

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Examination of Physical Properties of Native Tapioca Starch

Native tapioca starch from Siam Modified Starch Co, Ltd. had been examined for its general physical properties. It was bright white powder with the whiteness 94%. It contained moisture 14%. The granule of tapioca starch was rather a sphere, as shown in Figure 4.1, which is quite characteristic of most tapioca starch (11).

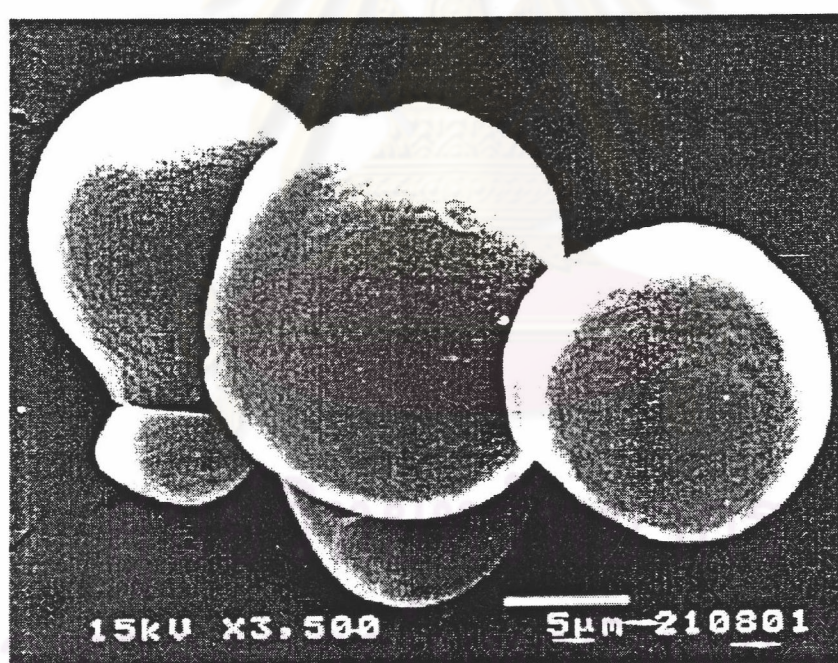


Figure 4.1 Scanning electron micrograph of native tapioca starch.

The pasting property of the native tapioca starch is shown in Figure 4.2. It indicated that the gelatinization temperature of native tapioca starch is normally 69.5°C and its peak viscosity is 625 BU (Brabender Unit). In general, the gelatinization of native tapioca starch ranges from $59-70^{\circ}\text{C}$ depending on the size of granule and the composition of amylose and amylopectin. It usually occurs over a narrow temperature range, with larger granules gelatinizing first and smaller granules later (9). It shall be noted that the higher the amylose is, the higher the gelatinization temperature will be. Since amylose molecules are linear, they can line up more readily and have more extensive hydrogen bonding. It thus requires more energy to break these bonds and gelatinize the starch (7). In this research, the native tapioca starch normally contained 15-18% amylose was used. It can then swell and gelatinize at low temperature.

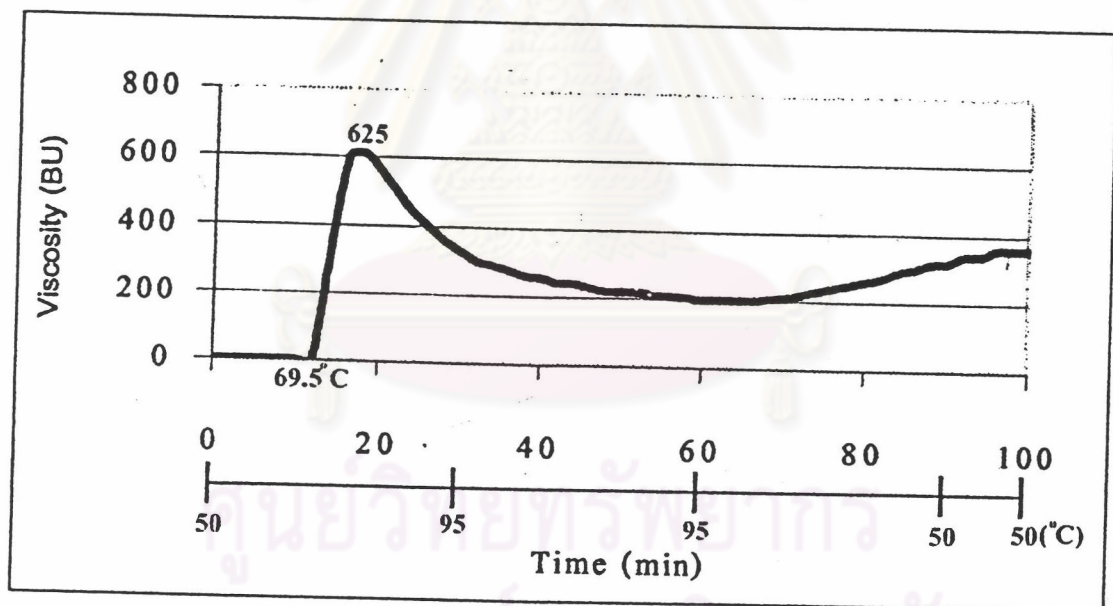


Figure 4.2. Brabender Viscograph of native tapioca starch (rate $1.5^{\circ}\text{C}/\text{min}$).

Accordingly, all reactions of tapioca starch must be handled at the temperature lower than its gelatinization temperature. This is to prevent the occurrence of gelatinized starch which will create the difficulty in the reaction work-up later. Therefore, all the reactions in this research were carried out at about 20-30°C lower than gelatinization temperature.

4.2 Preliminary Study of Hydroxypropylation of Tapioca Starch

Native starches differ in their morphological and physicochemical properties. Different types of starches will thus respond to the chemical modification differently. Pal (13) found that the reaction condition to yield the same degree of substitution in hydroxypropylation differed from one starch type to another. Wang (21) also reported that the degree of substitution and reaction yield of hydroxypropylated starch at the same condition was differing from one starch type to the others. Basically, the reaction efficiency correlates to the size of the starch granules, with larger granule, starch exhibited greater reaction efficiency.

However, almost hydroxypropylated reported starches came from corn and potato starches. Hydroxypropylation of tapioca starch was rarely to find. Therefore, the hydroxypropylation of tapioca starch was investigated in this study.

The primary condition of hydroxypropylation of tapioca starch had been taken as follows: 40% dry starch in water, 1% sodium hydroxide (3.5%w/v) and 7% propylene oxide, both based on the dry starch weight at 40°C with 24-hour reaction time. This reaction was carried out three times, repeatedly. The degree of substitution then was determined by colourimetric method (12) at least three times for each sample. Then the average value of degree of substitution was taken as shown in Table 4.1.

Table 4.1 Hydroxypropylation of tapioca starch at the primary condition.

Reaction No.	Degree of substitution (Average)	Reaction Yield (%)
1	0.0588	30.07
2	0.0518	26.49
3	0.0554	28.34

In the experiment, gelatinization in the reaction no.2 probably occurred earlier than the reaction no.3 and 1 in a sequence. Therefore, the resulted hydroxypropylated starch had lower degree of substitution and reaction yield. From Table 4.1, it was noticed that the degree of substitution and reaction yield for the repeated reactions were quite different. This was probably due to the gelatinization appeared after the hydroxypropylated starch was formed. Eventhough the reaction temperature was controlled to be not over 40°C, the gelatinization still occurred. This gel formation was not certainly attributed from the native tapioca starch, whose gelatinization was 69.5°C, but rather from the hydroxypropylated starch.

