes at low magnification (50x) of acetaminophen granules containing TE and TF. Higher magnification (500x) revealed that they were the dense aggregates of acetaminophen granules containing TD, while that of TE and TF showed the loose aggregates.

Acetaminophen granules containing commercial pregelatinized starches (E, N, S) showed no significant difference in surface and shape characteristics. The granules containing Era-Gel had somewhat dense surface.

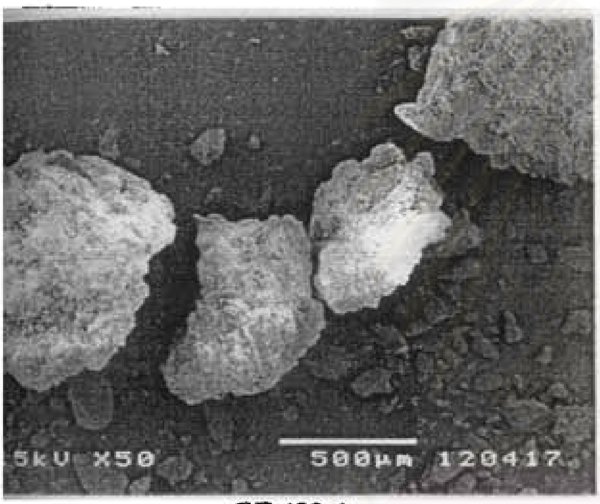
The results could be explained that the highly viscous fillers/binders tended to produce strength acetaminophen granules with smooth surface, leading to good properties in friability of granules and the tablet formations, however the unsatisfactory disintegration time and dissolution time were performed.



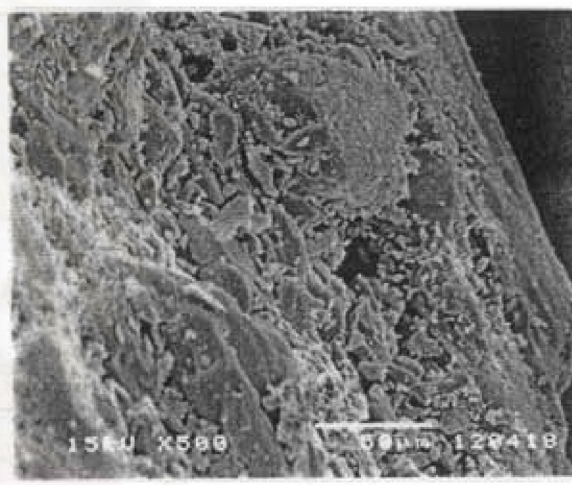
GD (50x)



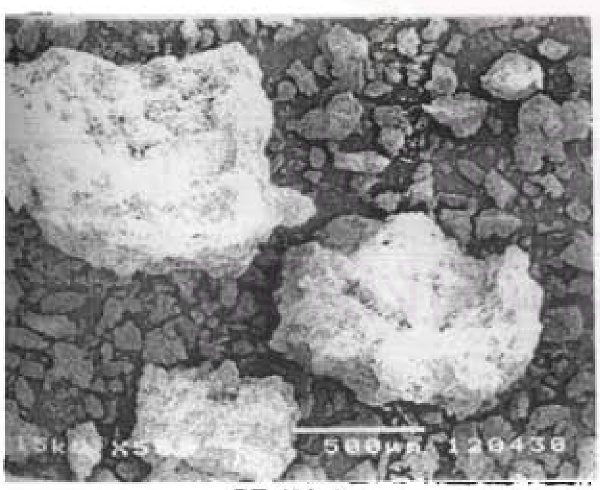
GD (500x)



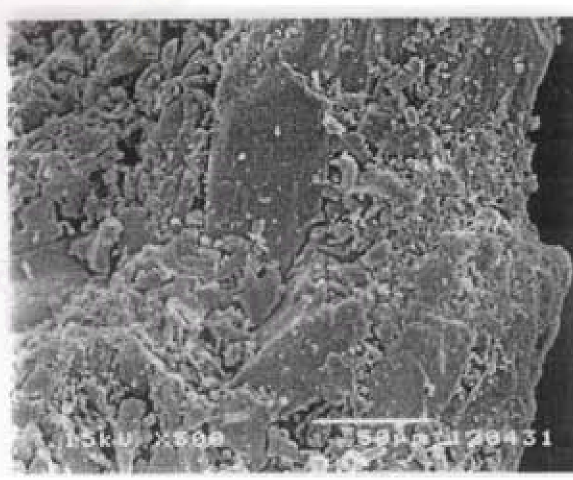
GE (50x)



GE (500x)

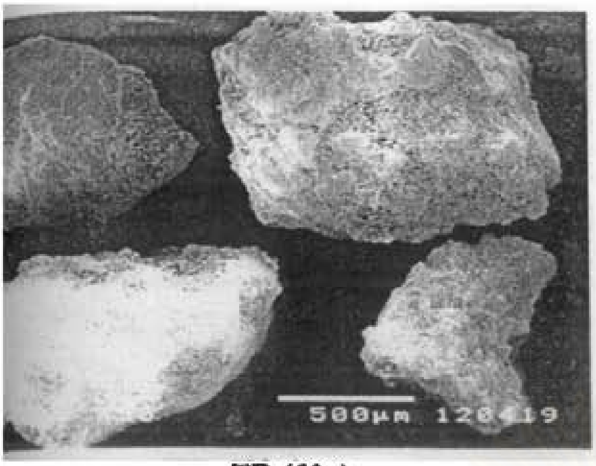


GF (50x)



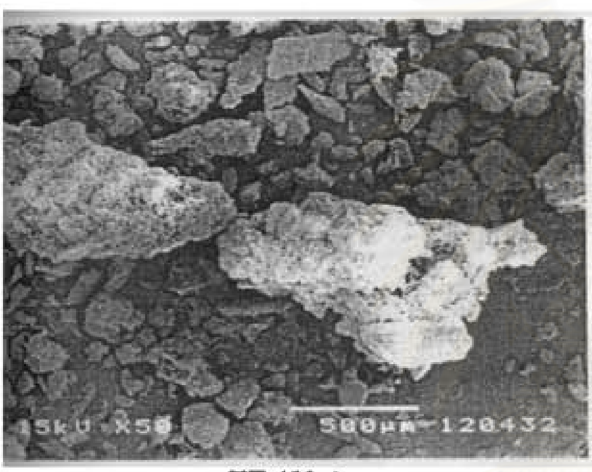
GF (500x)

Figure 99 Scanning electron micrographs of acetaminophen granules containing pregelatinized glutinous rice starches, GD, GE and GF

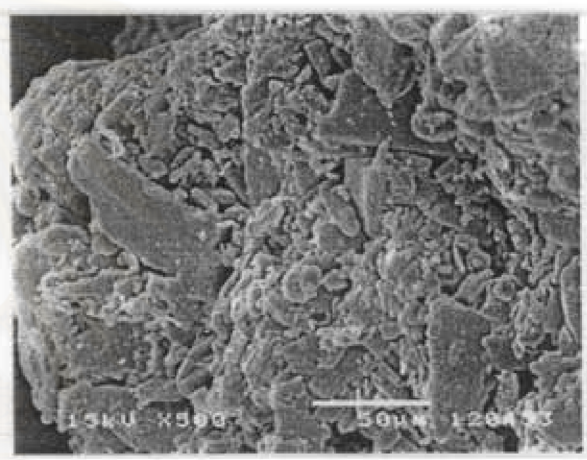


TD (50x)

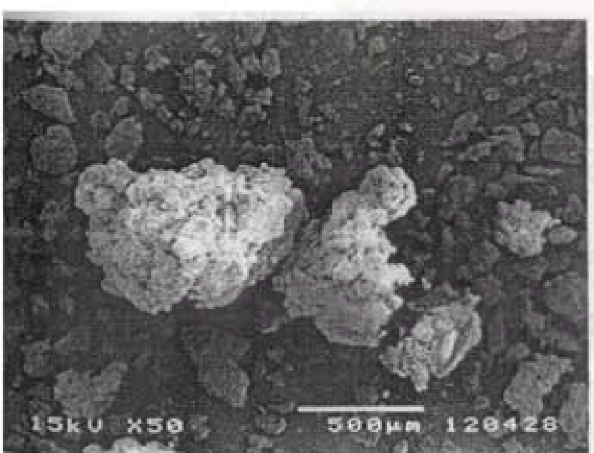
TD (500x)



TE (50x)



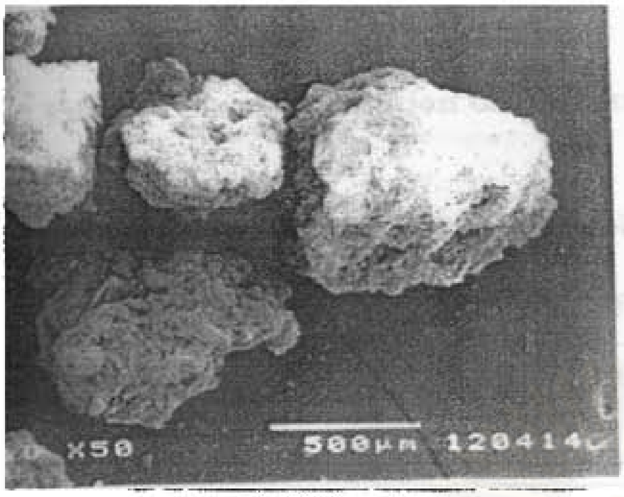
TE (500x)



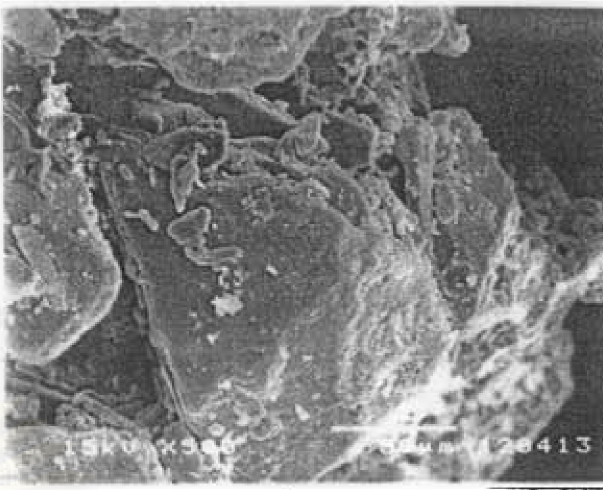
TF (50x)

TF (500x)

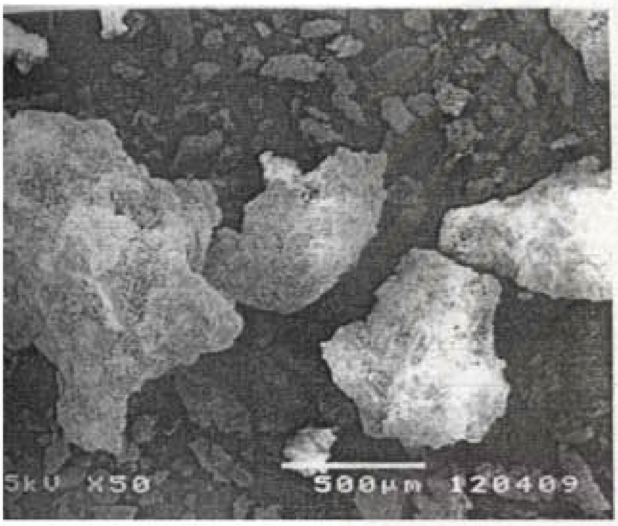
Figure 100 Scanning electron micrographs of acetaminophen granules containing pregelatinized tapioca starches, TD, TE and TF



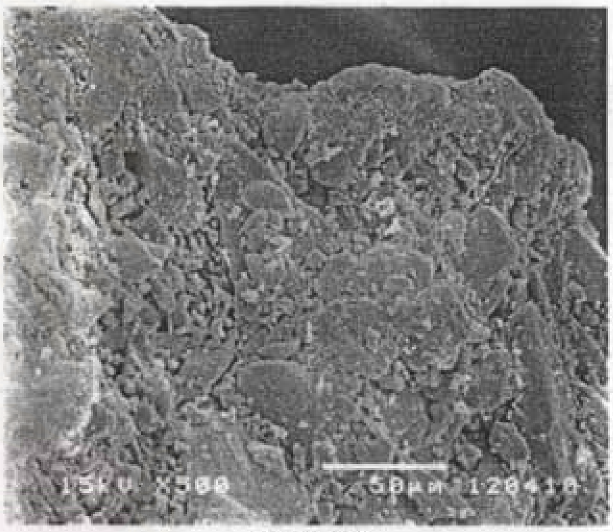
E (50x)



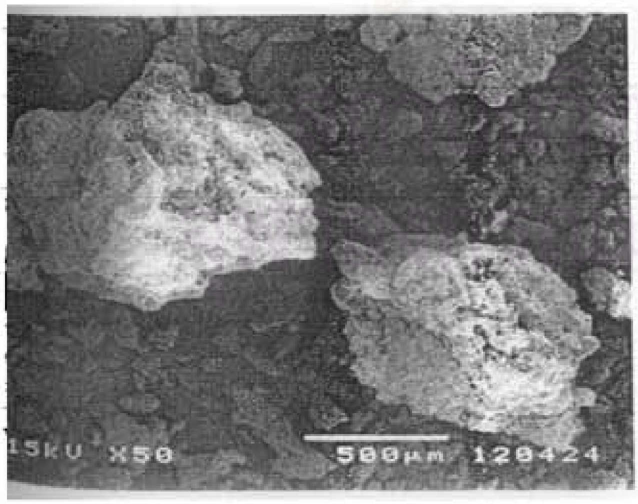
E (500x)



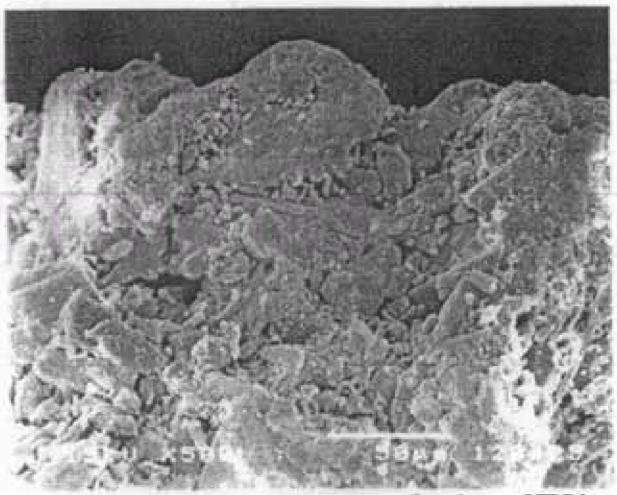
N (50x)



N (500x)

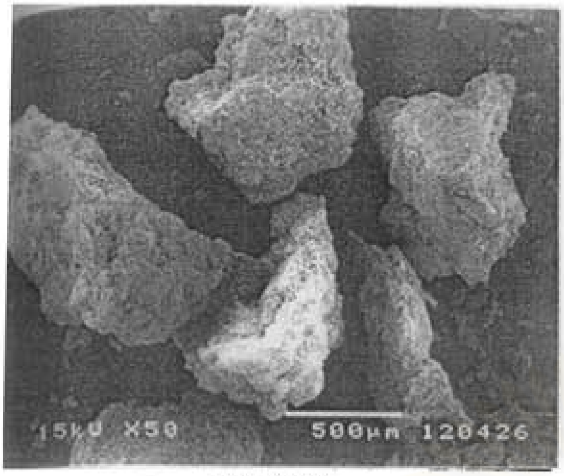


S (50x)

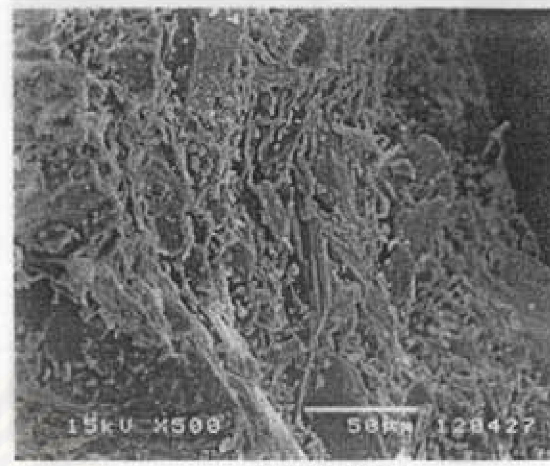


S (500x)

Figure **101** Scanning electron micrographs of acetaminophen granules containing commercial pregelatinized starches, E (Era-Gel), N (National 1551), S (Starch 1500)

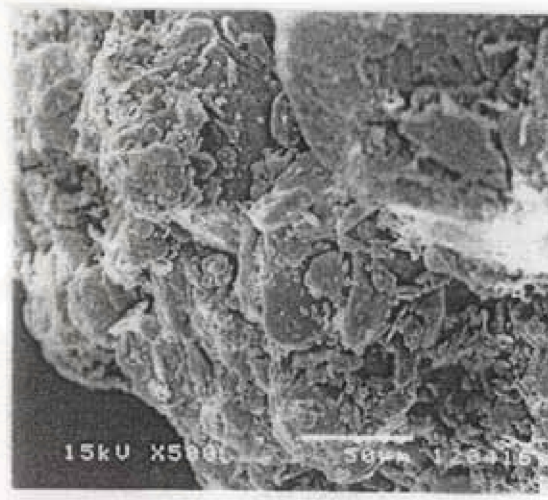


CD (50x)

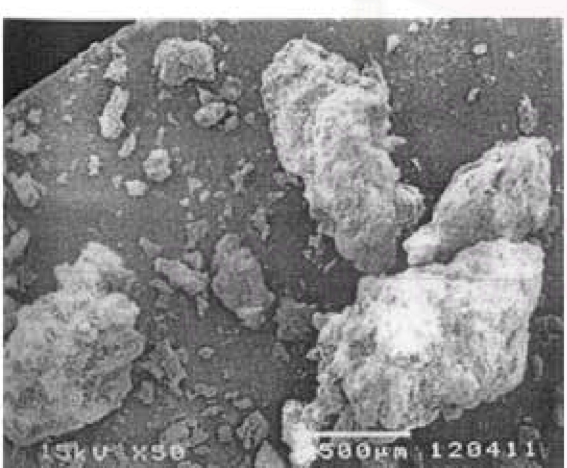


CD (500x)

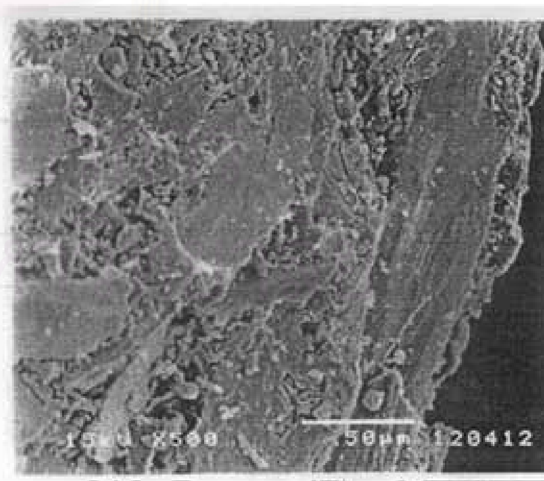
CE (50x)



CE (500x)



CF (50x)



CF (500x)

Figure 98 Scanning electron micrographs of acetaminophen granules containing pregelatinized corn starches, CD, CE and CF

1.2 Particle Size Distribution of Acetaminophen Granules

Table 15-16 and **Figure 102-104** display the size distribution and average size of acetaminophen granules prepared by dry addition method using 11.17% concentration (%w/w) of the different pregelatinized starches.