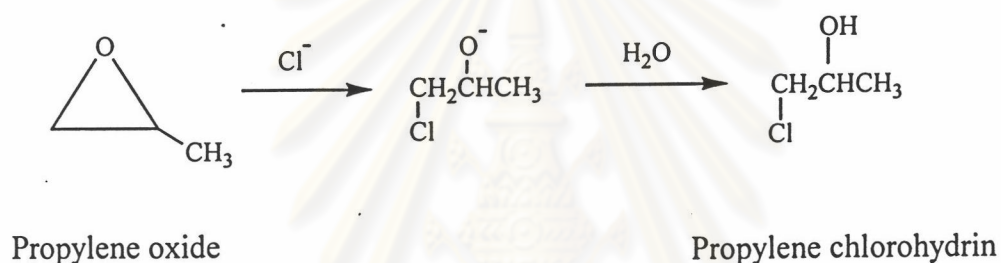
The gelatinization temperature of hydroxypropylated starch was varied depending on the degree of substitution (16). Once the gelatinization was induced to occur by the hydroxypropylated starch with higher degree of substitution, the further hydroxypropylation was interrupted caused by this gel. Therefore, it is quite vital to prevent gelatinization during the course of reaction.

This can be performed by varying the gelatinization inhibitor. The presence of the gelatinization inhibitor in the reaction shall prevent gelatinization before hydroxypropylation starts. Furthermore, its presence may allow the reaction to run at

more severe condition such as higher temperature, higher content of sodium hydroxide and propylene oxide.

4.3 Effect of Sodium Sulfate on Degree of substitution

Two common gelatinization inhibitors are sodium sulfate and sodium chloride. Although sodium chloride is cheaper than sodium sulfate, propylene chlorohydrin may be generated from the excess propylene oxide by reacting with chloride ion in the reaction (Scheme 4.1). Since propylene chlorohydrin is hazardous to human being, the



Scheme 4.1 The side reaction between propylene oxide and chloride ion (28).

chlorohydrin level in modified stuff for food application has been limited and regulated by Food and Drug Administration (FDA) (24). To avoid such problem, sodium sulfate was chosen as the appropriate gelatinization inhibitor for the slurry in this research.

Various amounts of sodium sulfate were used in hydroxypropylation reaction at the same condition as described in section 4.2 (Table 4.2). Each condition was carried out three times, repeatedly. The degree of substitution was then determined by colourimetric method at least three times for each sample. Then the average value of degree of substitution was taken as shown in Table 4.2

Table 4.2 Effect of the quantity of sodium sulfate on degree of substitution.

Sodium Sulfate (% by dry starch weight)	Degree of Substitution (Average)
8	0.0475 ± 0.0031
12	0.0549 ± 0.0034
15	0.0664 ± 0.0055

Figure 4.3 showed that when the amount of sodium sulfate increased, the degree of substitution was increased. The reaction with 8% sodium sulfate gave the minimum degree of substitution and the gelatinization was still occurred. In case of, the reaction with 12 and 15% sodium sulfate, higher degree of substitution was obtained and no gel formation appeared during the reactions. This can be due to the salt dissolved in water. Salt had interacted with water by surrounded sodium ions and sulfate ions. As the result, the water molecules could not approach the starch

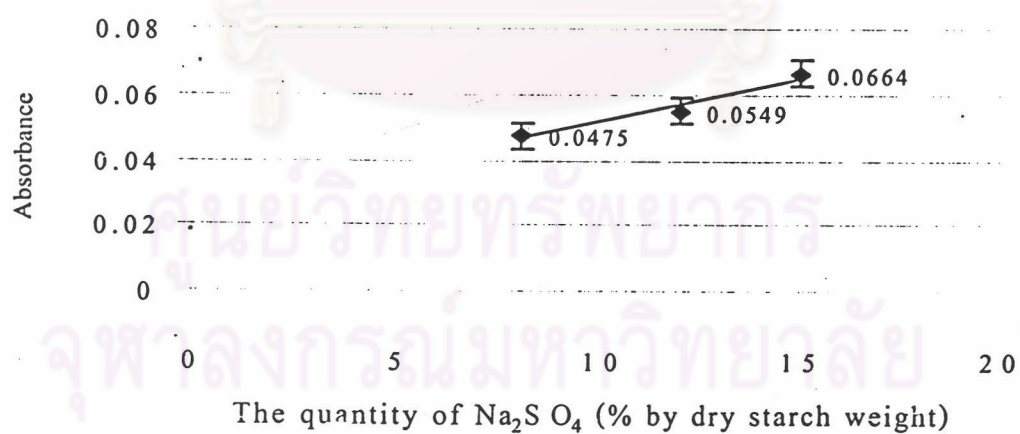


Figure 4.3 The plot of the quantity of Na₂SO₄ versus degree of substitution.

molecules. Thus the gelatinization could not occur. Bircan (25) reported that salt is added to the starch during modified process because it reduces granule swelling. Modification of the starch occurs in an alkali environment, which may increase. It is likely that the hydroxyl groups of starch bind sodium ions, similar to the binding action when sodium hydroxide is added.

The gelatinization in modified starch was occurred by the interaction between starch and water. Thus, if the gelatinization inhibitor like sodium sulfate is present in large amounts, water activity will be low and gelatinization will not occur to only a limited extent. The degree of substitution would be increased.

Accordingly, the prevention of gelatinization in hydroxypropylation reaction is necessary. However, the hydroxypropylated starch from the reaction which had salted over 15% by dry starch weight, was not good for using as thickener in food application. Furthermore, sulfate can be converted to hydrogen sulfide by anaerobic reduction during wastewater treatment, can have an undesirable effect on the environment (13).

4.4 Effect of Sodium Hydroxide on Degree of Substitution

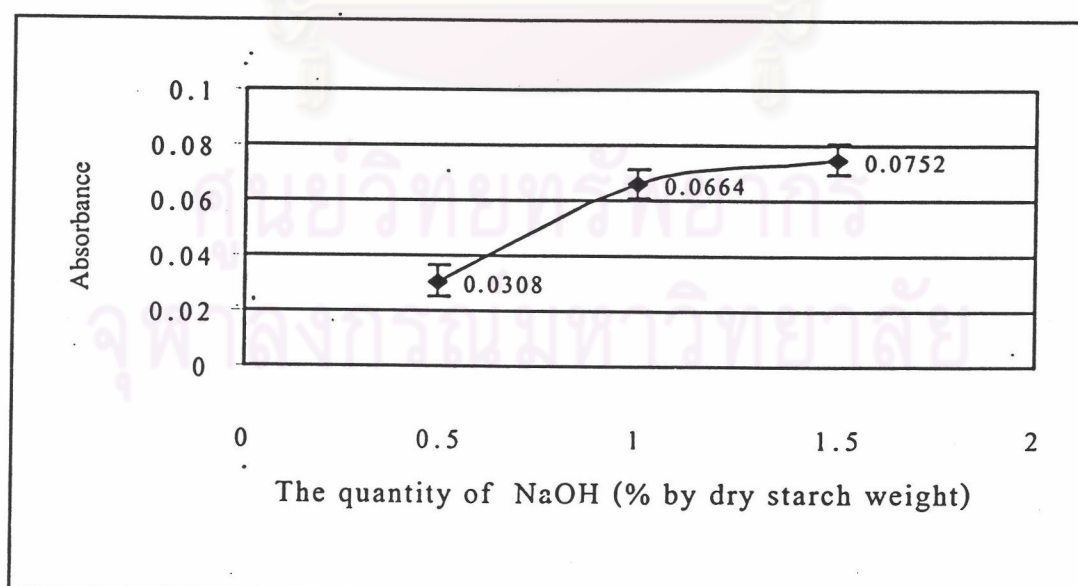
In hydroxypropylation reaction, the starch molecule is firstly activated to make the O-H bond nucleophilic and to facilitate the formation of starch-O⁻. This was done by using sodium hydroxide as a catalyst.