Table 15 Particle size distribution of acetaminophen granules containing various pregelatinized starches

Type of starches as filler/binder	% weight retained on sieves				
	< 250 μm	250-500 μm	500-710 μm	710-1000 μm	> 1000 μm
Corn starches					
CD	19.82	19.75	20.02	26.05	14.20
CE	23.94	19.72	16.52	24.90	14.28
CF	19.45	18.41	17.40	27.54	17.04
Glutinous rice starches					
GD	20.43	18.26	18.26	28.35	13.79
GE	18.33	16.81	16.81	30.14	18.66
GF	19.78	17.83	17.83	29.05	15.42
Tapioca starches					
TD	14.86	15.48	15.48	30.16	25.27
TE	26.56	16.84	16.84	24.47	11.22
TF	23.54	14.83	14.83	24.29	18.67
Commercial pregelatinized starches					
E	15.73	12.55	12.55	24.77	26.82
N	12.90	13.22	13.22	27.25	32.65
S	14.76	13.01	13.01	26.81	26.84

Table 16 Geometric mean diameter (D_{50}) and geometric standard deviation (δ_g) of acetaminophen granules containing various pregelatinized starches as fillers/binders

Types of starches as fillers/binders	Geometric mean diameter (D_{50}) (μm)	Geometric standard deviation (δ_g)
Corn starches		
CD	500.07	2.25
CE	528.03	2.10
CF	555.64	2.10
Glutinous rice starches		
GD	528.93	2.11
GE	547.31	1.68
GF	589.44	2.23
Tapioca starches		
TD	519.25	2.12
TE	528.00	2.42
TF	667.15	2.28
Commercial pregelatinized starches		
E	642.31	2.66
N	777.55	2.52
S	667.73	2.59

The sieve analysis data revealed minor difference in either pattern of granule size distributions or average size for the preparation using all types of pregelatinized starches. This can be attributed to the fact that all granulation were prepared by the same method.

As can be seen from the data, all pregelatinized-acid treated starches in both levels of viscosity produced coarser granules than pregelatinized of unmodified starches. This finding is in agreement with the data reported by Visavarungroj (1990) who concluded that the high viscosity of the binding agents could lead to the insufficient distribution of the paste during granulation, resulting in a smaller granule particle size.

Commercial pregelatinized starches used in this study produced somewhat larger granules than the others, especially National 1551.

These results obtained attributed that the pregelatinized starches of both acid treated and unmodified starches could be use as the binding agent by dry incorporation into the powder, while the granulating liquid can be added later.

The geometric mean diameter (D_{50}) were illustrated in **Table 16** Value of cumerative percent frequency undersize were transferred into Z value (standard) which presented in **Table 21** (see **Appendix 6**) and illustrated versus particle size in **Figure 212 – 223 (see Appendix 6)** D_{50} of acetaminophen granules containing pregelatinized starches decreased in the following orders: CF > CE > CD; GF > GE > GD and TF > TE > TF and N > S > E for the formulation containing pregelatinized corn starches, glutinous rice starches and tapioca starches respectively.

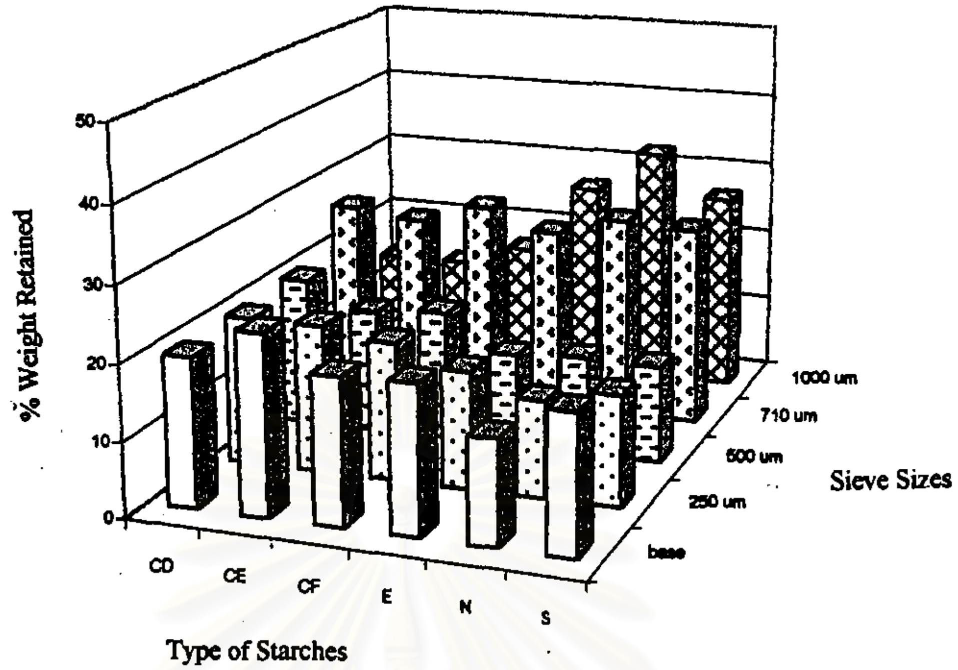


Figure 102 Particle size distribution of acetaminophen granules containing various pregelatinized corn starches and commercial pregelatinized starches.

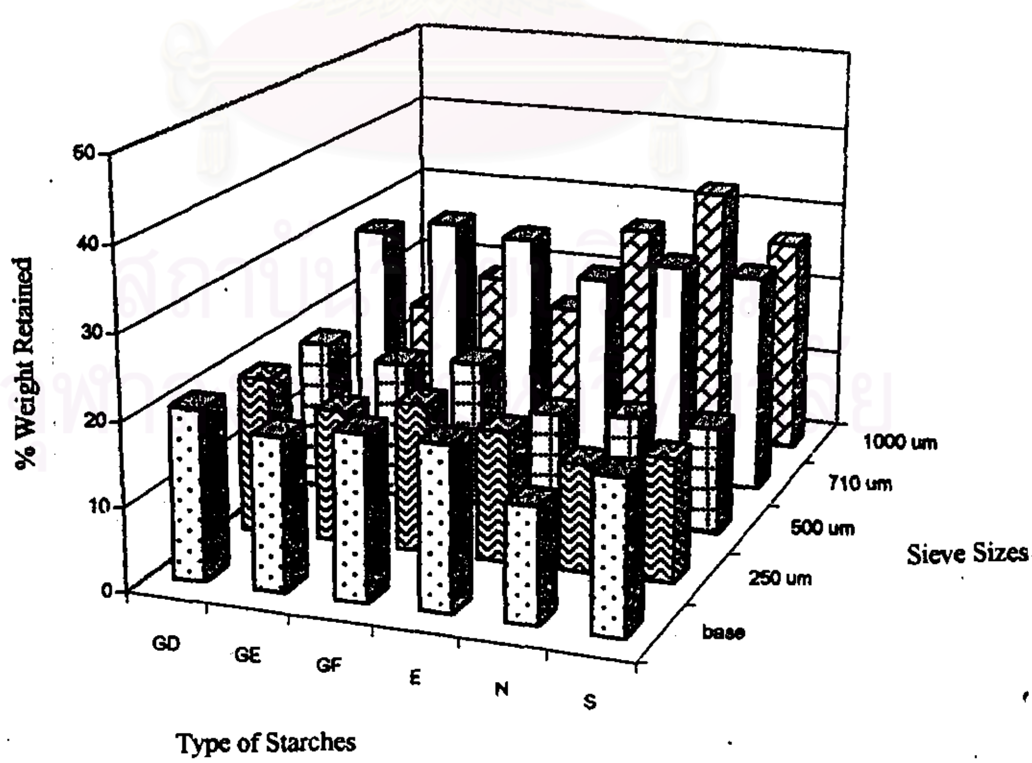


Figure 103 Particle size distribution of acetaminophen granules containing various pregelatinized glutinous rice starches and commercial pregelatinized starches.

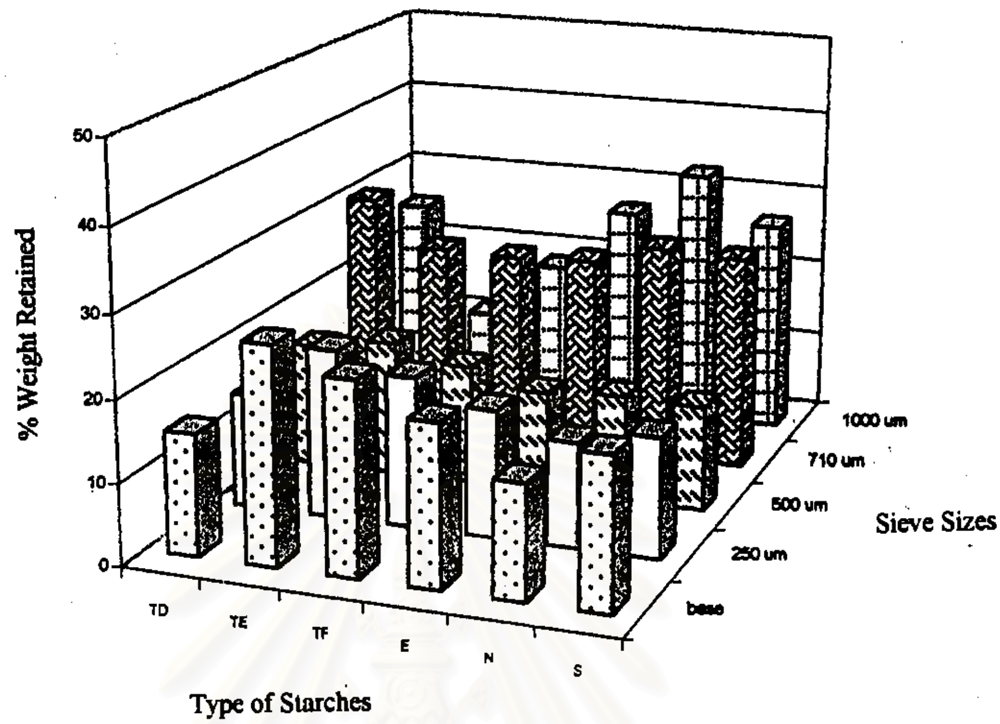


Figure 104 Particle size distribution of acetaminophen granules containing various pregelatinized tapioca starches and commercial pregelatinized starches.