From Table 4.3 and Figure 4.4, it obviously indicated that degree of substitution was increased when the amount of sodium hydroxide was increased. The maximum degree of substitution is 0.0752 by using 1.5% sodium hydroxide. The

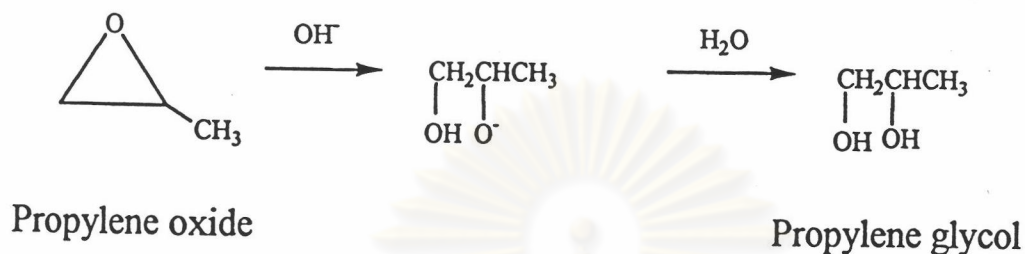
Table 4.3 Effect of the quantity of sodium hydroxide on degree of substitution.

Sodium Hydroxide (% by dry starch weight)	Degree of Substitution (Average)
0.5	0.0308 ± 0.0067
1.0	0.0664 ± 0.0055
1.5	0.0752 ± 0.0038
2.0	gelatinized

increase in degree of substitution of hydroxypropylated tapioca starch was because of the catalytic effect of sodium hydroxide on the hydroxypropylation reaction (Scheme 2.1). High alkalinity is needed for good reaction efficiency. Sodium hydroxide catalyzed to convert starch to a nucleophile (starch-O). Nucleophiles reacted with propylene oxide to yield hydroxypropylated starch. When sodium hydroxide concentration increased, the amount of nucleophile would be increased. The higher degree of substitution thus was obtained in a shorter reaction time.

**Figure 4.4** The plot of the quantity of NaOH versus degree of substitution.

The effect of sodium hydroxide concentration on degree of substitution can be explained by the following mechanism: sodium hydroxide could catalyze the hydrolysis of 1,2-propylene oxide as well. This would lead to the formation of propane 1,2-diol, a side product (Scheme 4.2). This reaction competed with the



Scheme 4.2. Base-catalyzed hydrolysis of propylene oxide (28).

catalysis of starch with the sodium hydroxide. So at 0.5%, lower degree of substitution resulted while at higher percentage of sodium hydroxide, degree of substitution was increased suggesting the catalytic effect of sodium hydroxide on the hydroxypropylation reaction.

With 2.0% sodium hydroxide, the starch slurry formed a very thick slurry that difficult to stir. At this sodium hydroxide concentration were presumably induced to occur rapidly more hydroxypropyl groups in a short time. A hydroxypropyl group was hydrophilic. Hydroxypropylated starch exhibited better dispersibility in cold water than native starch. However, gelatinization would easily occur due to the presence of a large number of hydroxypropylated groups. This explanation corresponds with the report by A.A. Ragheb (26). He observed that gelatinization of starch depended mainly on the concentration of sodium hydroxide on the paste and its rheological characteristics of pastes depended on both the temperature of treatment and on the concentration of sodium hydroxide.

Consequently, it indicated that the sodium hydroxide concentration had influenced on reaction efficiency and degree of substitution of hydroxypropylated starch. But the gelatinization occurred when the percentage of sodium hydroxide was too much. Therefore, the presence of sodium hydroxide was much or less depended on the other severe condition in each reaction such as higher temperature, higher content of sodium hydroxide and propylene oxide.

4.5 Effect of Propylene Oxide Concentration on Degree of substitution

Figure 4.5 presented the effect of propylene oxide concentration on degree of substitution. It obviously found that degree of substitution was increased when the propylene oxide concentration increased. From Table 4.4, it showed that the degree of substitution as high as 0.1013 was obtained at 9% propylene oxide. The explanation

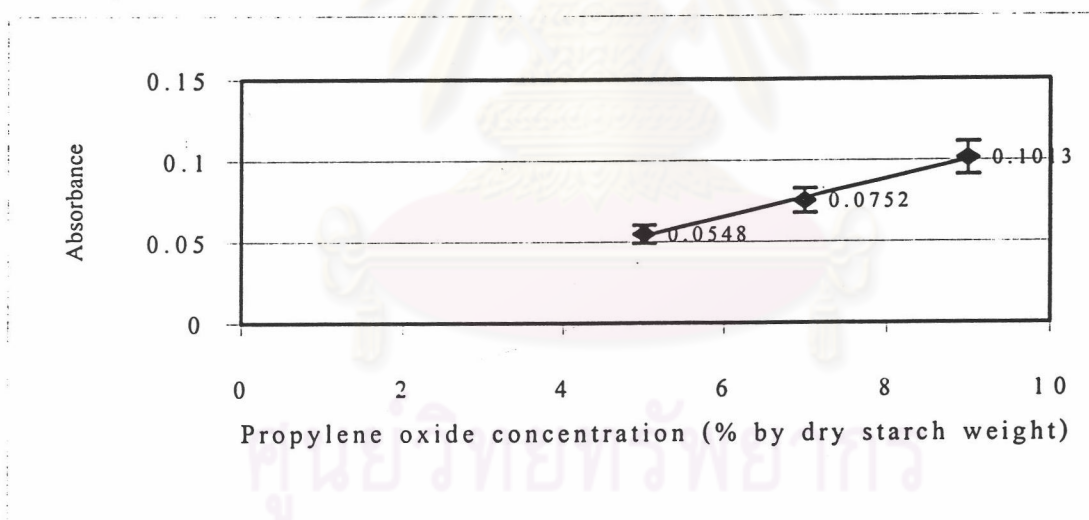


Figure 4.5 The plot of the concentration of propylene oxide versus degree of substitution.

was that the great amount of propylene oxide would allow more possibility for starch-O to react with leading to higher substitution. The same observation had been reported by other researchers who worked on the different types of starch (13,21).

At higher than 9% propylene oxide, gelatinization occurred. This was again due to the presence of more hydroxypropyl groups in starch. When they were introduced into starch granules, the internal bond holding the granule together was

Table 4.4 Effect of propylene oxide concentration on degree of substitution.

Propylene Oxide (% by dry starch weight)	Degree of Substitution (Average)
5	0.0548 ± 0.0048
7	0.0752 ± 0.0038
9	0.1013 ± 0.0044
10	gelatinized
20	gelatinized

weaken. Then hydration of starch granule occurred easily even at low temperature. On the other hand, it can be said that the hydroxypropylated starch was lower gelatinization temperature than the native starch.

Consequently, the high content of propylene oxide, but limited concentration was needed for preparing the high degree of substitution of hydroxypropylated starch. In order to yield higher degree of substitution at high propylene oxide concentration, other factors must be considered. Therefore, the next section would study the indirect condition which avoid the gelatinization when high propylene oxide concentration was used. Furthermore, FDA regulations defined the maximum amount of propylene oxide

and its derivative, propylene chlorohydrin that can be presented in the product (Scheme 4.1). This must be conceived if it was used for the food application.

4.6 Effect of the Reaction Time on Degree of substitution

To increase the degree of substitution, high amount of sodium sulfate, sodium hydroxide and propylene oxide were used. To avoid the gelatinization of modified starch, the shorter reaction time was thus attempted.

Table 4.5 Effect of the reaction time on degree of substitution.

Reaction Time (hrs.)	Degree of Substitution (Average)
6	0.0493 ± 0.0048
12	0.0927 ± 0.0037
18	0.1023 ± 0.0037
20	0.1018 ± 0.0019
24	0.1013 ± 0.0044

From Table 4.5 and Figure 4.6, it showed that the degree of substitution of hydroxypropylated tapioca starch increased significantly at early reaction. Greater contact time with continuous agitation led to efficient absorption or diffusion of propylene oxide into starch granules, which increased the chances of collisions between the starch nucleophile and propylene oxide, which induced a higher degree of substitution. However, after 12 hours no significant change in degree of substitution was observed. It implied that 12-hour reaction accomplished almost complete hydroxypropylation. The similar observation had been reported by several other researchers who worked on other types of starch (13,22).

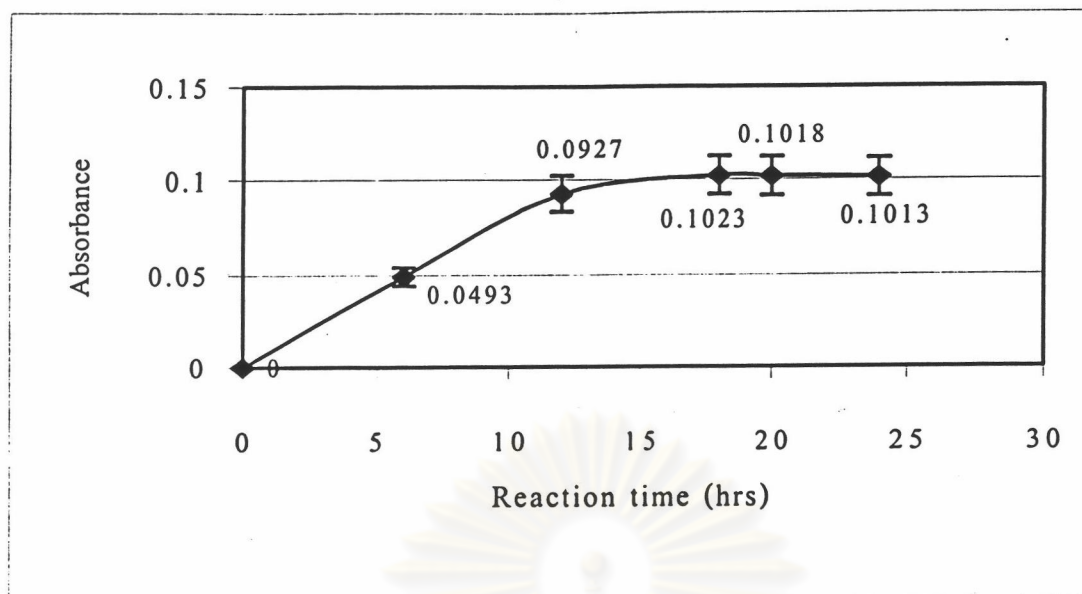


Figure 4.6 The plot of the reaction time versus degree of substitution.

Accordingly, 12 hours of reaction time was the appropriate reaction time for hydroxypropylation of tapioca starch when propylene oxide concentration was 9% by dry starch weight. The lower reaction time than 12 hours gave only slightly higher degree of substitution which was not good in term of economic wise.

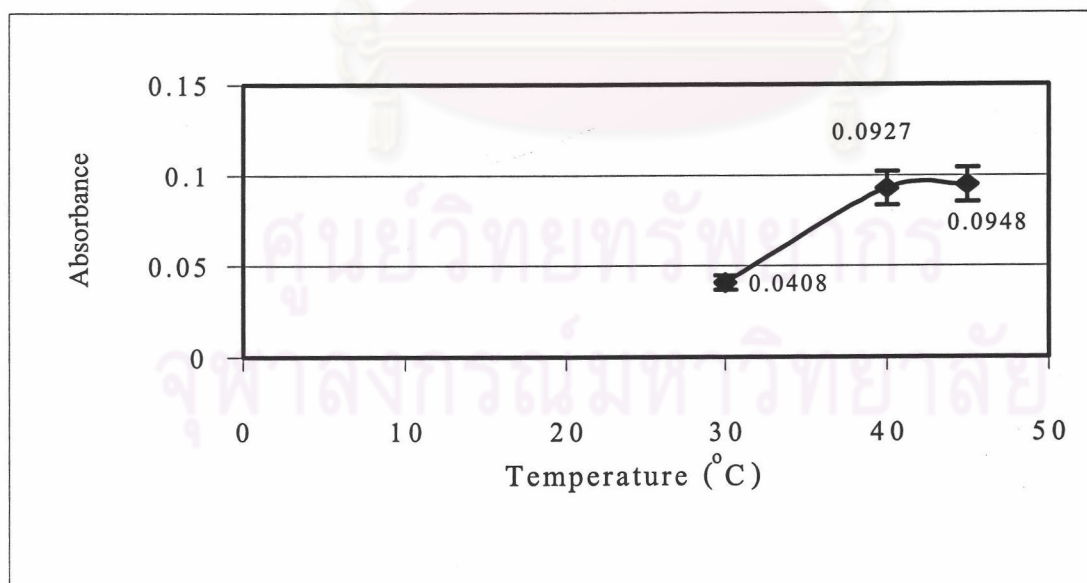
4.7 Effect of Temperature on Degree of Substitution

The elevated temperature of reaction helps in diffusion and penetration of sodium hydroxide and propylene oxide into the starch granule and thus economizes the reagent consumption. However, the elevated temperature must not be higher than the gelatinization temperature of native tapioca starch which was 59°C (9).

Table 4.6 Effect of temperature on degree of substitution.

Temperature (°C)	Degree of Substitution (Average)
30	0.0408 ± 0.0016
40	0.0927 ± 0.0037
45	0.0948 ± 0.0029
50	gelatinized

Table 4.6 and Figure 4.7 showed that the higher temperature was, the high degree of substitution was obtained. This was dependent on the chances of collision of the starch nucleophile with the propylene oxide molecules which was normally increased when the temperature was elevated. However, at 50°C, the gelatinization was observed. It can be rationalized that as the temperature was increased, the starch molecules vibrated more vigorously, breaking intermolecular bonds and allowing their

**Figure 4.7** The plot of temperature versus degree of substitution.

hydrogen bonding sites to engage more water molecules in the reaction caused gelatinization to occur. This was corresponded with the report by Ragheb (26). He observed that the degree of gelatinization depended on the temperature and the amount of water available in the process. When the temperature and the amount of water increased, thicker gel was observed.

Consequently, it indicated that the higher degree of substitution of hydroxypropylated tapioca starch could be prepared at the elevated temperature which was lower than the gelatinization temperature of native tapioca starch.

4.8 Effect of the Reaction Medium on Degree of Substitution

To avoid the gelatinization during reaction, it was necessary to conduct the hydroxypropylation in the presence of a limited amount of water medium. For example, it had been accomplished by working in aqueous alcohol medium such as ethanol, isopropanol and methanol. The hydroxypropylated starch had little or no tendency to swell in these mediums (20,22).

Table 4.7 Effect of the ethanol concentration on degree of substitution.