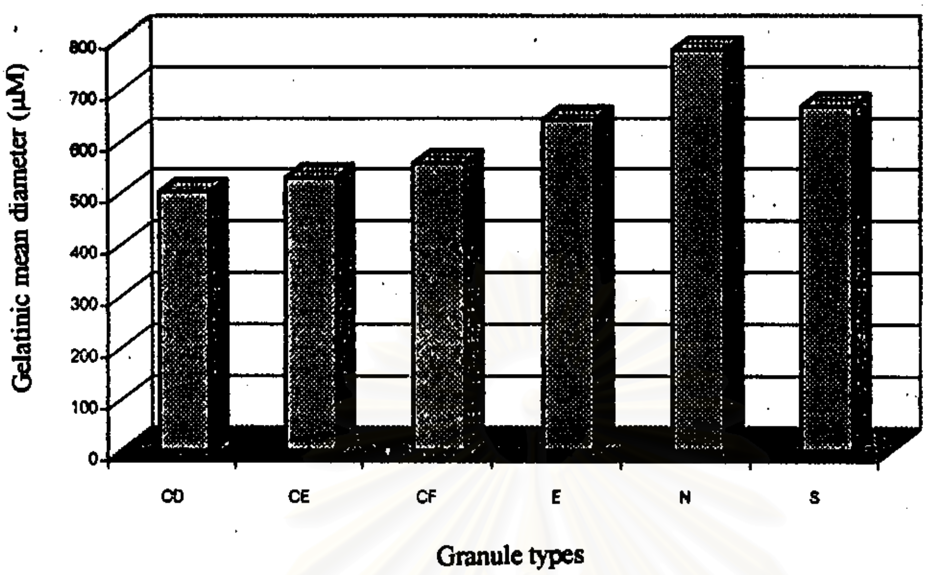


Figure 105 The histograms of geometric mean diameter (D_{50}) of acetaminophen granules containing pregelatinized corn starches and commercial pregelatinized starches

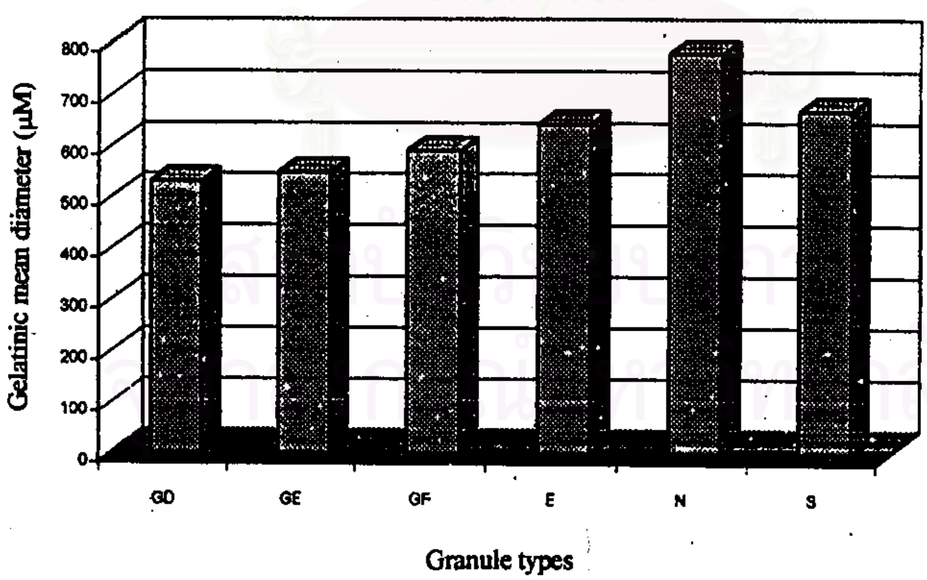


Figure 106 The histograms of geometric mean diameter (D_{50}) of acetaminophen granules containing pregelatinized glutinous rice starches and commercial pregelatinized starches

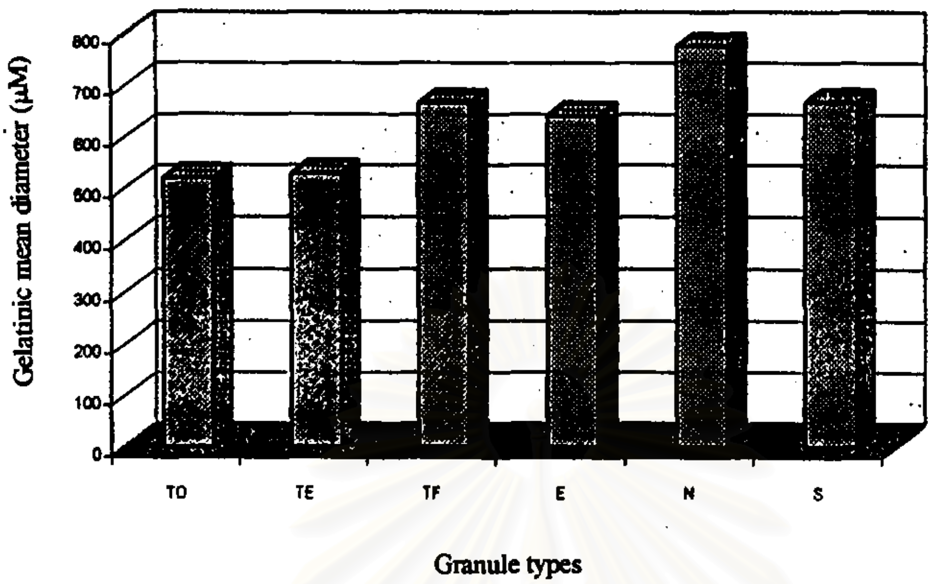


Figure 107 The histograms of geometric mean diameter (D_{50}) of acetaminophen granules containing pregelatinized tapioca starches and commercial pregelatinized starches

1.3 Bulk density, tapped density, percent compressibility, angle of repose and flow rate

Examination of the bulk, tapped density of the granulation (see **Table 17** and **Figure 108-110**) shows that those containing various pregelatinized starches have the minor difference in apparent bulk density. This is not entirely surprising since it was noted during the granulation process that they all showed not very importance difference in granule size and shape due to the same method used.

The term "compressibility" in this study refers to the packing characteristics of the materials and it has been suggested that the lower the value, the better is flow (Neumann, 1967).

In this study, the order of flowability could be described by percent compressibility (**Figure 111-113**). Comparing between the pregelatinized of all starches and commercial pregelatinized starches, the granules of E, N, S displayed the better flowability, the ranks of percent compresibility of granules using commercial pregelatinized starches were E > N >S, whereas the compressibility of the most types of acetaminophen produced from pregelatinized of unmodified starches and both levels of acid treated starches did not appear to differ from each others.

The angle of repose and flow rate of each granulations were evaluated by using powder characteristic tester. The construction of the flow meter was similar to that described in starch powder studies. Triplicate measurements revealed no significant differences between the all of the granulations in terms of their powder flow. As each granulation was prepared using the same method, this result is not necessary remarkable (Kottke, Chueh and Rhodes,1992).

All the results presented that the granules obtained from this study have the moderate flowability, according to the report of Gordon and Fornner (1989).

Table 17 Bulk density, tapped density, percent compressibility, angle of repose and flow rate of acetaminophen granules containing pregelatinized starches as fillers/binders

Types of starches as fillers/binders	Bulk density (g/ml) (SD)	Tapped density (g/ml) (SD)	compressibility (%) (SD)	Angle of repose (degree) (SD)	Flow rate (g/sec) (SD)
Corn starches					
CD	0.472 (0.002)	0.579 (0.003)	18.535 (0.766)	31.33 (0.67)	0.43 (0.00)
CE	0.460 (0.001)	0.561 (0.002)	18.110 (0.507)	31.97 (0.40)	0.32 (0.01)
CF	0.472 (0.002)	0.579 (0.002)	18.375 (0.332)	31.60 (1.35)	0.41 (0.05)
Glutinous rice starches					
GD	0.497 (0.006)	0.615 (0.001)	19.187 (1.015)	31.37 (1.40)	0.87 (0.11)
GE	0.506 (0.005)	0.612 (0.002)	17.421 (0.615)	28.40 (0.95)	0.60 (0.02)
GF	0.505 (0.005)	0.618 (0.001)	18.230 (0.866)	32.10 (1.68)	0.53 (0.01)
Tapioca starches					
TD	0.475 (0.009)	0.582 (0.004)	18.339 (1.407)	31.00 (0.56)	1.69 (0.18)
TE	0.437 (0.005)	0.537 (0.003)	18.623 (0.543)	34.60 (1.57)	0.43 (0.02)
TF	0.443 (0.005)	0.543 (0.001)	18.305 (0.835)	33.50 (1.94)	0.44 (0.04)
Commercial pregelatinized starches					
E	0.420 (0.002)	0.509 (0.008)	17.476 (0.919)	34.30 (2.54)	0.39 (0.04)
N	0.473 (0.008)	0.570 (0.004)	17.079 (0.955)	33.97 (1.20)	0.43 (0.03)
S	0.433 (0.001)	0.517 (0.004)	16.362 (0.745)	34.87 (2.82)	0.37 (0.01)

* Average and standard deviation were calculated from three determinations.

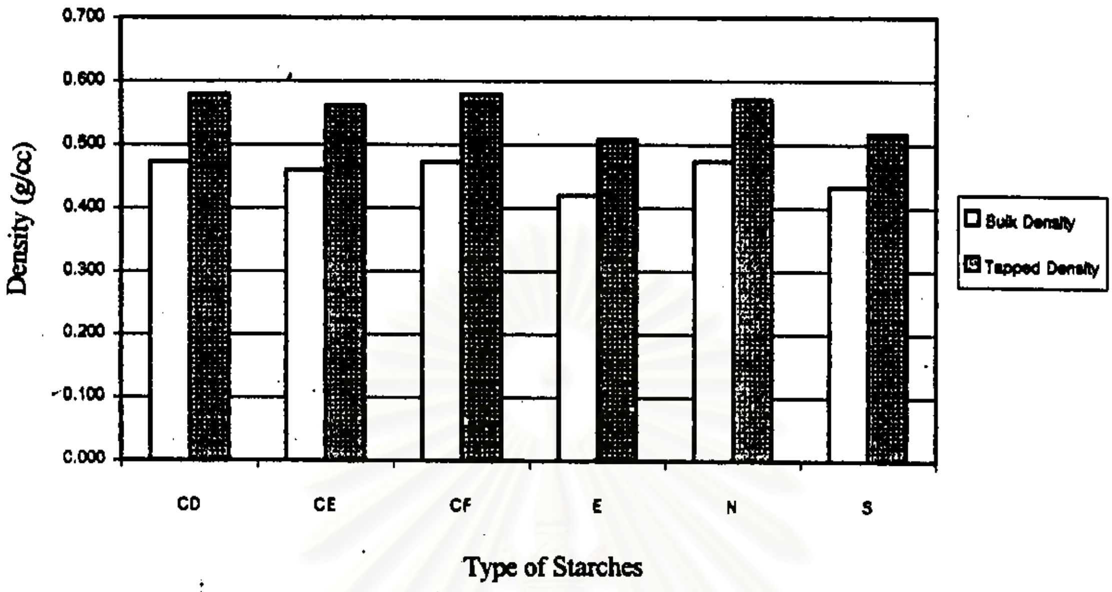


Figure 108 The histograms of bulk density and tapped density of acetaminophen granules containing pregelatinized corn starches and commercial pregelatinized starches