Ethanol : Water (% by starch weight)	Degree of Substitution (Average)
20 : 80	gelatinized
30 : 70	0.0522 ± 0.0031
70 : 30	0.1003 ± 0.0029

Table 4.8 obviously indicated that an amount of water had influenced on degree of substitution as well. The degree of substitution obtained from the reaction in 30% ethanol was less than 70% ethanol medium. It was noticed that in the first two reactions, little gel formation was observed. The rationalized to this observation was that higher amount of water was presented in the reactions using 20% and 30% ethanol. In this case, sodium sulfate was not worked since ethanol could not swell the starch molecule due to its structure, which was larger, and more hindrances than water molecules. However, at low percentage of ethanol in reaction, slight gelatinization was still observed. When the starch granule swelled, sodium hydroxide and propylene oxide, which penetrated to react with starch granules, get diluted. Therefore, the degree of substitution was decreased. Other reports were described the similar observation on the hydroxypropylation of different types of starch (20,22).

Accordingly, the amount of water in the reaction had influenced on the gelatinization of the hydroxypropylated tapioca starch. Thus hydroxypropylation of tapioca starch in aqueous ethanol medium was the appropriate medium for preparing the high degree of substitution of hydroxypropylated tapioca starch.

4.9 High Degree of Substitution of Hydroxypropylated Tapioca Starch

From the previous section, the most appropriate condition of the hydroxypropylation of tapioca starch was as follows: 40% dry starch in water, 15% sodium sulfate, 1.5% sodium hydroxide (3.5%w/v) and 9% propylene oxide, all of these based on the dry starch weight at 40°C with 24-hour reaction time. The reaction was repeated three times. The degree of substitution and reaction yield of hydroxypropylated tapioca starch were 0.1013 and 40.70% respectively. They were not high enough because the amount of propylene oxide was lost about 59.30%. Thus this section studied the preparation of high degree of substitution of hydroxypropylated

tapioca starch which decreased the loosening of propylene oxide. The reaction was repeated three times. The degree of substitution was determined at least three times for each sample. Then the average values of degree of substitution and reaction yield were taken as shown in Table 4.8.

From Table 4.8, it found that the degree of all three trials were very close to each other. The average degree of substitution of all three trials was 0.2057. The average reaction yield was 49.10%.

Table 4.8 Degree of substitution of hydroxypropylated tapioca starch.

Reaction No.	Degree of Substitution	Average Degree of Substitution	Average Reaction Yield (%)
1	0.2043	0.2057 ± 0.0062	49.10
2	0.2130		
3	0.1990		

Y.J. Choi (27) also prepared the hydroxypropylated corn starches at high degree of substitution in an aqueous ethanol (70%). Sodium hydroxide 1.08% and propylene oxide 30% by dry starch weight was used at 65°C. Reaction yield reached about 50% (DS 0.4) by a 24-hour reaction. Therefore, hydroxypropylation of tapioca starch was carried out as the same condition as Choi (27) but the temperature had kept at 45°C to prevent gel formation. It was found that only 0.1076 of degree of substitution and 12.84% of reaction yield was obtained. It is unbelievably that he could get high degree of substitution 0.4 since very low concentration of sodium hydroxide was used which was not conformed with this research.

4.10 Determination of Degree of Substitution by $^1\text{H-NMR}$

Degree of substitution of hydroxypropylated tapioca starch can be determined by two different methods: a colourimetric and proton nuclear magnetic resonance ($^1\text{H-NMR}$) method. The determination of degree of substitution of hydroxypropylated starch was thus performed by using $^1\text{H-NMR}$ technique. The hydroxypropylated starch with the highest degree of substitution, 0.2130, taken as a sample for $^1\text{H-NMR}$ recording compared with the $^1\text{H-NMR}$ spectrum of the native tapioca starch. Table 4.9 showed degree of substitution values obtained by colourimetric method and $^1\text{H-NMR}$.

Table 4.9 Degree of substitution values of hydroxypropylated tapioca starch determined by colourimetry and $^1\text{H-NMR}$.

DS (Colourimetry)	DS ($^1\text{H-NMR}$)
0.2130	0.2324

With $^1\text{H-NMR}$ spectroscopy, the degree of substitution was calculated by using the integrated intensities of the signals in two regions as detailed in Appendix J. Figure 4.8 showed the $^1\text{H-NMR}$ spectrum of native tapioca starch, where the signal of equatorial proton of the anhydroglucose unit, protons of the anhydroglucose units and water appeared at δ 5.6-5.8, 3.8-4.4 and 4.5-4.8, respectively. This spectrum did not appear the signal from the methyl protons in the hydroxypropyl groups. To compare with Figure 4.9, hydroxypropylated starch had another characteristic proton signal of hydroxypropyl group at δ 1.4-1.6 ppm (a doublet). The degrees of substitution values obtained from $^1\text{H-NMR}$ were higher than colourimetric method. The reason for this significant difference in degree of substitution values between two methods was probably due to the error from colourimetric method. The colourimetric method was the conventional method for determining degree of substitution of hydroxypropylated