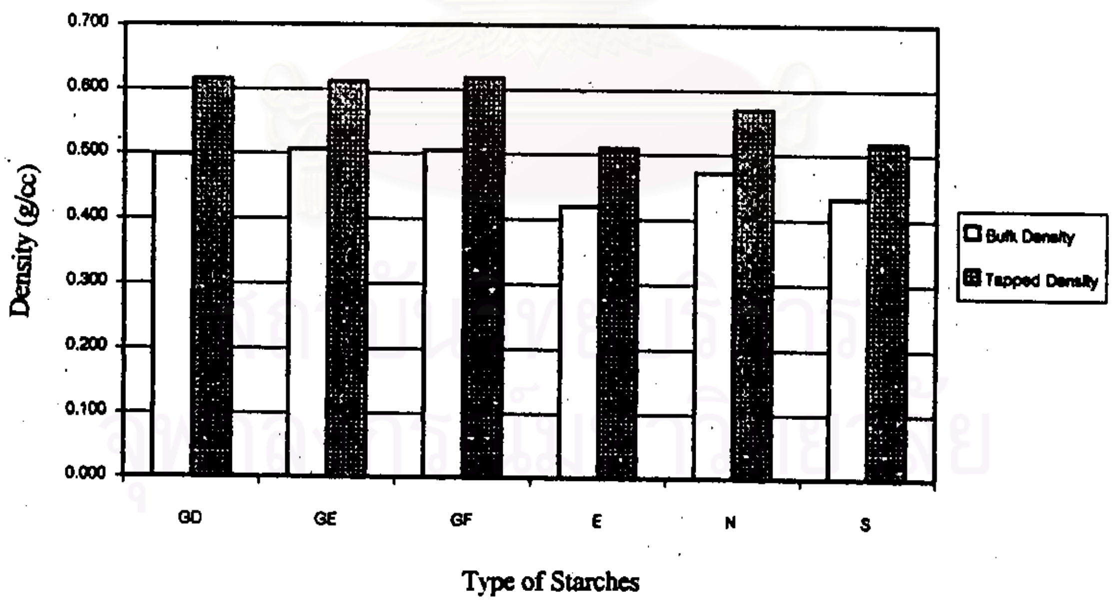


Figure 109 The histograms of bulk density and tapped density of acetaminophen granules containing pregelatinized glutinous rice starches and commercial pregelatinized starches

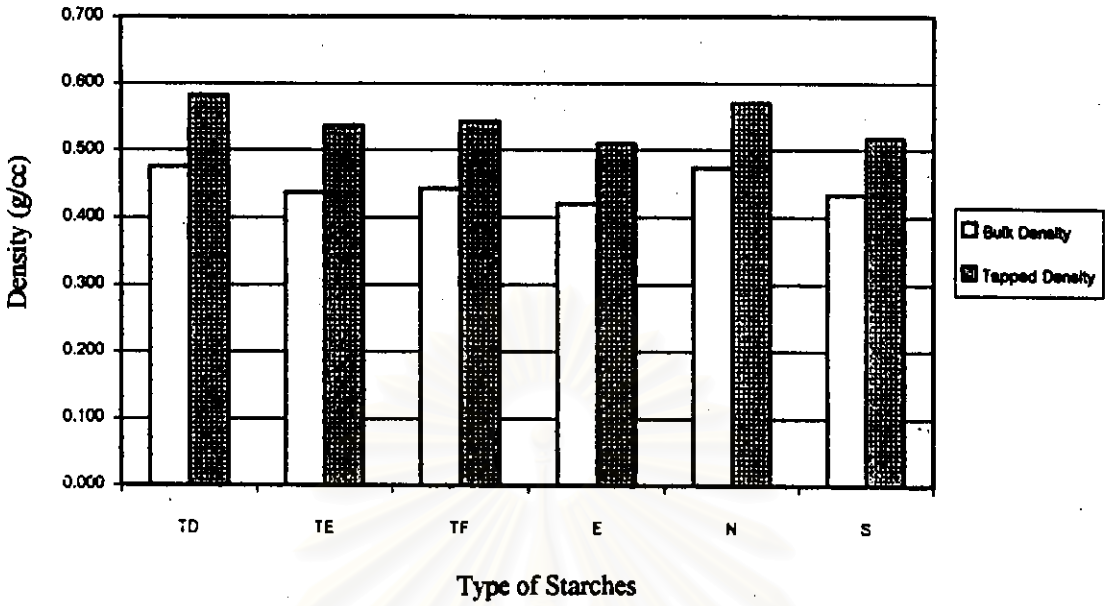


Figure 110 The histograms of bulk density and tapped density of acetaminophen granules containing pregelatinized tapioca starches and commercial pregelatinized starches

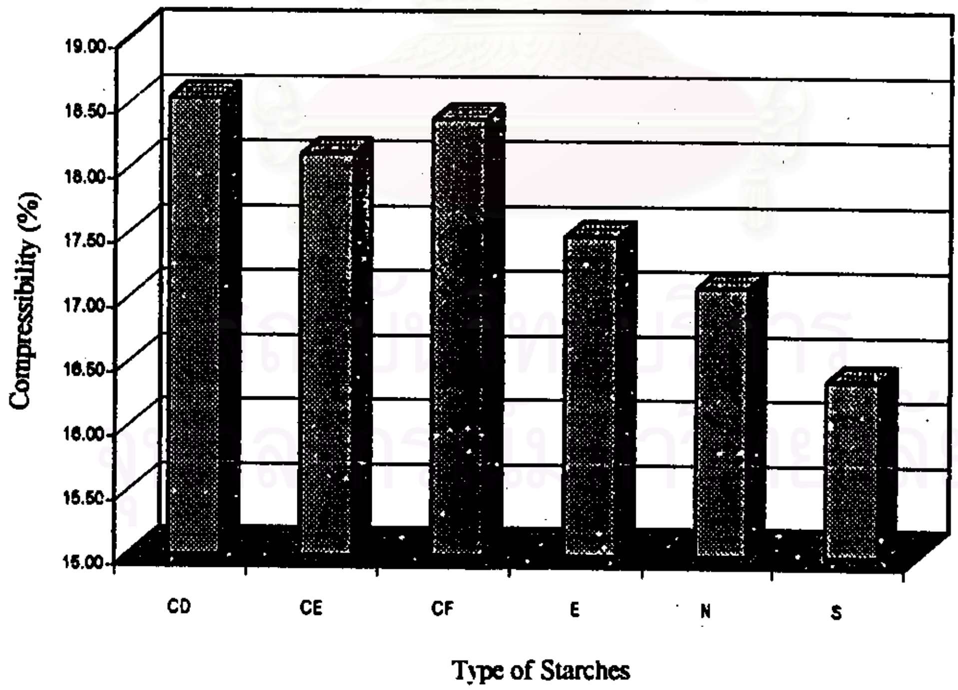


Figure 111 The histograms of percent compressibility of acetaminophen granules containing pregelatinized corn starches and commercial pregelatinized starches

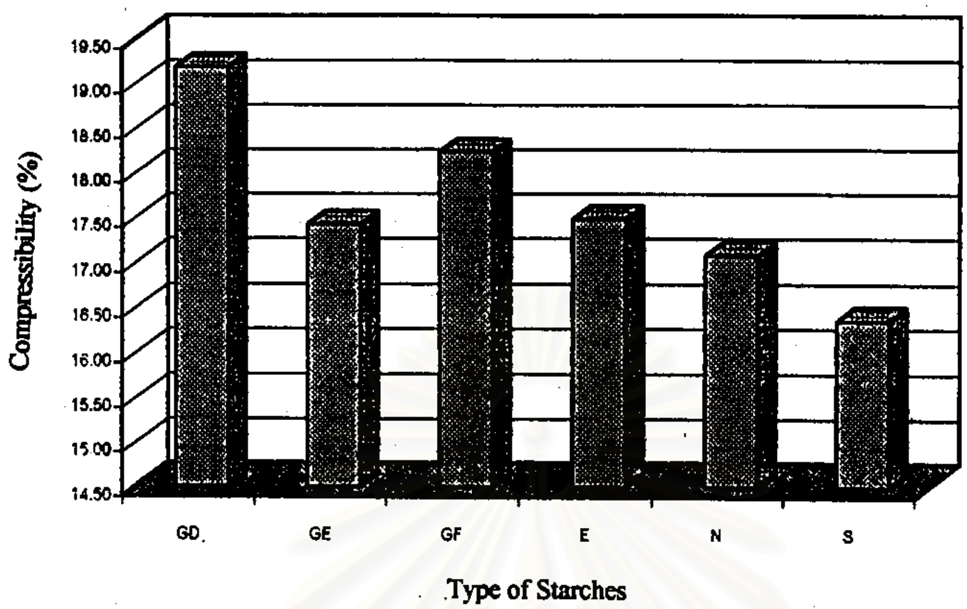


Figure 112 The histograms of percent compressibility of acetaminophen granules containing pregelatinized glutinous rice starches and commercial pregelatinized starches