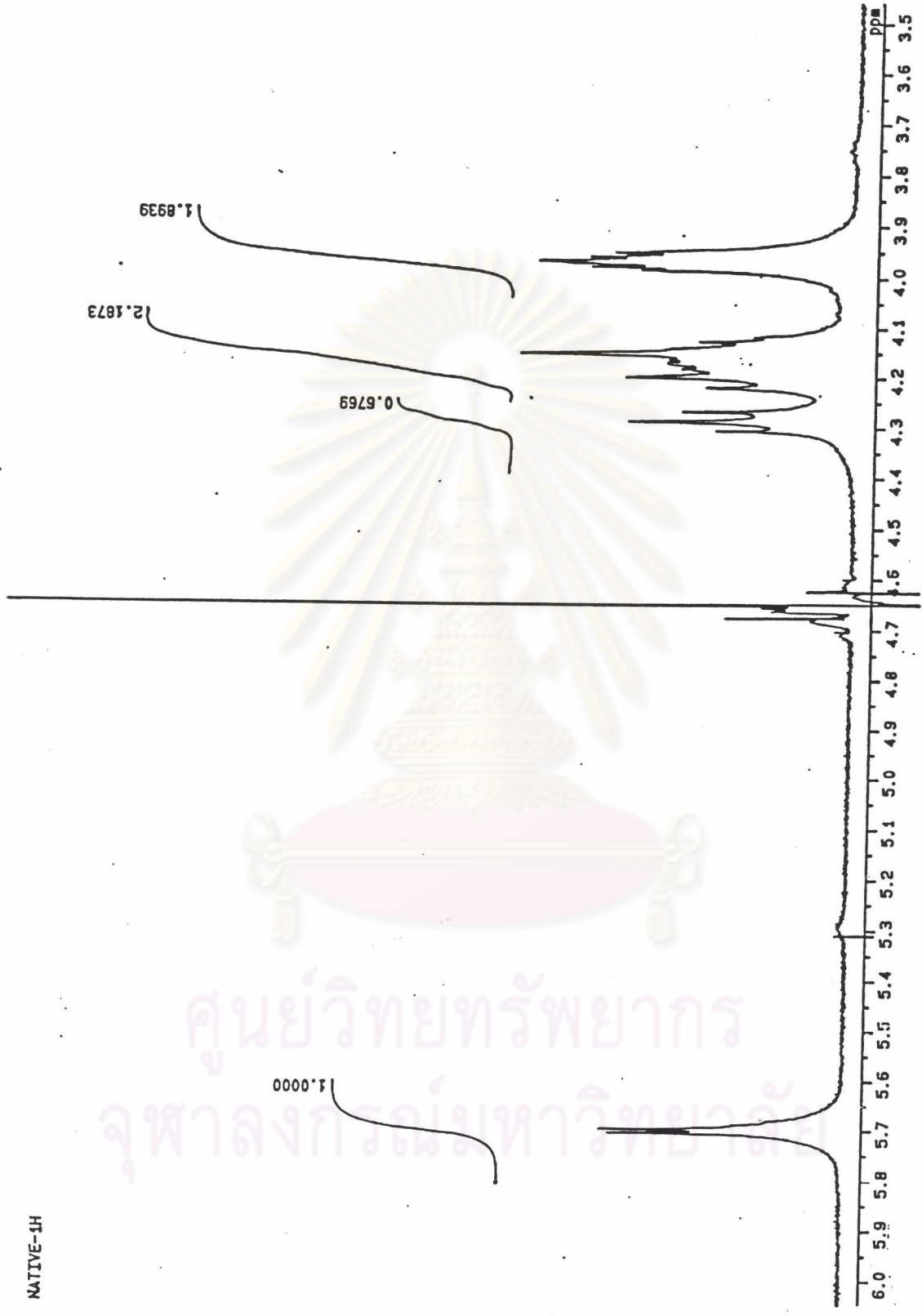


Figure 4.8 The $^1\text{H-NMR}$ spectrum of native tapioca starch.

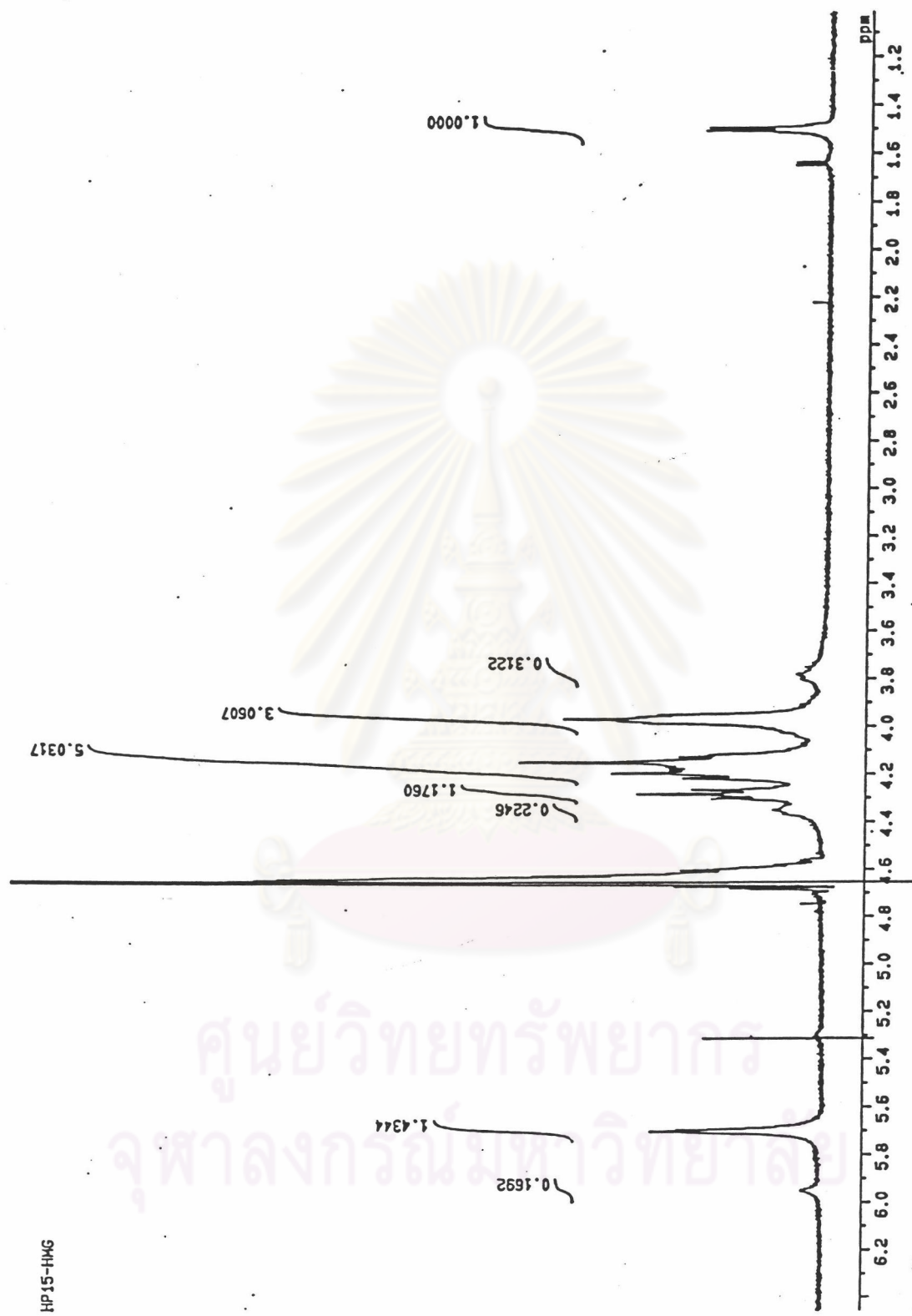


Figure 4.9 The ¹H-NMR spectrum of hydroxypropylated tapioca starch (DS=0.2130).

starch. This method had taken a long time and procedure to prepare the starch samples involved several steps, while $^1\text{H-NMR}$ method has taken a short time and better precision can be obtained. However, $^1\text{H-NMR}$ instrument cost high expense but it gives more accurate results than colourimetric method. This similar technique had been reported in different types of starch by the other researchers (18,19). In the present, colourimetric method is still used to determine the degree of substitution of hydroxypropylated starch.

Accordingly, it showed that $^1\text{H-NMR}$ spectroscopy can be used as an easy and accurate tool for analysis of degree of substitution. This method had saved time for determining degree of substitution.

4.11 Examination of Physical Properties

4.11.1 Gelatinization Temperature

Native tapioca starch begins to gelatinize between $59-70^\circ\text{C}$. Different starches exhibit different gelatinization temperature. The gelatinization range refers to the temperature range over which all the starch granules are fully swollen. The gelatinization of starch was observed by increased viscosity of the starch slurry. As the starch undergoes hydroxypropyl substitution, the gelatinization temperature is decreased. Therefore, another indirect method for determining degree of substitution of hydroxypropylated tapioca starch is the starch gelatinization temperature drop. The Brabender Viscoamylograph is a convenient instrument to use for determining the decrease of gelatinization temperature (6).

Table 4.10 Effect of degree of substitution on gelatinization temperature of hydroxypropylated tapioca starch.

Samples	Gelatinization Temperature (°C)	Peak Viscosity (BU)	Viscosity at 95 °C (BU)	Viscosity after holding at 95 °C for 30 min (BU)	Viscosity after cooling to 50 °C (BU)
Native tapioca	69.5	625	330	200	320
DS=0.0664	60.5	710	400	310	450
DS=0.0752	60.5	715	400	320	390
DS=0.0927	59.0	720	420	340	490
DS=0.1013	54.5	730	390	320	520
DS=0.2130	54.0	650	315	255	380

Table 4.10 showed the Brabender characteristics of the hydroxypropylated tapioca starches having degree of substitution of 0.0664, 0.0752, 0.0927, 0.1013 and 0.2130 compared with native tapioca starch. It was observed that all the hydroxypropylated starches had lower gelatinization temperature than their native starch. It also showed that the gelatinization temperature decreased gradually with an increase of degree of substitution. This can be easily explained by the fact that the hydroxypropyl group is hydrophilic in nature, which facilitates the penetration of water molecules inside the starch granule by weakening the internal bond holding the granule together. Then it increases the ease of hydration of the starch granule. The similar observation had been reported by the other researchers (14, 16, 22).