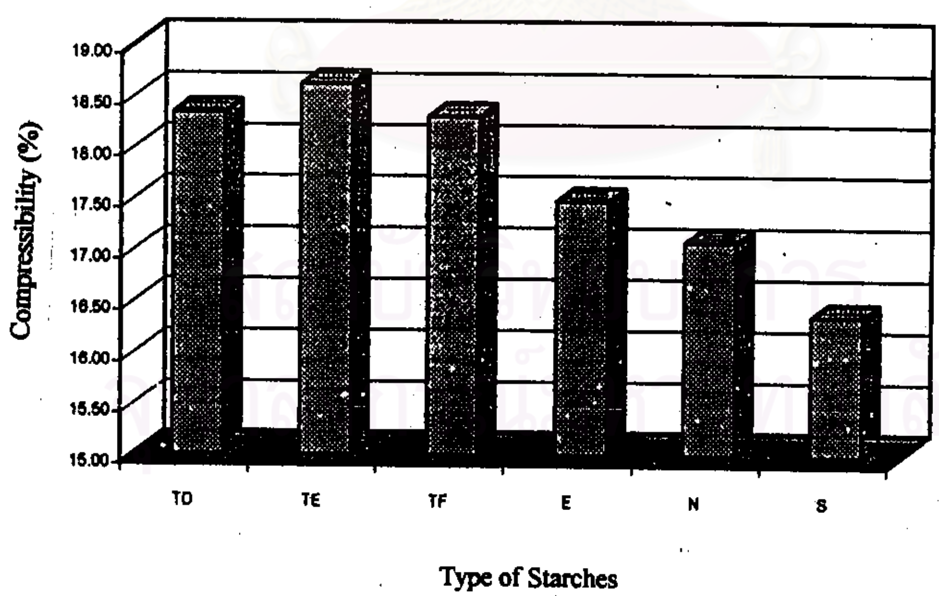


Figure 113 The histograms of percent compressibility of acetaminophen granules containing pregelatinized tapioca starches and commercial pregelatinized starches

1.4 Granule Friability

Granule friability is related to the strength of the granules and their ability to withstand during normal handling. In this study, the pregelatinized of unmodified starches tended to produce granules with lower friability than that of pregelatinized-acid treated starches. This can be explained by the fact that the pregelatinized of unmodified starches provided the high viscosity binders, thereby aiding in the agglomeration of acetaminophen particles and improving the bonding strength of granules after drying. The result showed that pregelatinized corn starches gave the friable granules in all types.

No difference in granule friability was seen between both levels of pregelatinized of acid treated starches.

In this study, it was found that the pregelatinized glutinous rice starches gave the granules with the lowest friability while the Era-Gel displayed the highest. The National 1551 and Starch 1500 produced the similar friable granules as the other pregelatinized starches obtained. This finding confirms the viscosity of pregelatinized starches used.

1.5 Moisture Analysis

The result was shown that there was no difference in moisture content (**Table 18**) of all granule obtained from the study. The moisture content was about 1.06-1.65 % after drying

As a result of the approximately equal moisture levels for each type of granulation, the influence of moisture upon variations in granule properties should be minimal.

The granule friability and percent moisture were shown in **Table 18** and **Figure 114-116**.

Table 18 Percent friability and moisture content of acetaminophen granules containing various pregelatinized starches as fillers/binders

Types of starches as fillers/binders	Friability (% loss)* (SD)	Moisture (%)* (SD)
Corn starches		
CD	8.87 (0.36)	1.39 (0.04)
CE	10.63 (0.40)	1.33 (0.03)
CF	10.12 (0.07)	1.28 (0.02)
Glutinous rice starches		
GD	7.09 (0.44)	1.56 (0.02)
GE	8.25 (0.50)	1.65 (0.39)
GF	8.37 (1.58)	1.39 (0.04)
Tapioca starches		
TD	7.35 (0.60)	1.27 (0.04)
TE	8.04 (0.25)	1.06 (0.04)
TF	8.79 (0.66)	1.61 (0.02)
Commercial pregelatinized starches		
E	11.25 (0.69)	1.38 (0.03)
N	7.58 (0.15)	1.22 (0.03)
S	9.45 (1.05)	1.32 (0.03)

* Average and standard deviation were calculated from three determinations.

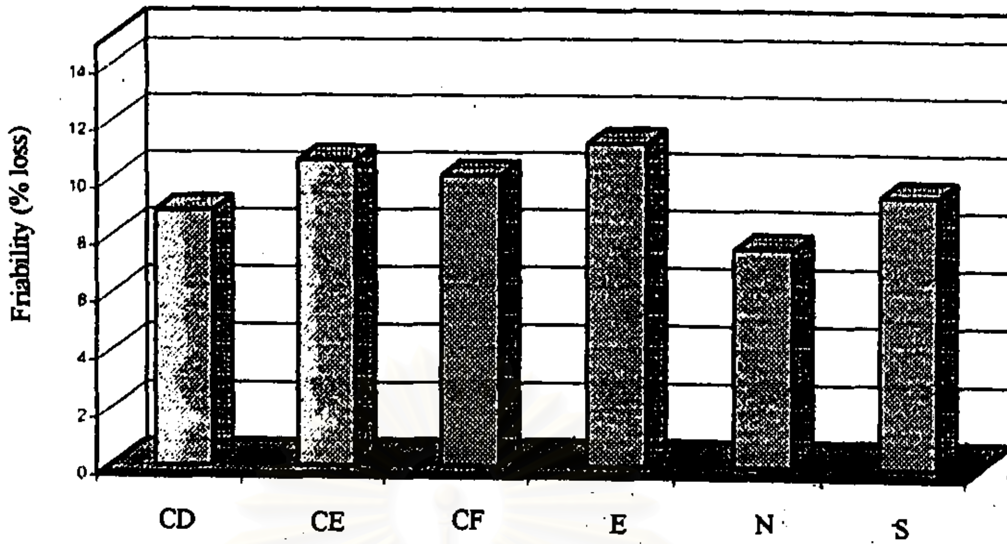


Figure 114 Percent friability of acetaminophen granules containing pregelatinized corn starches and commercial pregelatinized starches

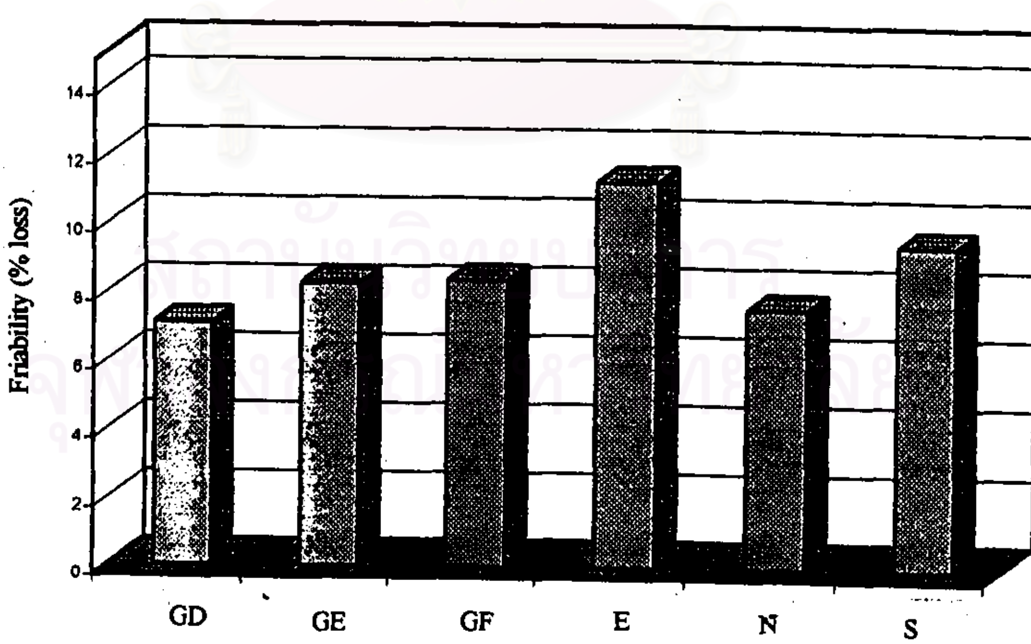


Figure 115 Percent friability of acetaminophen granules containing pregelatinized glutinous rice starches and commercial pregelatinized starches

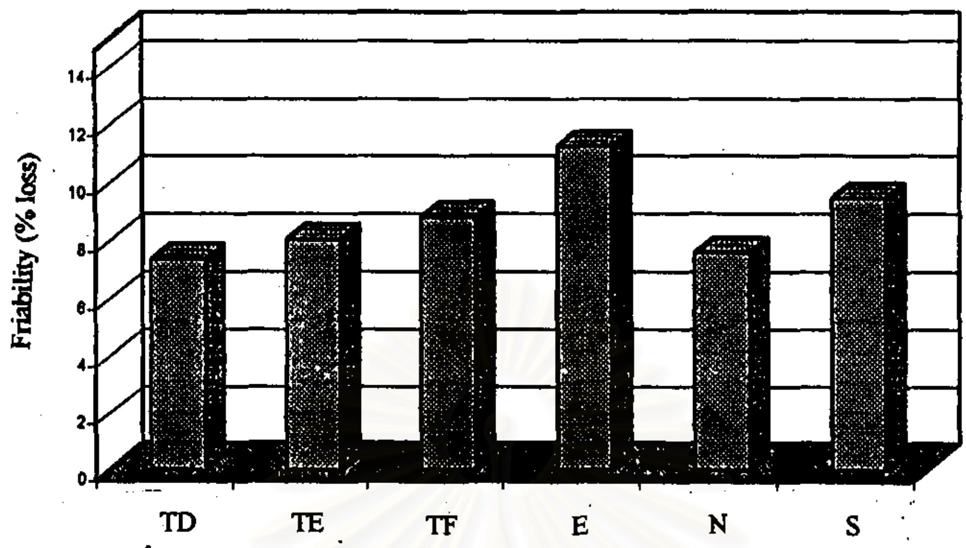


Figure 116 Percent friability of acetaminophen granules containing pregelatinized tapioca starches and commercial pregelatinized starches

2. Tablet Evaluation

2.1 Hardness, thickness, weight variation, compression force and percent friability

The hardness of all types of tablets were fixed in the ranged of 6-8 Kp except that containing CE and TD which yielded slightly harder tablet (9.56 and 8.84 Kp,. respectively). Also, tendency for 'capping' or 'lamination' at such exaggerated hardness was not seen in any formulations.

The tablet thickness was in the narrow range of 3.8-4.2 mm., although the compaction force was varied in each formulation. The result presented that the tablet thickness of all formulations could be controlled in the acceptable variation (5%) (Banker and Anderson, 1986), as well as the weigh variation which conformed the limit of USP 23 (within ±5% variation).