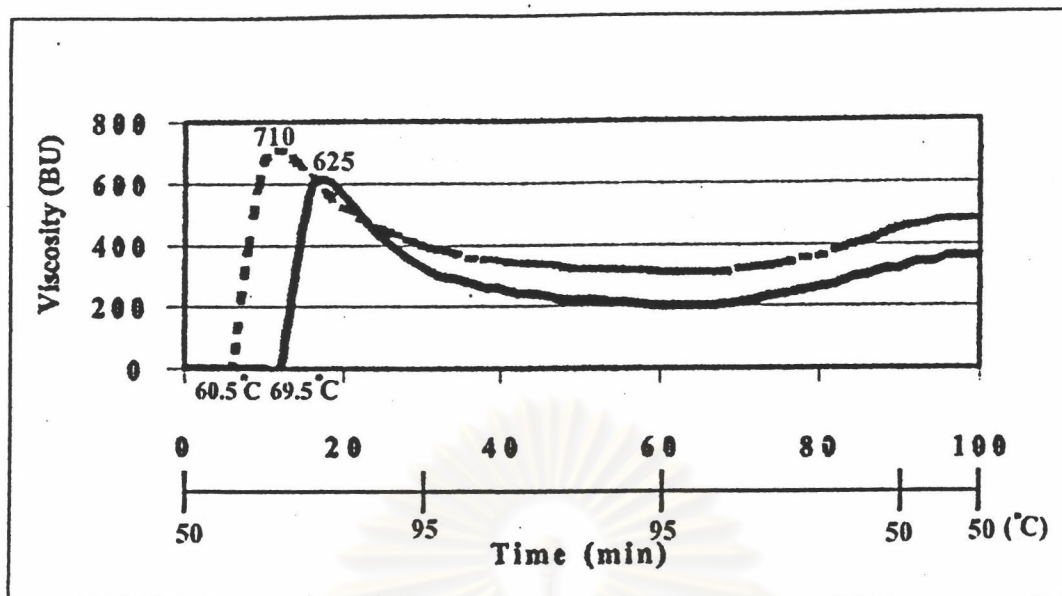


Figure 4.10 Brabender Viscograph of hydroxypropylated tapioca starch

(DS = 0.0664) compare with native tapioca starch (rate 1.5°C/min).

— Native tapioca starch Hydroxypropylated tapioca starch

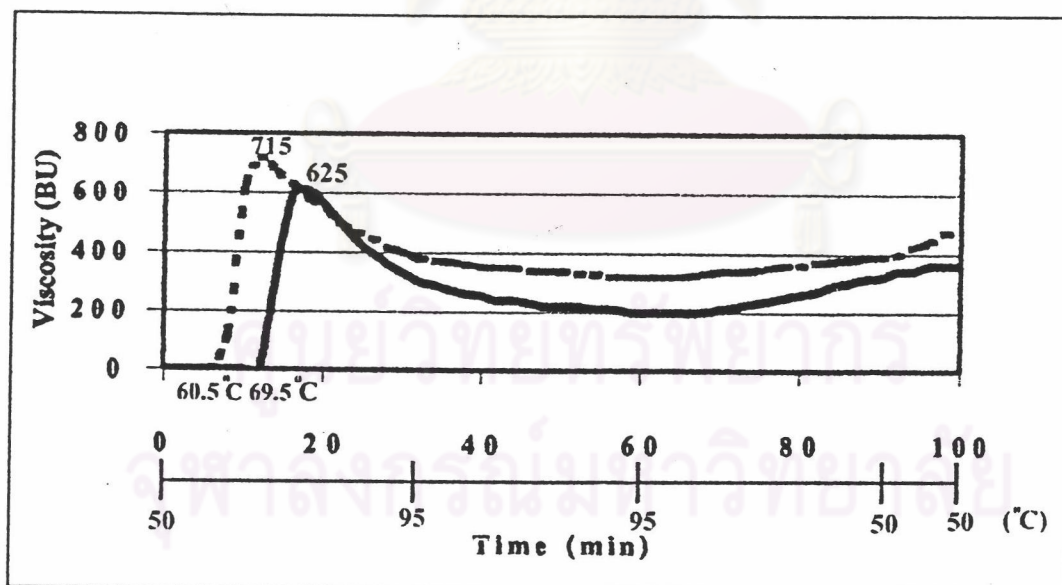


Figure 4.11 Brabender Viscograph of hydroxypropylated tapioca starch

(DS = 0.0752) compare with native tapioca starch (rate 1.5°C/min).

— Native tapioca starch Hydroxypropylated tapioca starch

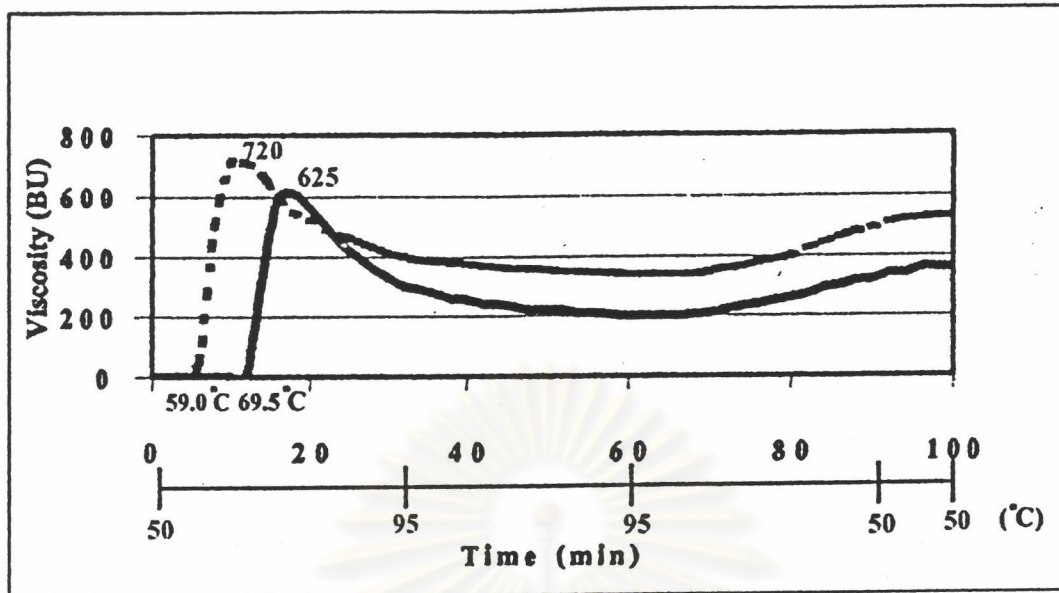


Figure 4.12 Brabender Viscograph of hydroxypropylated tapioca starch
(DS = 0.0927) compare with native tapioca starch (rate 1.5°C/min).
— Native tapioca starch Hydroxypropylated tapioca starch