The mean compression forces were also listed in **Table 19** and showed by the histograms in **Figure 117-119**. It was found that the amount of compression force required for all types of granules containing pregelatinized of acid treated starches were higher than those for all other granulations. In addition, the amount of compression force required for granules containing commercial pregelatinized starches were lower than that for other granulations, especially the formulation contained National 1551 require the lowest compression force.

Comparing between the pregelatinized of acid treated starches, the compression force for that of corn starches was the highest, while the force for pregelatinized of unmodified starches is lower in both glutinous rice starches and tapioca starches which nearly that of commercial product, except the pregelatinized of unmodified corn starch that still required high compression force.

The results showed that all typed of pregelatinized of unmodified starches obtained provide the excellent binding property cause of the lower compression was needed. In the case of pregelatinized of acid treated starches, which required higher compression force. This might be that they had ultrastructure changes during the acid modification process, leading to lower viscosity and poor binding property.

The binding power of starch was provided by the amylopectin fraction (Schwartz and Zeilinskie, 1978). This could explain the data obtained from corn and tapioca starches, which the first has lower fraction of amylopectin thereby the high compression force were used. Anyway this did not agree with in the case of glutinous rice starch, which has a high fraction of amylopectin but still required high compression force. This might be the physical property of these starches, which were so sticky and stiff.

Friability is a measure of interparticular cohesiveness in tablets. Since interparticulate coheseiveness increase, the friability of tablets decreased (Taige Gebre, 1993).

Acetaminophen tablets in this study, showed neither capping nor lamination at filler/binder concentration 11.17% when tested for friability. Capping in acetaminophen tablets has been attributed to a low degree of plastic flow and bonding

(Obiorah and Shotton,1976). This indicated that the binding agents used in this study were in appropriate amount.

All the obtained tablets, however, showed the slightly higher in percent friability (0.90-1.98%) than the industry standard of 1% (Kottke, 1992). This might be the punch used during the tabletting procedures which results the round, flat face with the sharp edge, leading high friability loss.

Table 19 The hardness, thickness, weight/tablet, weight variation, compression force and perfriability of acetaminophen tablet containing various types of pregelatinized starches as fillers/binders

Types of starches as fillers/binders	Hardness* (Kp) (SD)	Thickness *(mm) (SD)	Wt/tab ⇧(mg) (SD)	Weight variation (%)	Compression force (kg)	Friability (%)
Corn starches						
CD	6.61 (0.92)	4.114 (0.060)	592.71 (0.02)	+2.90, -2.56	1252	1.04
CE	9.56 (0.59)	3.904 (0.053)	577.22 (0.01)	+1.77, -1.94	1568	1.02
CF	7.95 (0.61)	4.078 (0.026)	590.54 (0.01)	+2.30, -2.79	1765	0.96
Glutinous rice starches				-		
GD	7.82 (0.71)	4.096 (0.033)	598.78 (0.01)	+1.47, -3.33	976	1.15
GE	6.44 (1.05)	4.112 (0.088)	592.23 (0.01)	+2.97, -3.17	1298	1.22
GF	7.61 (0.46)	4.087 (0.053)	597.73 (0.01)	+1.64, -2.71	1371	1.08
Tapioca starches						
TD	8.84 (0.50)	4.088 (0.126)	595.65 (0.01)	+2.79, -3.09	786	0.90
TE	6.36 (1.43)	4.146 (0.063)	594.55 (0.02)	+ 2.10, -2.14	1025	1.36
TF	6.03 (1.34)	4.264 (0.106)	599.68 (0.01)	+1.90, -2.57	1252	1.98
Commercial pregelatinized starches						
E	6.69 (0.88)	3.821 (0.945)	599.33 (0.02)	+2.29, -2.89	1055	1.92
N	8.24 (1.65)	4.137 (0.050)	598.09 (0.02)	+2.55, -1.25	779	0.95
S	7.50 (1.41)	4.017 (0.057)	588.30 (0.02)	+3.93, -2.90	1174	1.32

* : Average and standard deviation were calculated from ten determinations.
⇧ : Average and standard deviation were calculated from twenty determinations.

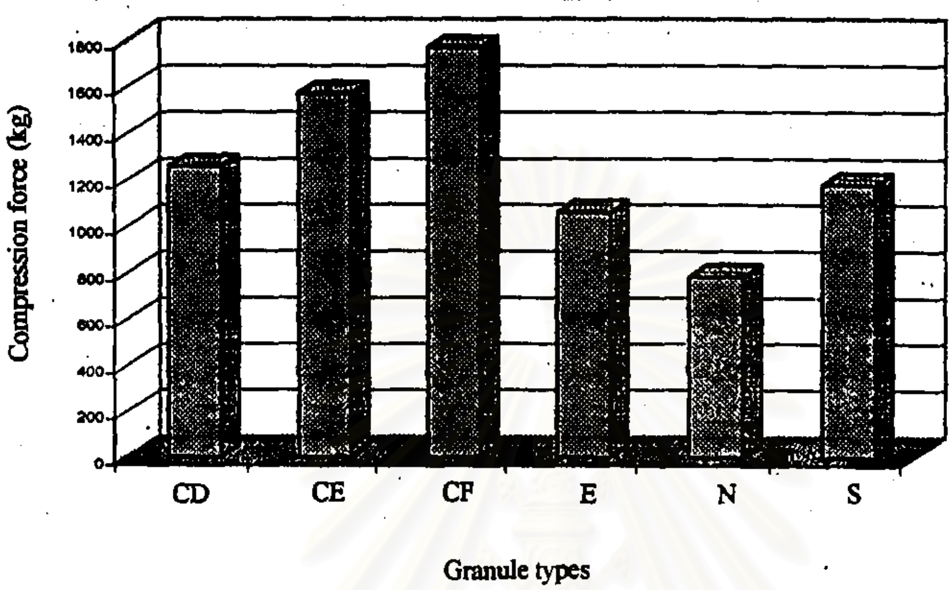


Figure 117 The histograms of compression force required for acetaminophen granules containing pregelatinized corn starches and commercial pregelatinized starches

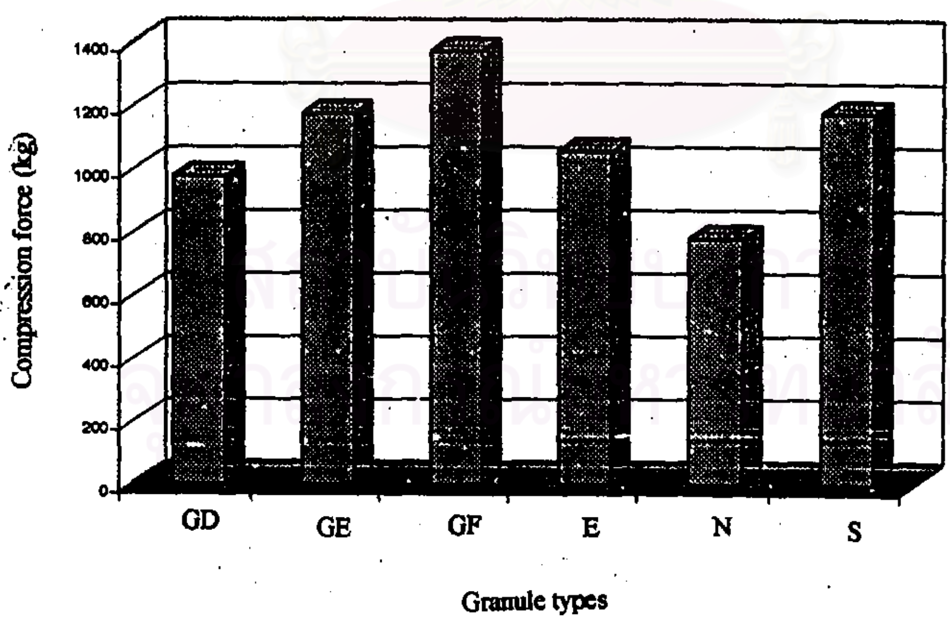


Figure 118 The histograms of compression force required for acetaminophen granules containing pregelatinized glutinous rice starches and commercial pregelatinized starches

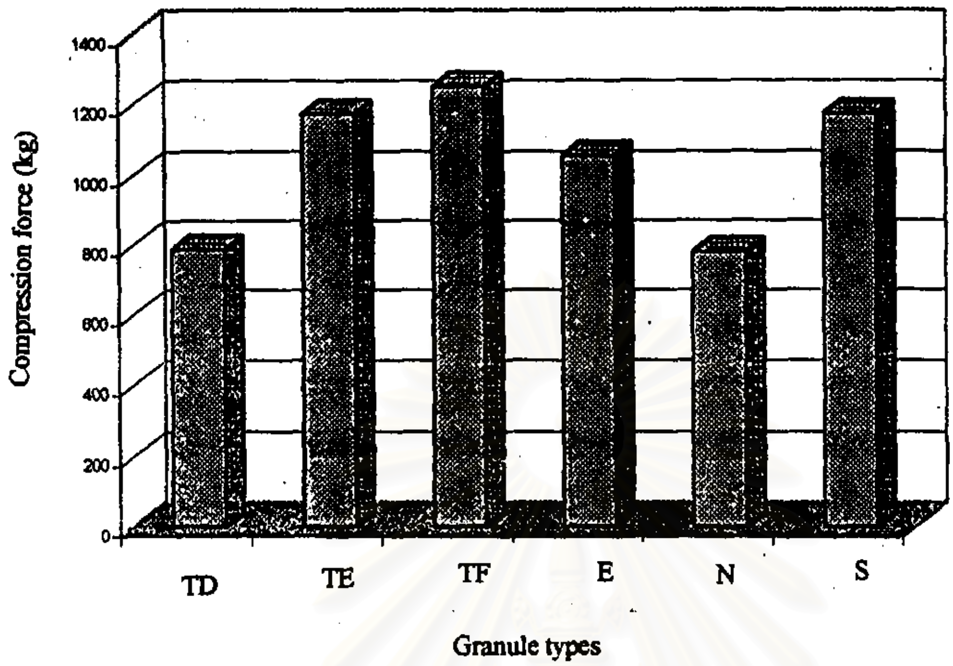


Figure 119 The histograms of compression force required for acetaminophen granules containing pregelatinized tapioca starches and commercial pregelatinized starches

2.2 Disintegration time

Table 20 shows the effects of types of pregelatinized starches as the binding agents on the disintegration times of acetaminophen tablets. The tablets containing TD, GD, GE and GF did not disintegrate within 60 min. This result demonstrated the poor disintegrating character of such binder in these formulas.

The increase in disintegration time with the pregelatinized starches used as filler/binder was expected as it has been shown by previous study (Daranee Pencharoen, 1999) that a thin film of starch mucilage around the granules is formed with a thickness depending on the type of pregelatinized starches used. It mentioned that the disintegration time of tablets containing pregelatinized tapioca starches were unsatisfied, providing the disintegration time longer than 60 min, which was an agreement of the result obtained in this study, as well as that of tablets containing pregelatinized glutinous rice starches.

It has also been noted that, in the presence of water, the thin film is converted into a mucilaginous, viscous barrier between the granules and the water, retarding the disintegration of the granules. Accordingly, it is assumed that at given equal concentrations of pregelatinized starches as binders, pregelatinized glutinous rice starches forms a more viscous film round the granules, thus causing a longer disintegration time than the others.

The result indicated that the present study could improve the disintegration time of the acetaminophen tablet containing pregelatinized tapioca starch by treating the native starch used in the proper acid conditions prior to pregelatinization. The pregelatinized-acid treated starches produced tablets with the disintegration time in the acceptable range of 4.2 min and 2.27 min for those containing TE and TF respectively, whereas the tablets prepared from TD did not disintegrate within 60 min. Anyway, this elimination could not be used in the case of glutinous rice starches. All tablets containing in either pregelatinized glutinous rice starch or both levels of pregelatinized of acid treated glutinous rice starches fell within the USP specification for disintegration time. This is in good agreement with the results obtained from the study of powder viscosity earlier which reported the very high viscosity of all types of pregelatinized glutinous rice starches. It would appear that glutinous rice starch is a good binder as it gave greater crushing strength and less friable tablets. As a disintegrant, however, it is less effective.

As can be seen in **Table 20**, the acceptable levels of the disintegration time of acetaminophen tablets could be ranked the following : CD > TE > TF > CE > N > CF > S > E. The statisticcal differences ($p<0.05$) were depicted in **Table 45** (Appendix 9). Tablets containing all types of pregelatinized corn starches (CD, CE, CF) gave the acceptable levels of disintegration time.

The CF as well as commercial pregelatinized starches (E, N, S) produced tablets which disintegrated with in 1 min. This could be explained that the disintegration property seemed to be responsible by the viscosity of filler/binder. The higher viscosity of filler/binder is, the lower disintegration time will be.

Table 20 Disintegration time and $T_{80\%}$ of acetaminophen tablets containing various type of pregelatinized starches

Types of starches as fillers/binders	Disintegration time (min)* (SD)	$T_{80\%}$ (min)** (SD)
Corn starches		
CD	5.23 (0.58)	7.00 (0.90)
CE	1.96 (0.37)	3.58 (0.38)
CF	0.78 (0.04)	2.92 (0.38)
Glutinous rice starches		
GD	> 60	-
GE	> 60	-
GF	> 60	-
Tapioca starches		
TD	> 60	-
TE	4.27 (1.37)	6.58 (0.95)
TF	2.27 (0.38)	4.50 (0.91)
Commercial pregelatinized starches		
E	0.65 (0.02)	3.25 (0.25)
N	0.93 (0.04)	5.67 (0.58)
S	0.68 (0.04)	3.58 (0.88)

* : Average and standard deviation were calculated from six determinations.
** : Average and standard deviation were calculated from three determinations.

2.3 Dissolution time

The official USP dissolution test for acetaminophen tablets was used to evaluate the eight formulations, which exhibited the acceptable disintegration time from 2.2 corresponding to the USP XXIII. The selected formulations were that containing CD, CE, CF, TE, TF, E, N and S.

The dissolution profiles of acetaminophen tablets containing the selected pregelatinized starches and commercial pregelatinized starches could be observed in **Figure.120-121.** The time required for 80% of the acetaminophen ($T_{80\%}$) to be released from the compressed tablets was shown in **Table 20**. The dissolution performances of tablets containing two levels of pregelatinized-acid treated tapioca starches (TE, TF) and all types of pregelatinized corn starches (CD, CE, CF) were evaluated by comparing with that of commercial pregelatinized starches (E, N, S). It was found that a minor difference was observed in the time to reach 100% dissolved, with all system, in the study taking only 15 min. All formulas selected had dissolution met the USP XXIII requirement. The dissolution of acetaminophen tablets were enhanced by the effect of pregelatinized starches used. The ranks of $T_{80\%}$ of the tablets containing pregelatinized corn starches comparing with those of commmercial pregelatinized starches were as follows: CD > N > S ≅ CE > E >CF, while the another profile, of tapioca starch was TE > N > TF >S > E. The statistical were illustrated in **Table 46** (Appendix 9). It showed no significant differences of T_{80}% were observed in acetaminophen tablets containing CE and CF, while the significant differences were observed in those of TE and TF.

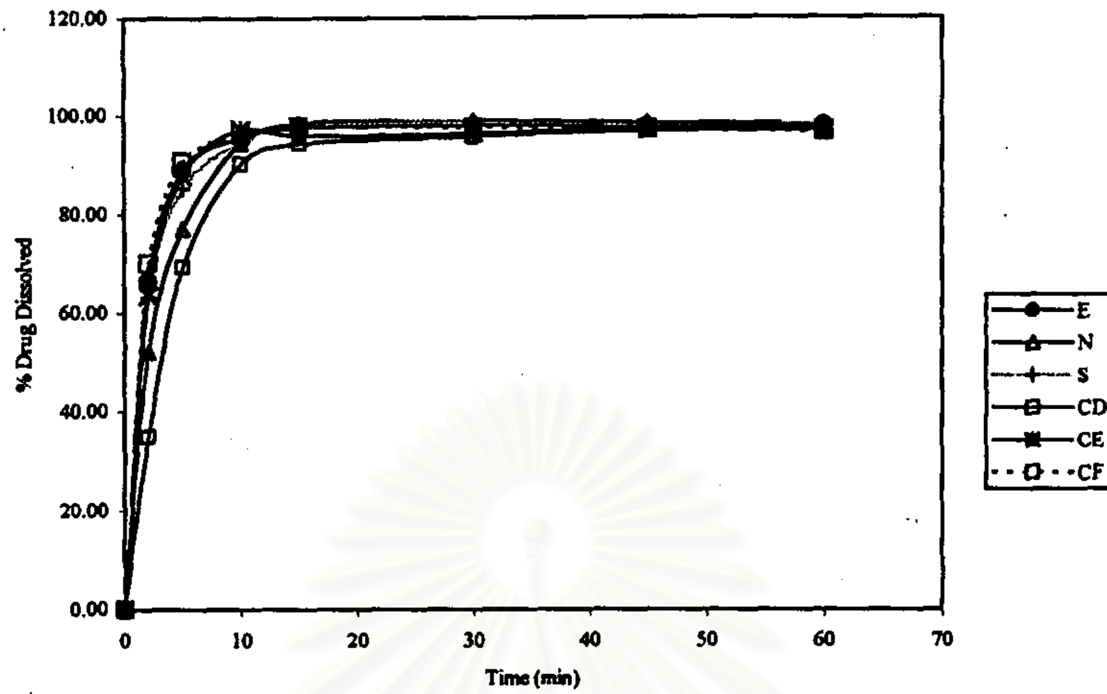


Figure 120 Dissolution Profiles of Acetaminophen Tablets Containing Pregelatinized Corn Starches and Commercial Pregelatinized Starches.

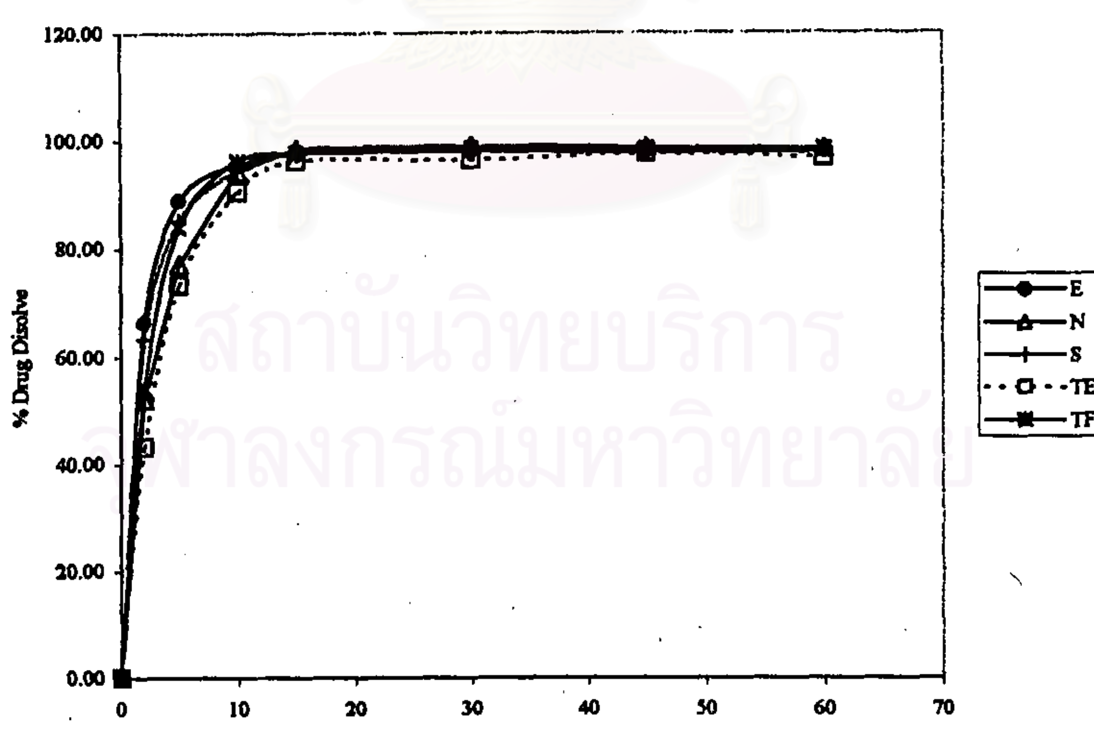


Figure 121 Dissolution Profiles of Acetaminophen Tablets Containing Pregelatinized Tapioca Starches and Commercial Pregelatinized Starches