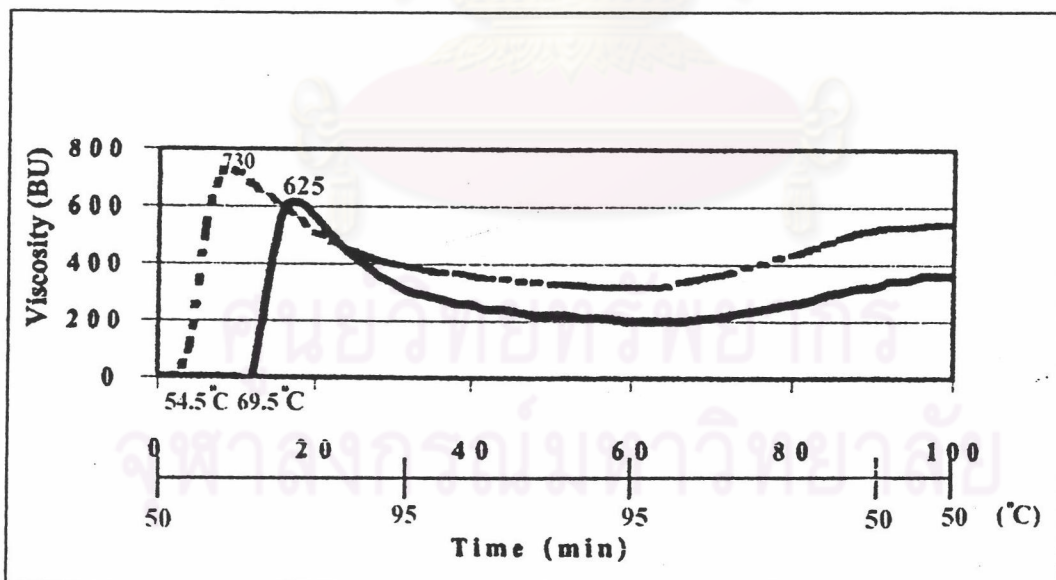


Figure 4.13 Brabender Viscograph of hydroxypropylated tapioca starch
(DS = 0.1013) compare with native tapioca starch (rate 1.5°C/min).
— Native tapioca starch Hydroxypropylated tapioca starch

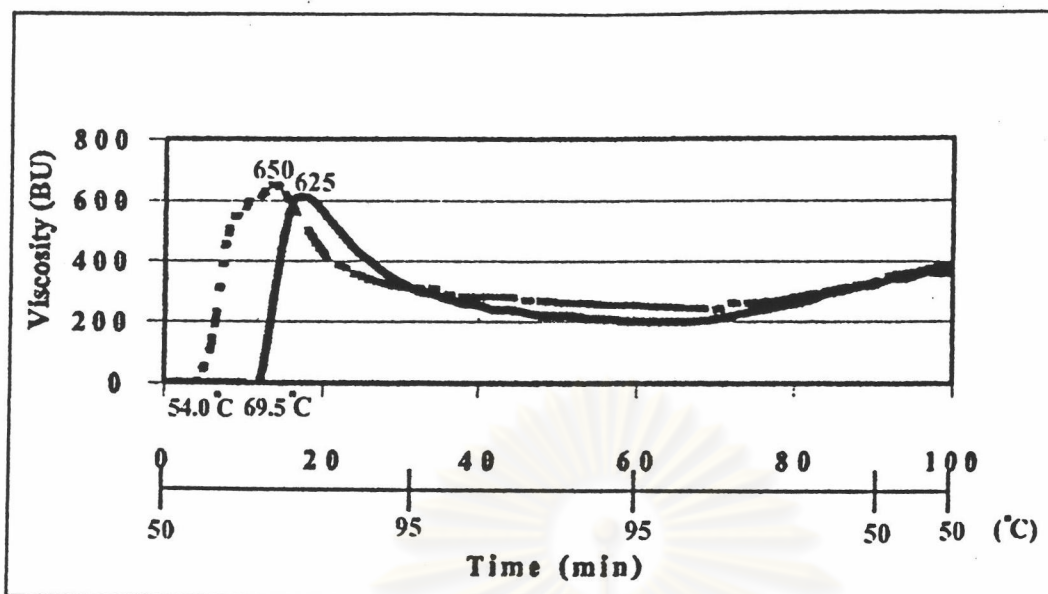


Figure 4.14. Brabender Viscograph of hydroxypropylated tapioca starch

(DS = 0.2130) compare with native tapioca starch (rate 1.5°C/min).

— Native tapioca starch Hydroxypropylated tapioca starch

From Table 4.11 (DS 0.0664, 0.0752, 0.0927 and 0.1013) and Figures 4.10 - 4.13, it also indicated that the gel from hydroxypropylated starch was highly viscous as compared to native tapioca starch. This was probably depended on the hydroxypropyl group in modified starch. The hydroxypropyl group caused loosening of the network and allowing additional water to enter starch granule. Thus the increase in hydration volume resulted in higher viscosity. In this case, cohesive forces in the starch granular structure still remained after hydroxypropylated groups slightly occurred. But hydroxypropylated tapioca starch of degree of substitution 0.2130 (Figure 4.14) showed remarkable decrease in peak viscosity as compared to the other hydroxypropylated starches probably caused by very weak cohesive force in the granular structure because the amount of hydroxypropyl groups was higher than previous reactions. The similar observation had been reported by J. Pal (16).

As heating was continued to 95°C, the starch granules tended to rupture, collapse and fragment released the smaller molecules of the starch chain. Then the viscosity dropped. When the gelatinized starch was cooled to 50°C, the viscous tended to rise, caused by molecular association from amylose chains. It formed a network that increased the viscosity (16).

Consequently, the gelatinization temperature of hydroxypropylated tapioca starch was dropped. The peak viscosity increased because of hydrophilic nature of hydroxypropyl groups. Therefore, the Brabender Viscoamylograph was the one of all methods to use for determining degree of substitution of hydroxypropylated tapioca starch.

4.11.2 Moisture

Hydroxypropylated tapioca starches from this research had moisture between 12-17% by dry starch weight. This was probably depended on the physical properties of these starches because the swelling power of starch was increased by hydroxypropylation:

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จุฬาลงกรณ์มหาวิทยาลัย

4.11.3 Granule Morphology

SEM used to determine granule morphology of hydroxypropylated tapioca starch. The granule morphology of tapioca starch before and after hydroxypropylation was presented in Figure 4.15. The size, shape and the granule surface remained unchanged on hydroxypropylation. It showed that the starch granules were not damaged after hydroxypropylation had completed.

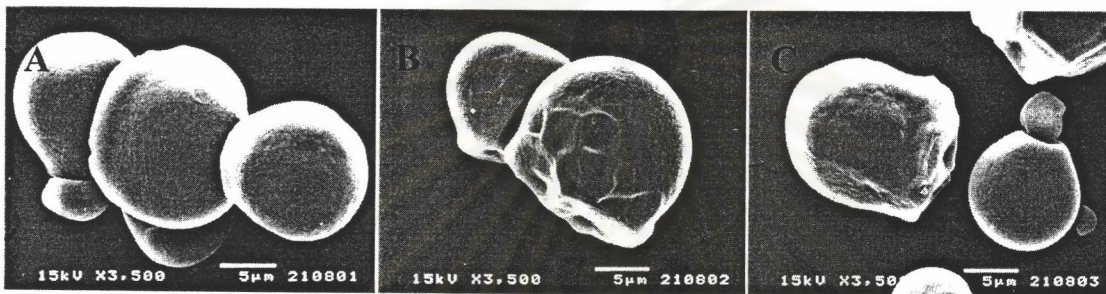


Figure 4.15 Scanning electron micrographs of native (A), hydroxypropylated: preparing in water medium (B) and hydroxypropylated: preparing in aqueous ethanol medium (C) tapioca starch granules.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย