

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Research Objective

As described in Chapter II, previous studies on graft copolymerization of styrene onto starch were concentrated on method using ^{60}Co -irradiation initiation. However, several approaches have indicated that starch-*g*-polystyrene can also be prepared by free radical reactions using other types of initiation such as thermal initiation and redox initiation. With concerning of safety, cost and simplicity of the preparation method, the main objective of this research was to develop such method that can be used to synthesize starch graft copolymers.

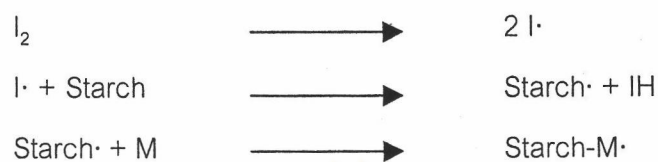
The following sections will cover the synthesis and characterization of starch-*g*-polystyrene copolymers prepared via free radical polymerization using benzoyl peroxide as an initiator in aqueous medium. Spectroscopic and physical properties of these copolymers and grafted polystyrenes will also be discussed.

4.2 Mechanism and Products of Graft Copolymerization

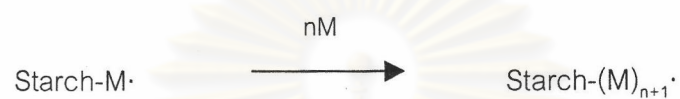
The following mechanism is proposed for graft copolymerization of styrene monomer onto starch using BPO as an initiator. Several reactions can occur during the process. It can be seen that free radicals obtained from BPO dissociation can react either with styrene monomer via addition to carbon-carbon double bond or with starch via hydrogen abstraction (or hydrogen atom transfer). Then propagation occurs. After termination or chain transfer reaction, several products including starch-*g*-polystyrene, homopolystyrene and crosslinked starch are obtained.

In order to obtain starch-*g*-polystyrene copolymer, the following reactions are preferred.

Initiation:



Propagation:



Termination:

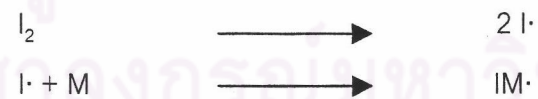


Chain Transfer Reaction:

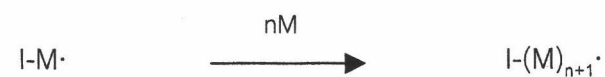


However, the following side reactions can occur and this results in the formation of homopolystyrene.

Initiation:



Propagation:



Termination:



Chain Transfer Reaction:



The crosslinked starch may be possibly formed from termination by combination as shown below.

Termination:



According to the above mechanism, the product obtained from graft copolymerization process would mostly be a mixture of starch-g-polystyrene and homopolystyrene. From the experiment, this product was hard, white, and opaque solid. After homopolystyrene removal by soxhlet extraction, the resulted product expected to be starch-g-polystyrene became soft, white, and opaque solid. In order to characterize the starch-g-polystyrene, acid hydrolysis was employed and the brown translucent residue expected to be grafted polystyrene was obtained. By using some characterization techniques, the existances of these products were proved as presented in later sections.

4.3 Effects of Mixing Methods, BPO Purity and Reaction Parameters on Graft Copolymerization

4.3.1 Effect of Mixing Methods

Many reports suggested that the percent of grafting was higher when the reaction temperatures were near or above gel temperature of the starch [43, 56, 60, 61]. Therefore, three different mixing methods were employed as previously mentioned

in Chapter III (Method A: using the starch pre-gel and adding the initiator at room temperature, Method B: using the starch pre-gel and adding the initiator at the pre-gel temperature, and Method C: mixing all the raw materials at the same time). Table 4.1 shows percent add-on, percent conversion, amount of homopolystyrene formed, grafting efficiency, grafting ratio, and yield of starch-g-polystyrene copolymers prepared from 5 g of starch, 5 g of styrene monomer and 1.0 g of unpurified BPO using reaction time of 2 hours and reaction temperature of 80°C with different mixing methods.

Table 4.1 Grafting characteristics of starch-g-polystyrene copolymers prepared with different mixing methods

Mixing Method	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
A	28.04	96.93	61.76	38.24	37.04	86.42
B	20.49	83.45	69.77	30.23	25.22	82.75
C	25.76	94.23	65.28	34.72	32.70	85.75

It can be seen that the best mixing method is Method A since it gives highest percent add-on (28.04%) and percent grafting efficiency (38.24%). This is because, at pre-gel stage, the starch chains completely expand so the probability of hydrogen abstraction from starch chains would increase. However, adding BPO at pre-gel temperature (80°C) as was done in Method B results in the lowest percent add-on (20.49%) and percent grafting efficiency (30.23%). This may be due to the cage effect caused by the viscous starch gel that results in recombination of the radicals formed from BPO dissociation; consequently, the number of the radicals involving in initiation process decreases. In the case of Method C, this method gives the moderate results but it seems to be the simplest and easiest method because less time and energy are consumed. In addition, this method has a potential to apply for pilot scale. Therefore,

this mixing method was used to synthesize starch-*g*-polystyrene copolymers for further studies.

4.3.2 Effect of BPO Purity

Table 4.2 shows grafting characteristics of starch-*g*-polystyrene copolymers prepared from 5 g of starch and 5 g of styrene monomer using reaction time of 2 hours and reaction temperature of 80°C with 1.0 g of unpurified and purified BPO.

Table 4.2 Grafting characteristics of starch-*g*-polystyrene copolymers prepared with unpurified and purified BPO

Type of BPO	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
Unpurified	25.76	94.23	65.28	34.72	32.70	85.75
Purified	28.28	96.56	61.95	38.04	36.76	86.37

It was found that when purified BPO was used, the obtained copolymer had better grafting characteristics. This is because the impurities in BPO can possibly destroy the radicals present in the system so the number of the radicals involving in initiation process decrease. From this result, it was preferred to use purified BPO to prepare starch-*g*-polystyrene copolymers for further studies.

4.3.3 Effect of Reaction Parameters

The effects of several reaction parameters including initiator concentration, reaction temperature, reaction time, and ratio of starch and styrene monomer were studied. The results are reported below.

4.3.3.1 Effect of Initiator Concentration

Table 4.3 and Figure 4.1 show all grafting characteristics of starch-g-polystyrene copolymers prepared from 5 g of starch and 5 g of styrene monomer using reaction time of 2 hours and reaction temperature of 80°C with different amounts of BPO. It can be seen that percent add on and percent grafting efficiency continuously increase as the concentration of BPO increases. This is because more free radicals are formed when higher amounts of BPO is used. As a result, the probability of graft initiation increases. But as the amounts of BPO are higher than 0.5 g, both percent add on and percent grafting efficiency significantly decrease. This may be because at high BPO concentration, too many free radicals are formed from BPO dissociation; therefore, recombination of these free radicals is more thermodynamically favorable than hydrogen abstraction which results in graft initiation. Consequently, the probability of graft initiation decreases. Similar observation has been reported by Misra et al. [39]. Thus, it can be concluded that the optimum weight of BPO should be 0.5 g.

Table 4.3 Grafting characteristics of starch-g-polystyrene copolymers prepared with different amount of BPO

Weight of Initiator (g)	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
0.01	4.14	55.90	92.59	7.41	4.14	75.81
0.05	17.19	62.77	68.59	31.41	19.72	78.40
0.1	31.19	87.34	52.71	47.29	41.30	88.14
0.2	32.48	88.11	50.53	49.47	43.55	87.54
0.3	33.35	92.10	50.71	49.29	45.38	88.70
0.4	34.03	92.75	48.86	51.14	47.43	88.71
0.5	35.87	95.64	46.09	53.91	51.26	88.08
1.0	28.28	96.56	61.95	38.04	36.76	86.37
1.5	20.23	106.15	77.14	22.86	24.24	87.67
2.0	16.04	115.95	84.31	15.69	18.80	89.39

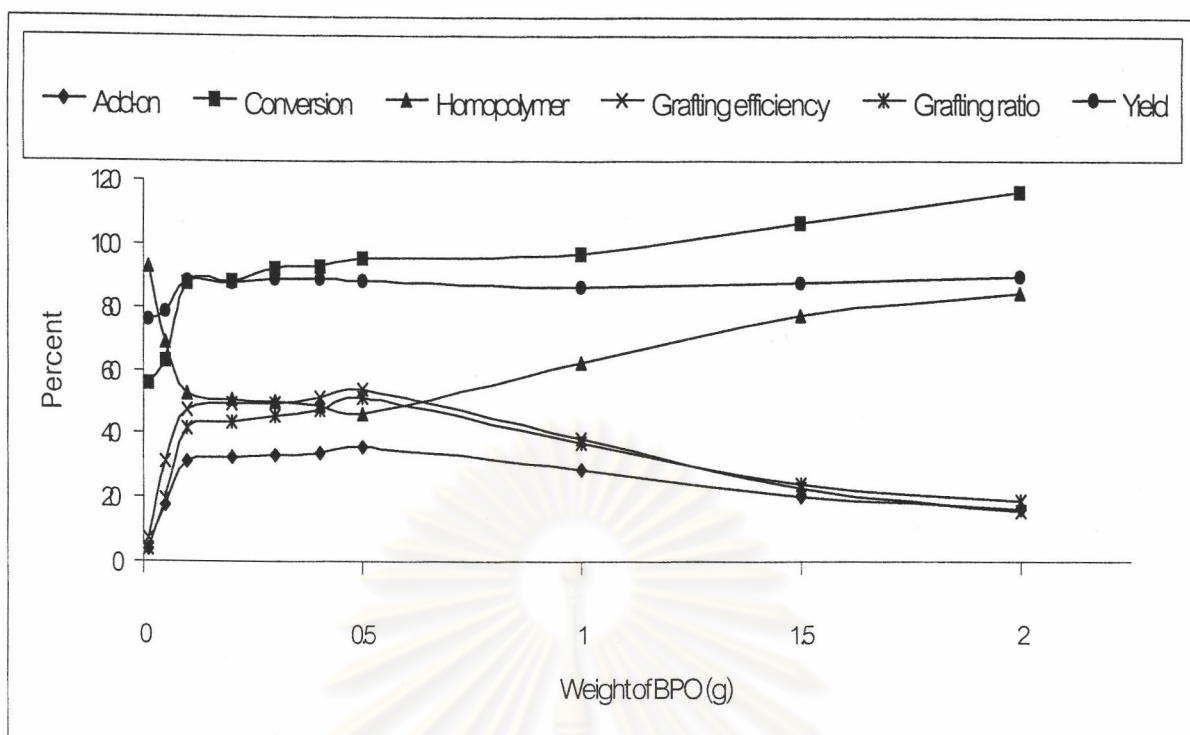


Figure 4.1 Grafting characteristics of starch-g-polystyrene copolymers prepared with different amount of BPO.

4.3.3.2 Effect of Reaction Time

To study the effect of reaction time, starch-g-polystyrene copolymers were prepared from 5 g of starch, 5 g of styrene monomer and 0.5 g of BPO using reaction temperature of 80°C and reaction time of 1, 2 and 3 hours. Table 4.4 and Figure 4.2 show that maximum grafting characteristics can be achieved at reaction time of 2 hours. However, at reaction time of 1 hour, they are very low. Percent conversion of 39.79% indicates that the reaction were far from completion. On the other hand, at reaction time of 3 hours, most grafting characteristics are slightly lower than those obtained with reaction time of 2 hours. This may be due to thermal degradation of polymeric chains. From these results, it can be concluded that the reaction time of 2 hours is suitable for this graft copolymerization system.

Table 4.4 Grafting characteristics of starch-*g*-polystyrene copolymers prepared with different reaction times

Reaction time (hour)	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
1	29.26	39.79	52.80	47.19	39.76	85.97
2	35.87	95.64	46.09	53.91	51.26	88.08
3	33.08	89.55	49.86	50.14	44.87	86.68

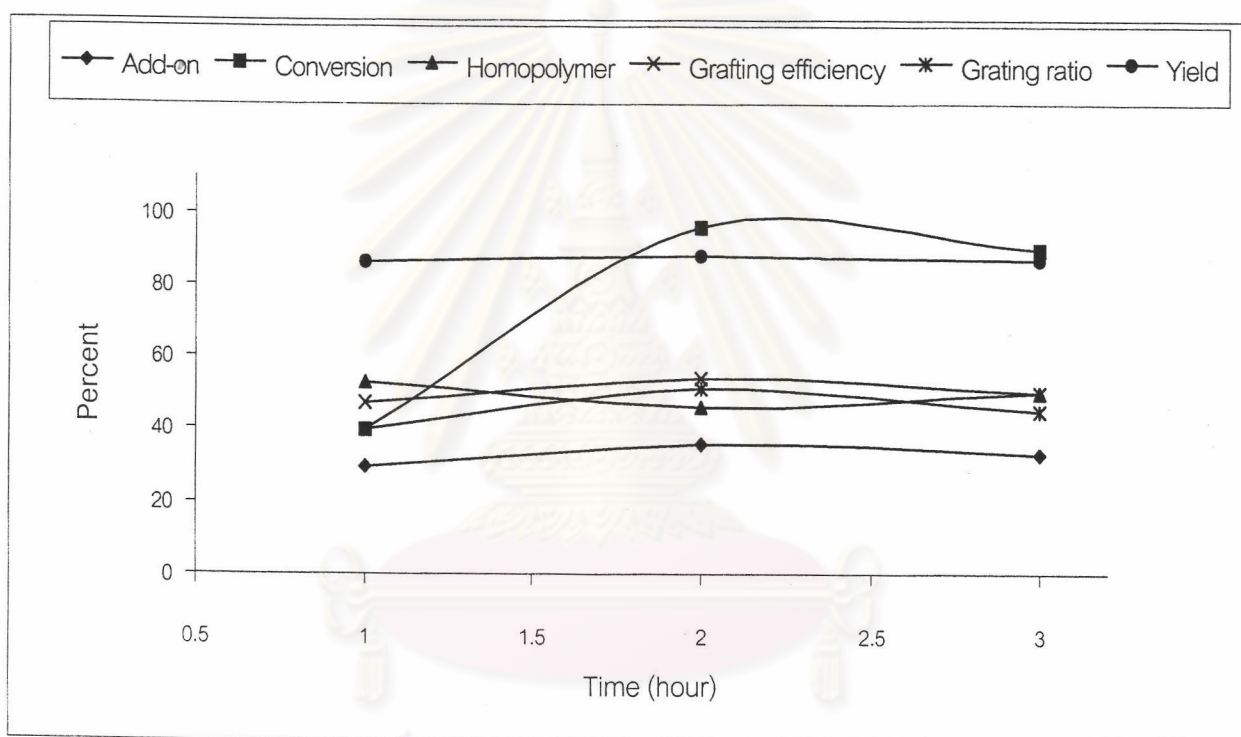


Figure 4.2 Grafting characteristics of starch-*g*-polystyrene copolymers prepared with different reaction times.

4.3.3.3 Effect of Reaction Temperature

To study the effect of reaction temperature, starch-*g*-polystyrene copolymers were prepared from 5 g of starch, 5 g of styrene monomer and 0.5 g of BPO using reaction time of 2 hours and reaction temperature of 70, 80 and 90°C. Table 4.5 and Figure 4.3 show grafting characteristics of the obtained copolymers.

Table 4.5 Grafting characteristics of starch-g-polystyrene copolymers prepared with different reaction temperatures

Reaction Temperature (°C)	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
70	22.49	77.73	63.36	36.63	28.47	83.68
80	35.87	95.64	46.09	53.91	51.26	88.08
90	31.79	92.11	53.30	46.67	42.99	87.70

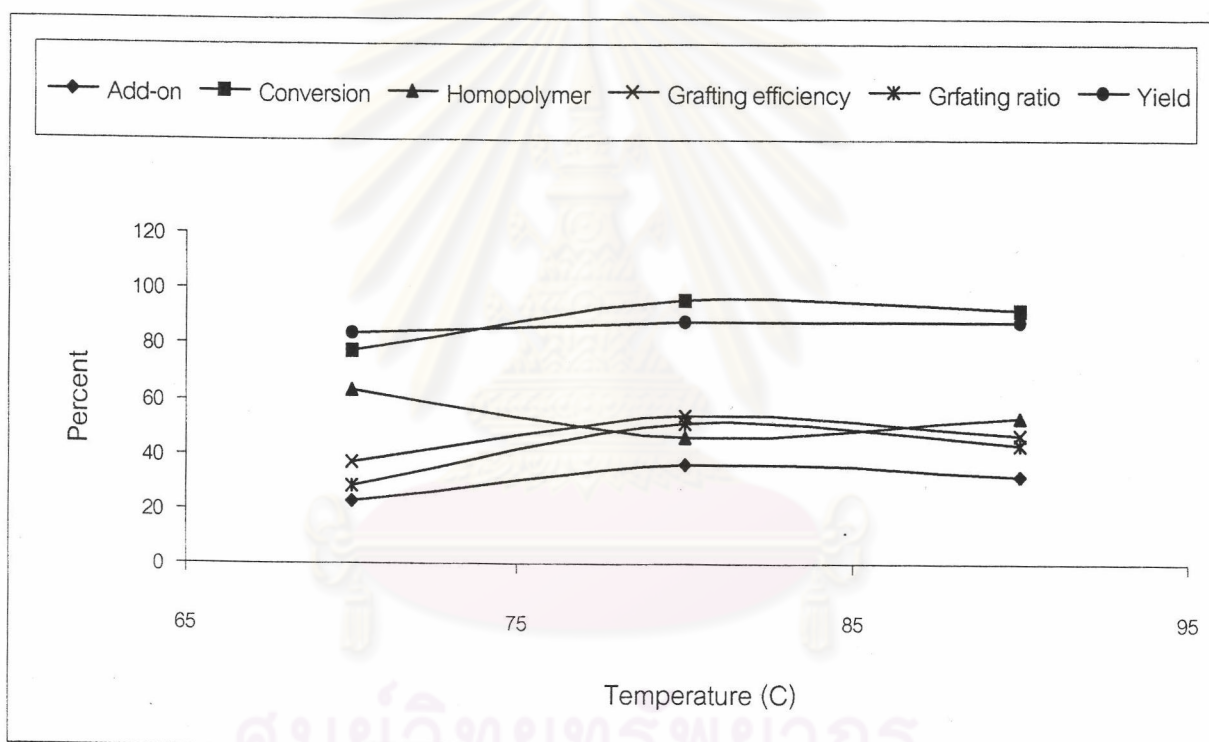


Figure 4.3 Grafting characteristics of starch-g-polystyrene copolymers prepared with different reaction temperatures.

It can be seen that the maximum grafting characteristics can be achieved at 80°C which is the most suitable temperature for dissociation of BPO into free radicals. Therefore, more free radicals are obtained at this temperature than at lower temperature such as 70°C. Furthermore, 70°C is closed to gel temperature of starch so the viscosity of the system is higher than that at 80°C. Consequently, cage effect in the

former system is higher. At 90°C, grafting characteristics of the copolymer are lower than those of copolymer prepared at 80°C. This may be due to an acceleration of some termination processes whose exact nature remains to be elucidated [38].

4.3.3.4 Effect of Ratio of Starch and Styrene Monomer

To study the effect of the ratio of styrene monomer and starch used in grafting, starch-g-polystyrene copolymers were prepared using different ratios of both reactants and the same amount of BPO (0.5 g). The reaction time and the reaction temperature for all systems were 2 hours and 80°C, respectively. The results are shown in Table 4.6 and Figure 4.4.

Table 4.6 Grafting characteristics of starch-g-polystyrene copolymers prepared with different ratios of starch and styrene monomer

Ratio of Starch:Styrene monomer (g:g)	Percent Add-on	Percent Conversion	Percent Homopolymer Formed	Percent Grafting Efficiency	Percent Grafting Ratio	Percent Yield
1:9	23.71	73.19	95.32	4.68	30.75	72.15
2:8	29.77	69.37	84.77	15.23	42.13	71.77
3:7	36.85	77.58	69.02	30.98	56.02	79.20
4:6	35.74	79.09	53.41	46.59	55.27	83.00
5:5	35.87	95.64	46.09	53.91	51.26	88.08
6:4	25.23	98.03	49.13	50.87	33.25	93.41
7:3	16.99	96.83	50.84	49.16	20.40	94.20
8:2	10.55	99.05	52.46	47.54	11.78	94.70
9:1	-	-	-	-	-	-

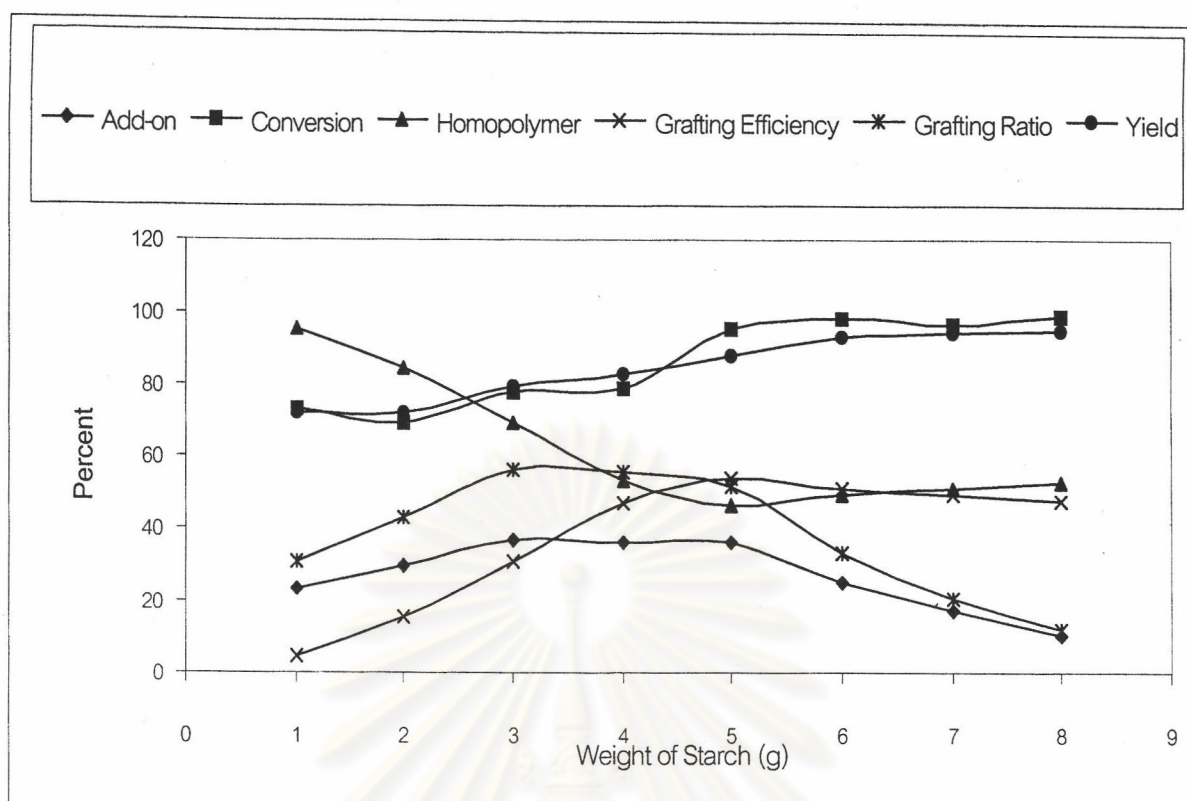


Figure 4.4 Grafting characteristics of starch-g-polystyrene copolymers prepared with different ratios of starch and styrene monomer.

As shown in Table 4.6 and Figure 4.4, the suitable ratio that gives the best grafting characteristics is 5:5. Since the viscosities of the systems increase with increasing the amount of the starch, it is more difficult for free radicals to diffuse to starch backbone. Therefore, grafting initiation decreases. On the other hand, increasing the amount of styrene monomer means increasing the probability for homopolymerization; consequently, initiation of grafting decreases.

4.4 Characterization of Graft Copolymer

As previously mentioned in Section 4.2, the product obtained from graft copolymerization process would be a mixture of starch-g-polystyrene and homopolystyrene. Therefore, soxhlet extraction was used to separate these two components. Then acid hydrolysis was used to hydrolyze starch-g-polystyrene in order

to obtain grafted polystyrene. All polymers were then characterized by the several techniques and the results are given as follows:

4.4.1 Analysis of Chemical Structures

Fourier Transform Infrared Spectroscopy (FT-IR) was used to analyze chemical structures of cassava starch powder, cassava starch gel, polystyrene reference, starch-g-polystyrene copolymer before extraction, the graft copolymer after extraction, and the hydrolyzed product as shown in Figure 4.5 (a) to 4.5(f), respectively.

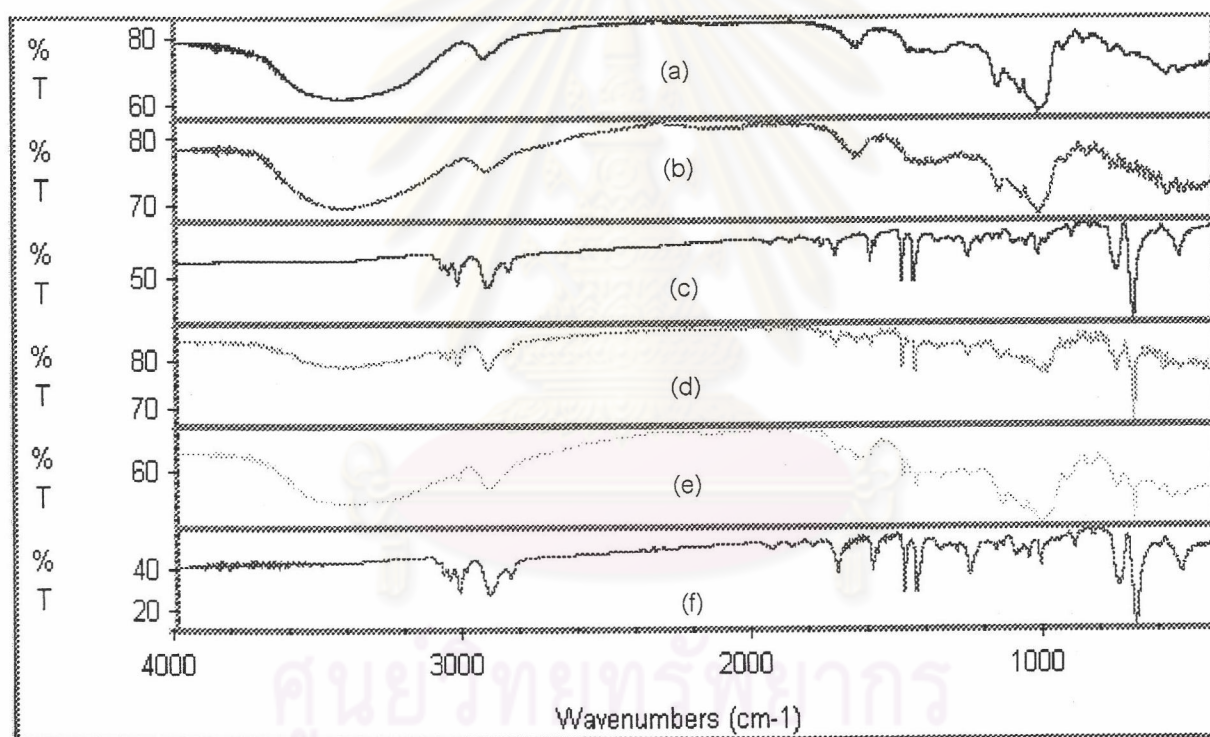


Figure 4.5 Infrared spectra of (a) starch powder, (b) starch gel, (c) polystyrene reference, (d) starch-g-polystyrene copolymer before extraction, (e) starch-g-polystyrene copolymer after extraction, and (f) hydrolyzed product.

It can be seen that infrared spectra of cassava starch in the powder and gel forms are identical. They show the O-H stretching peak at $3300\text{--}3500\text{ cm}^{-1}$, the C-H

stretching peak of CH_2 group at $2850\text{-}2950\text{ cm}^{-1}$, and the C-O stretching peak at $950\text{-}1200\text{ cm}^{-1}$. The spectrum of polystyrene reference indicates the peaks corresponding to aromatic ring at 3050 cm^{-1} , 1650 cm^{-1} , and $650\text{-}800\text{ cm}^{-1}$.

Before soxhlet extraction, it is clearly seen that the product shows the characteristic peaks of both starch and polystyrene. This suggests the possibility of grafting. After soxhlet extraction, those characteristic peaks are still observed but with lower intensities of those peaks corresponding to polystyrene and higher intensities of those peaks corresponding to starch. This indicates that homopolystyrene was removed. After acid hydrolysis of the copolymer, the hydrolyzed product gives the spectrum which resembles to homopolystyrene reference. This suggests that this hydrolyzed product is grafted polystyrene. From this results, it can be concluded that graft copolymer of starch and styrene monomer was achieved.

4.4.2 Determination of Molecular Weight Distribution of Grafted Polystyrene

By using GPC, it was found that the molecular weights and molecular weight distributions of grafted polystyrene and homopolystyrene were comparable as shown in Table 4.7. This suggests that once the initiations occur, the propagation rates of both polystyrenes are the same.

Table 4.7 GPC characteristics of homopolystyrene and grafted polystyrene formed in starch-g-polystyrene copolymerization

	M_n	M_w	M_z	M_{z+1}	Polydispersity
Homopolystyrene	4917	11984	23538	39541	2.44
Grafted polystyrene	4761	10103	17354	26228	2.12

4.4.3 Determination of Grafting Frequency

The grafting frequency, being defined as the number of anhydroglucose units between two polystyrene chains which graft onto starch backbone, can be determined from the following equation [59].

$$\text{Grafting frequency} = \frac{(100 - \% \text{add-on}) / 162}{\% \text{add-on} / \text{MW graft}}$$

The grafting frequency of this copolymer is 111.50. This means that at approximately every 111 anhydroglucose units the polystyrene chain can be observed.

4.4.4 Thermal Properties Measurements

4.4.4.1 Thermogravimetric Analysis (TGA)

TGA technique was used to determine percent weight loss and decomposition temperature (T_d) of the polymers. All TGA results and TGA thermograms of the samples are shown in Table 4.8 and Figures 4.6 to Figure 4.11, respectively.

Thermograms of starch powder and starch gel as shown in Figures 4.6 and 4.7, respectively, are comparable. They both show two decomposition stages. The initial weight loss of both starches begins at approximately 50°C. This corresponds to the loss of moisture absorbed in both starches. Further weight loss occurs at approximately 310°C which is a decomposition temperature of the starch. At 800°C, less than 1.5% of starch powder and about 8% of starch gel do not decompose. On the other hand, TGA thermogram of homopolystyrene reference shows that polystyrene has only one decomposition stage which is at 390°C and it completely decomposes at 450°C.

Table 4.8 Thermogravimetric data of all polymers involving in graft copolymerization of starch and styrene monomer

Polymer	Number of decomposition stage	Onset decomposition temperature (°C)	% Weight loss	% Residue at 800°C
Starch powder	1	50	6.7	1.5
	2	312.8	91.8	
Starch gel	1	50	6.6	8.5
	2	308.6	92.9	
Polystyrene reference	1	389.4	100.4	0
StOH-g-St [#] with homopolystyrene	1	50	4.6	7
	2	303.0	35.8	
	3	387.6	52.5	
StOH-g-St [#] without homopolystyrene	1	50	4.3	8.5
	2	200	3.3	
	3	301.8	53.7	
	4	393.0	28.9	
Grafted polystyrene	1	372.9	100.3	0

Where [#] represents starch-g-polystyrene copolymer

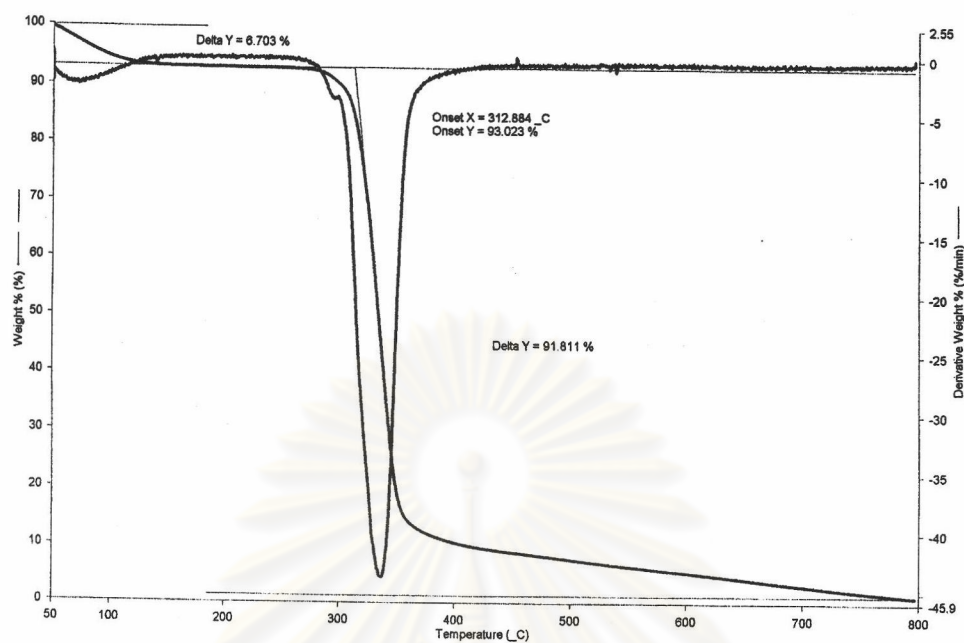


Figure 4.6 TGA thermogram of cassava starch powder.

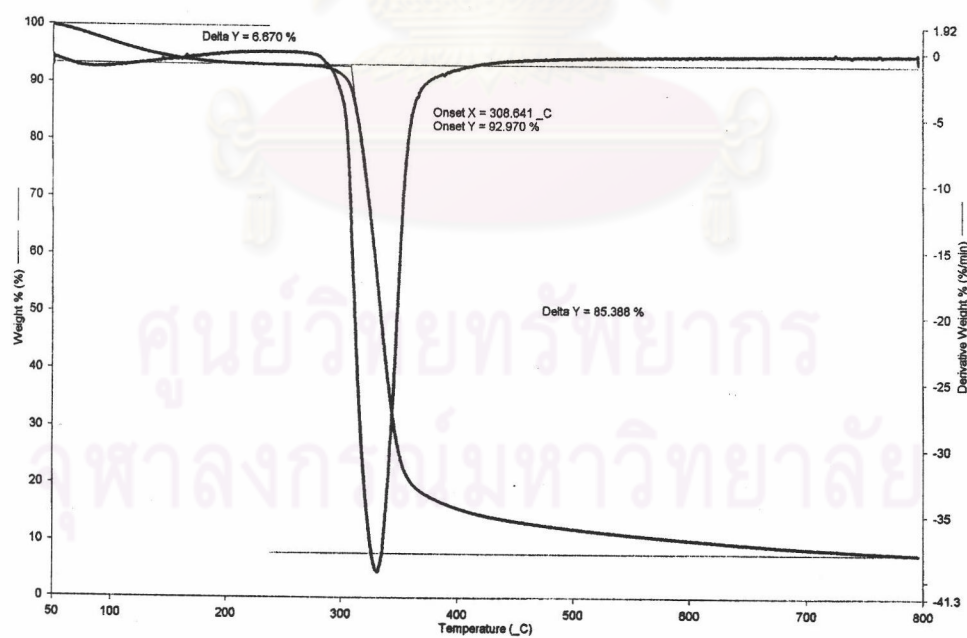


Figure 4.7 TGA thermogram of cassava starch gel.

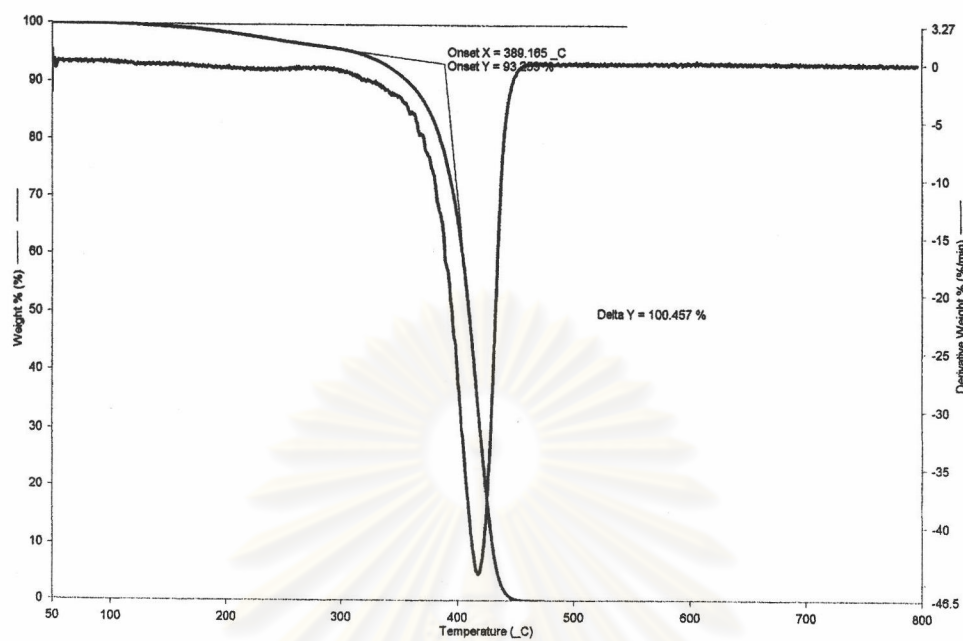


Figure 4.8 TGA thermogram of polystyrene reference.

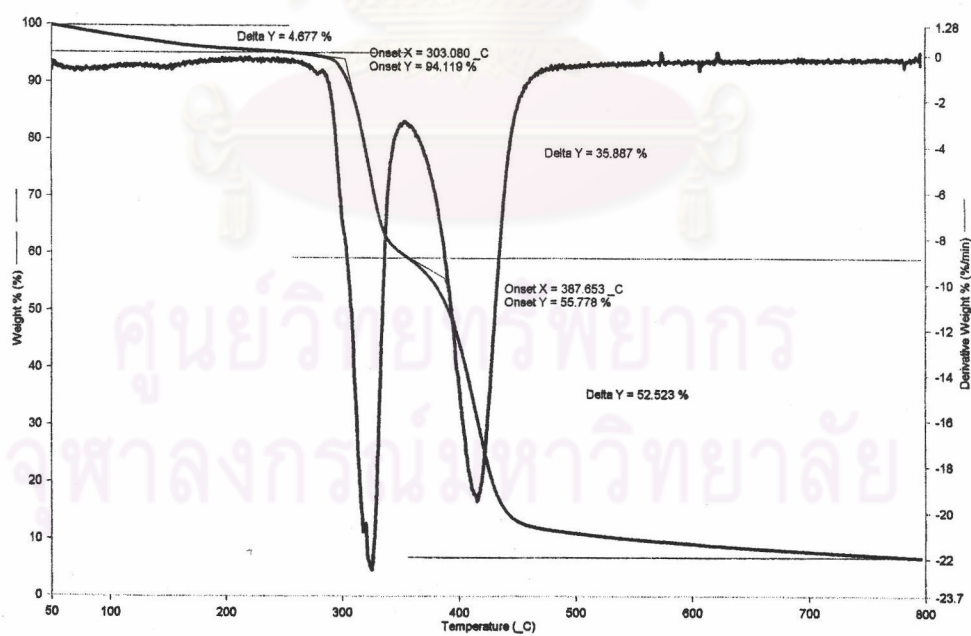


Figure 4.9 TGA thermogram of starch-g-polystyrene copolymer with homopolystyrene.

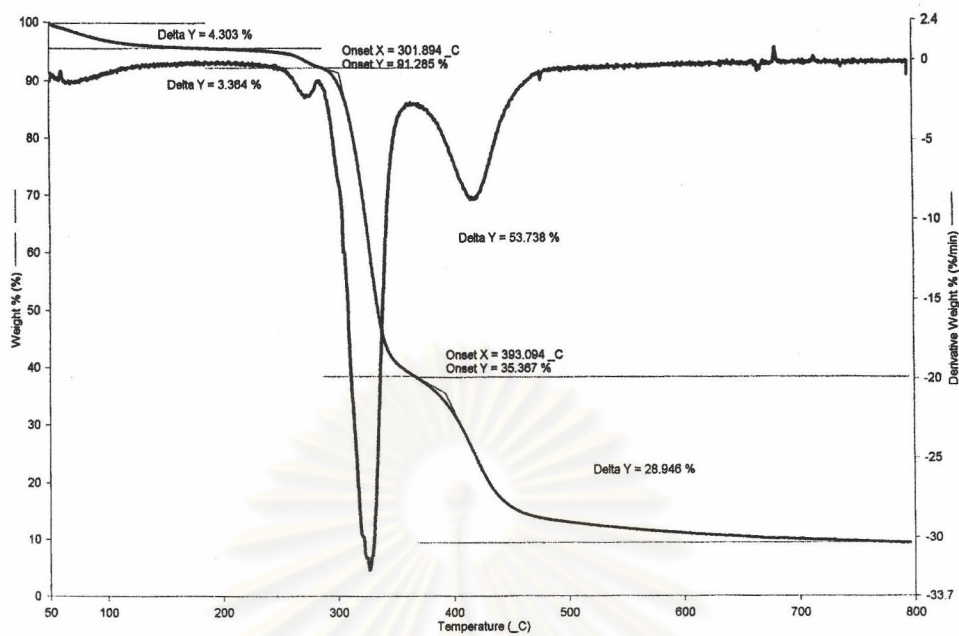


Figure 4.10 TGA thermogram of starch-g-polystyrene copolymer without homopolystyrene.

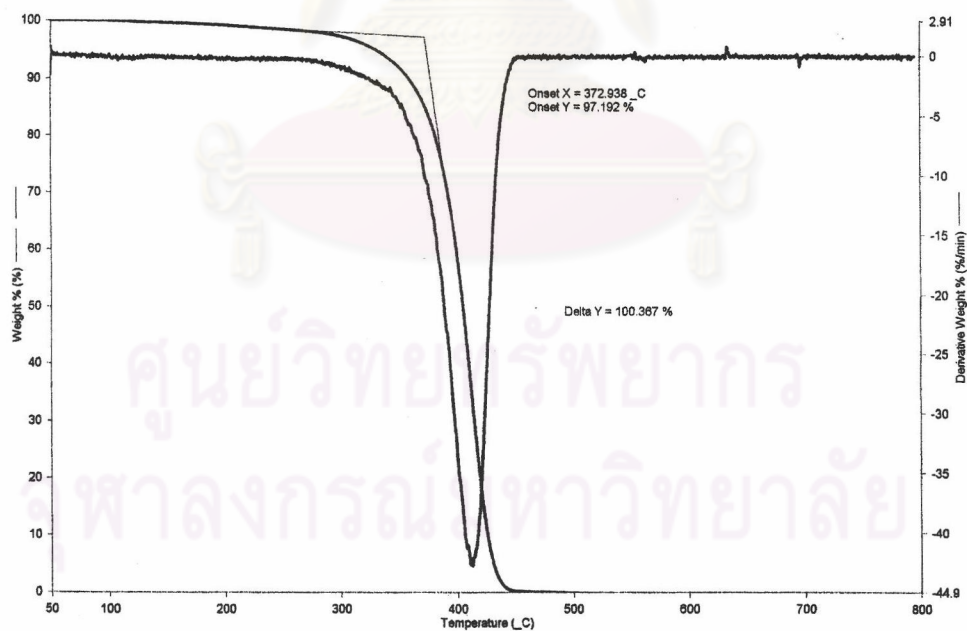


Figure 4.11 TGA thermogram of grafted polystyrene.

Three decomposition stages were observed for starch-*g*-polystyrene copolymer with homopolystyrene (before extraction) as shown in Figure 4.9. The initial weight loss at 50°C is due to the loss of the moisture absorbed in starch portion. The next decomposition stage is at 303°C. This stage corresponds to the decomposition of starch portion of the graft copolymer. The last decomposition stage at 387°C is a result of a decomposition of polystyrene portion of the graft copolymer. Starch-*g*-polystyrene copolymer without homopolystyrene have four decomposition stages (Figure 4.10). The loss of moisture absorbed in starch portion results in the first decomposition stage whereas the small weight loss at second stage may be caused by decomposition of some impurities. The decompositions of starch and polystyrene occur at third stage (303°C) and fourth stage (387°C), respectively. It was also observed that the ratio of weight loss in third and fourth stages can be used to determine percent add-on and grafting ratio as follows:

$$\text{Percent add-on} = \frac{\text{weight loss in stage four}}{\text{weight loss in stage three} + \text{weight loss in stage four}}$$

$$\text{and Grafting ratio} = \frac{\text{weight loss in stage four}}{\text{weight loss in stage three}}$$

Table 4.9 shows the results of percent add-on and grafting ratio calculated by the theoretical method [15, 65] and by TGA results. It can be seen that the values obtained from both methods are comparable. This suggests that TGA analysis can be used to determine percent add-on and grafting ratio of a graft copolymer.

Table 4.9 Percent add-on and grafting ratio of starch-*g*-polystyrene copolymer

	Theoretical Method	TGA results	Different of Calculation
Percent Add-on (%)	35.87	35.01	0.86
Grafting Ratio (%)	51.26	53.87	2.61

However, it can be seen that the graft copolymer has lower decomposition temperature than starch powder and starch gel. This result is in contrast with the result obtained by Vilas and Vidyagauri who grafted acrylamide onto granular maize starch [44]. Since using granular form of starch results in grafting only onto the surface of the granules, the grafted polyacrylamide can reduce the direct thermal attack at the starch molecules. On the other hand, using starch powder or starch gel as done in this research increases the possibility of polystyrene chains to graft onto starch backbone at random positions. Therefore, the starch molecules do not closely pack as they do before grafting and this makes thermal attack become easier. Consequently, the decomposition temperature of starch-g-polystyrene is lower than that of cassava starch.

It can be seen from Figure 4.11 that grafted polystyrene shows one decomposition stage at 372°C which is lower than that of polystyrene reference (390°C). This may be because the acid and the temperature (about 110°C) used for starch hydrolysis decrease the stability of the grafted polystyrene.

4.4.4.2 Differential Scanning Calorimetry (DSC)

DSC is an important tool for evaluating the glass transition temperature (T_g) of a polymer. The glass transition temperature can be determined by two methods: (i) using the onset point of the transition and (ii) using the mid point of the transition [44]. In this research, the second method was used to determine T_g . Two heating cycles were employed to all polymers except for starch powder and starch gel. This is because second heating cycle provides more information on reversible transitions by erasing any prior thermal histories associated with the sample. The results are concluded in Table 4.10 and DSC thermograms of all samples are shown in Figures 4.12 - 4.17.

Table 4.10 T_g of the polymers involving in graft copolymerization of starch and styrene monomer

Polymer	T_g at 1 st running (°C)	T_g at 2 nd running (°C)
Starch powder	-	-
Starch gel	-	-
Polystyrene reference	98	85.012
StOH-g-St [#] with homopolystyrene	97	87.717
StOH-g-St [#] without homopolystyrene	102	-
Grafted polystyrene	98	87.548

Where [#] represents starch-g-polystyrene copolymer

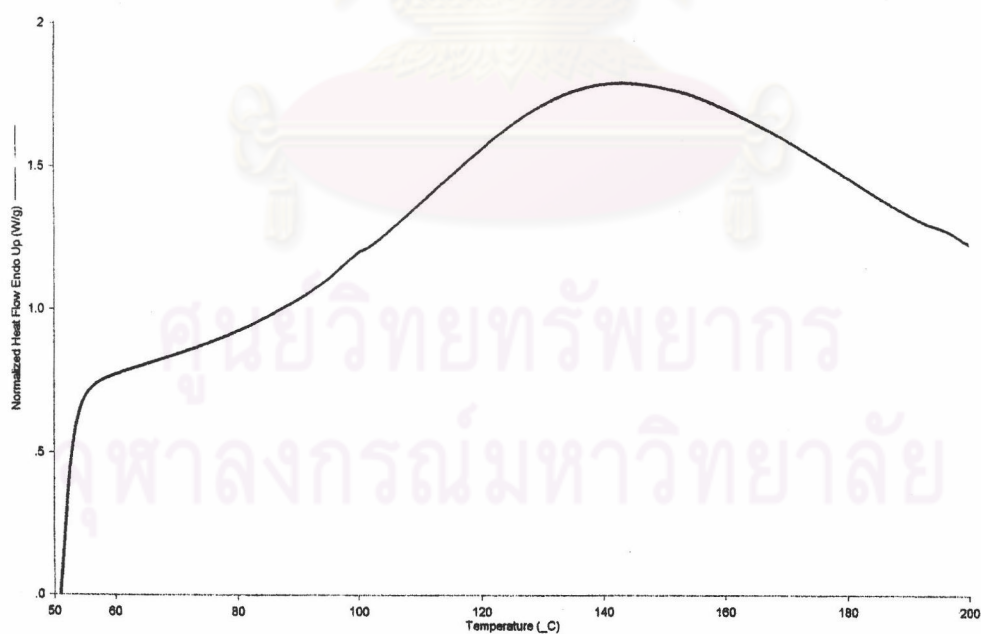


Figure 4.12 DSC thermogram of cassava starch powder.

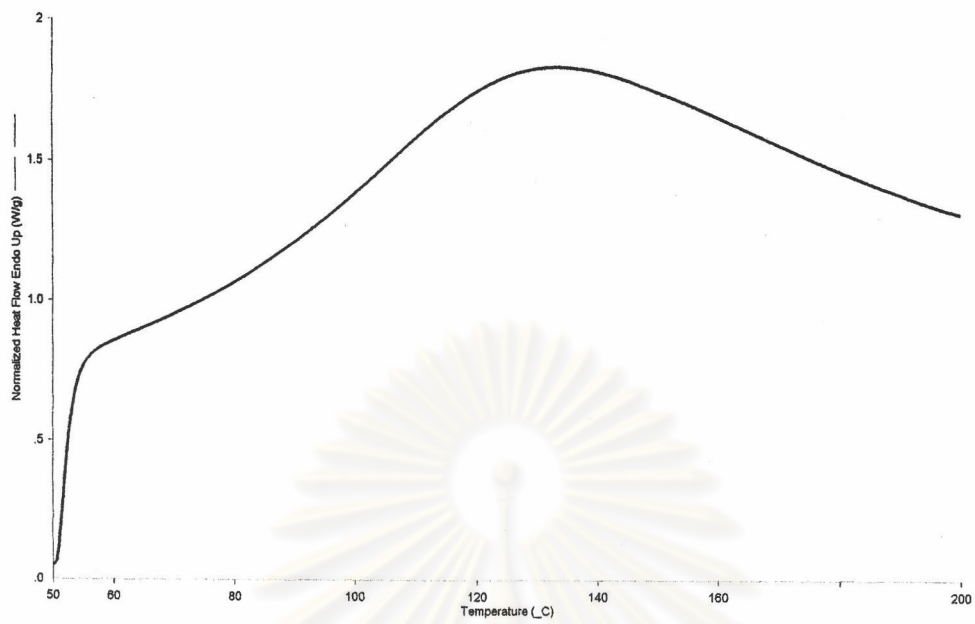


Figure 4.13 DSC thermogram of cassava starch gel.

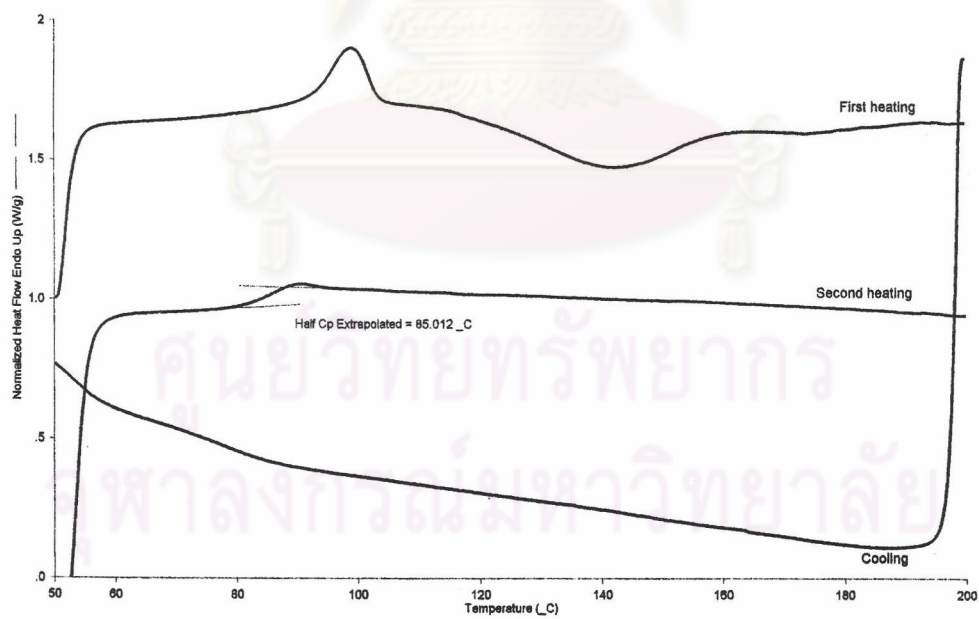


Figure 4.14 DSC thermogram of polystyrene reference.

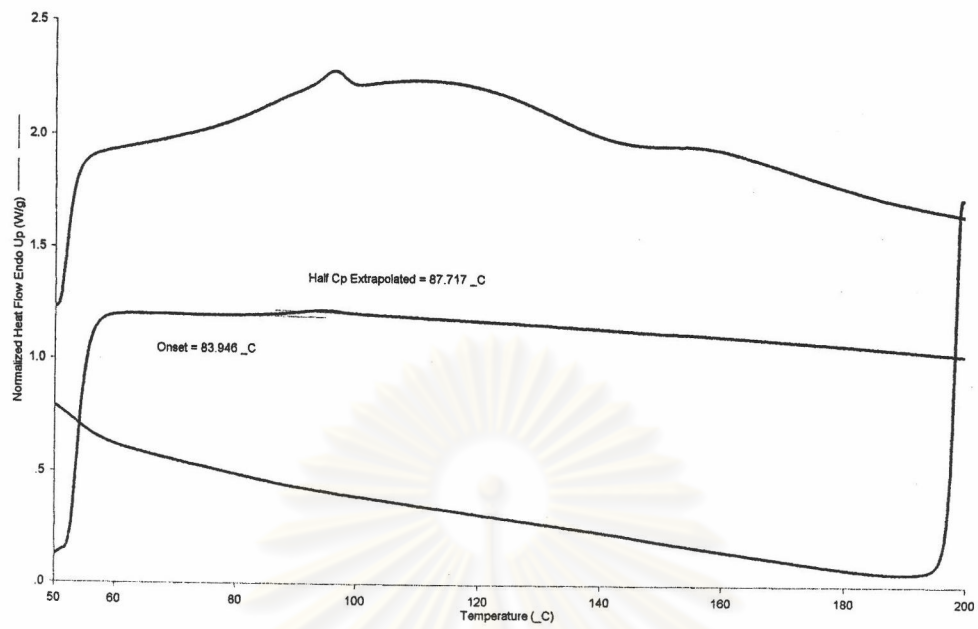


Figure 4.15 DSC thermogram of starch-*g*-polystyrene copolymer with homopolystyrene.

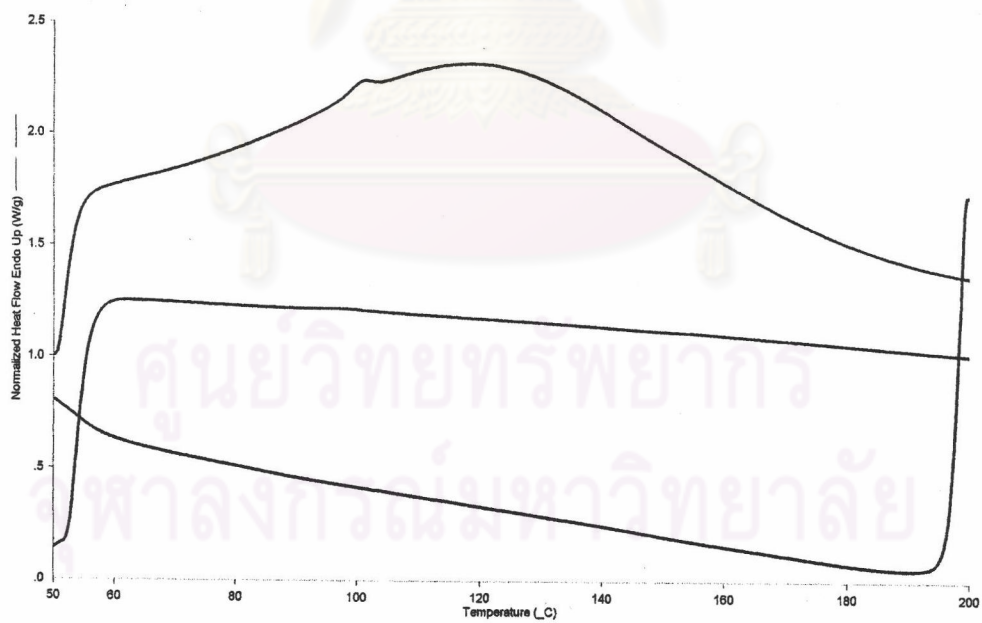


Figure 4.16 DSC thermogram of starch-*g*-polystyrene copolymer without homopolystyrene.

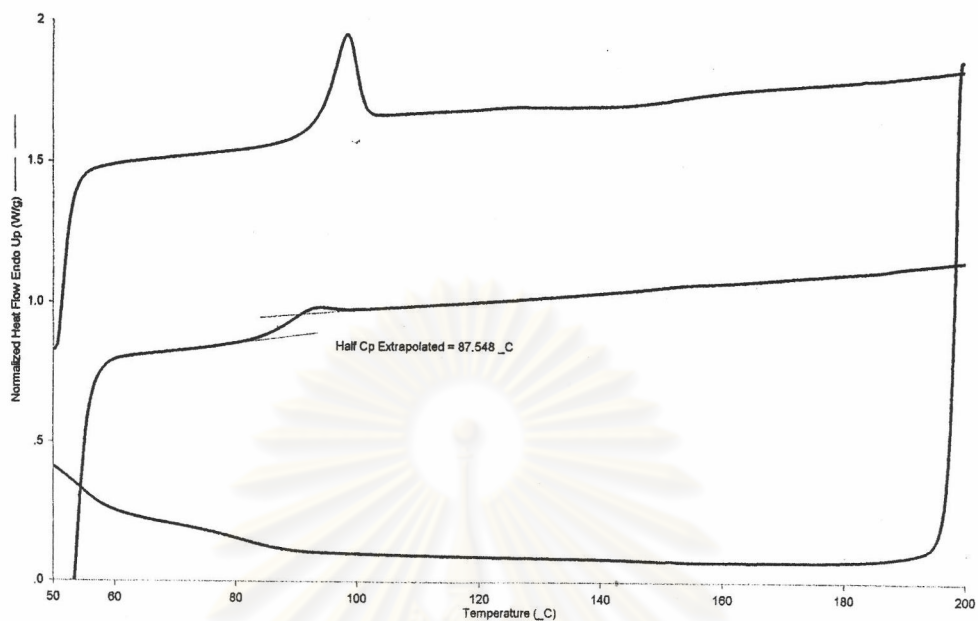


Figure 4.17 DSC thermogram of grafted polystyrene.

DSC thermograms of starch powder and starch gel are shown in Figures 4.12 and 4.13, respectively. Both exhibit one broad peak. While the top of endothermic peak of starch gel is 135°C, the top of that peak of starch powder is 145°C. This may be attributed to the moisture content in both samples. As previously reported by Véronique, et al. [66], T_g of starch depends on the amount of water present in the starch since it acts as a plasticizer for starch. They found that T_g of starch decreased with increasing the amount of water. They also found that the DSC thermogram showed one broad endothermic peak in the range of 90 to 160°C and the temperature at the top of this peak increased with decreasing the amount of water. In this research, the water was not intentionally added to starch powder and starch gel but the samples can absorb moisture from atmosphere. Since the molecules of starch gel are more expandable than those of starch powder, they can absorb more moisture. Therefore, the starch gel shows lower temperature at the top of endothermic peak.

DSC thermogram of polystyrene reference in Figure 4.14 indicates that T_g of polystyrene is 98°C for first heating cycle and decreases to 85°C for

second heating cycle. This may be because after first heating cycle at 200°C, some polystyrene molecules start degrading.

On the other hand, DSC thermograms of starch-*g*-polystyrene copolymer with and without homopolystyrene show both starch and polystyrene characteristic peaks in the first heating cycle as shown in Figures 4.15 and 4.16, respectively. This suggested that both samples compose of starch and polystyrene. However, after second heating cycle, both samples do not show starch characteristic peak and polystyrene characteristic peak only appears in starch-*g*-polystyrene copolymer with homopolystyrene sample. This may be because after first heating cycle, starch molecules degrade and cause degradation of grafted polystyrene chains. Furthermore, grafted polystyrene can also self-degrade by heat as shown in Figure 4.17. Therefore, grafted polystyrene molecules encounter more degradation than homopolystyrene until it loses the properties that results in T_g existence. The same phenomenon was also reported by Bershtein who studied the grafting of styrene onto butadiene rubber [67].

4.4.5 Morphological Analysis

Morphological characteristics of all polymers were obtained from SEM as shown in Figure 4.18 to Figure 4.23. Figure 4.18 shows that cassava starch powder composes of granules with different sizes and shapes. The surface of these granules are smooth even the distorted ones. When starch was gelatinized, it shows rough surface as shown in Figure 4.19. For polystyrene, its surface is smooth as shown in Figure 4.20.

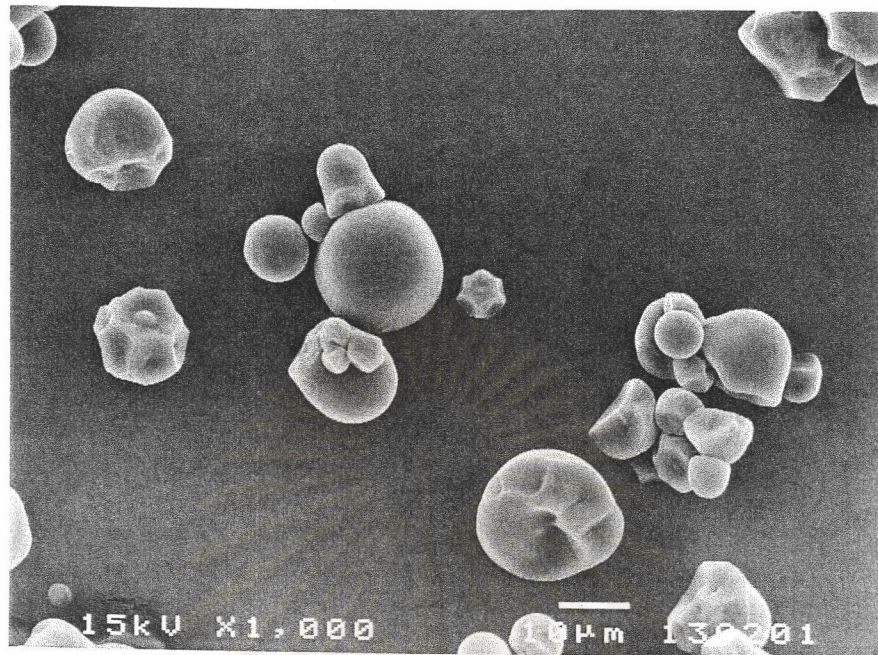


Figure 4.18 Scanning electron micrograph of cassava starch powder.

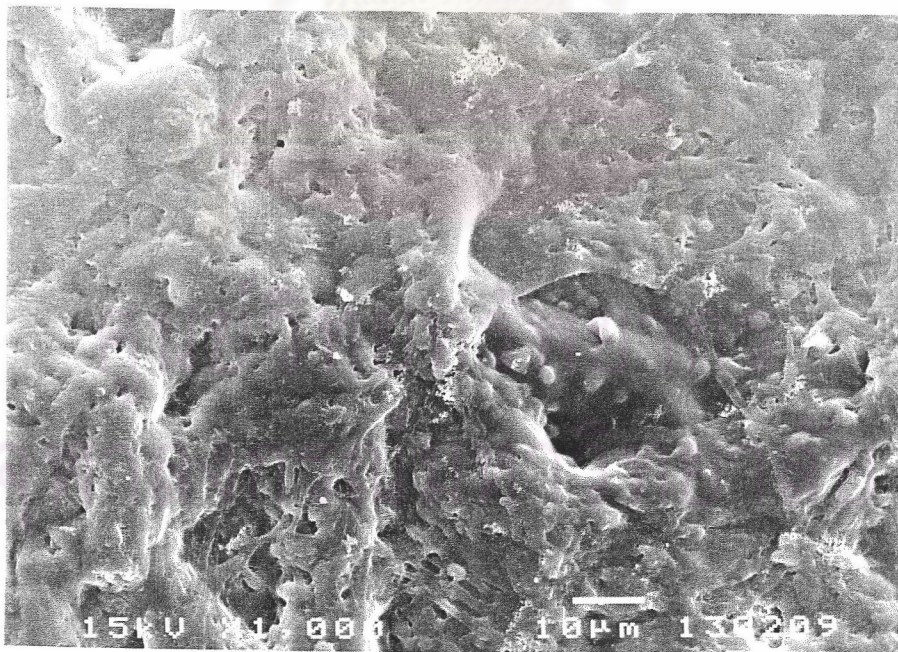


Figure 4.19 Scanning electron micrograph of cassava starch gel.



Figure 4.20 Scanning electron micrograph of polystyrene reference.

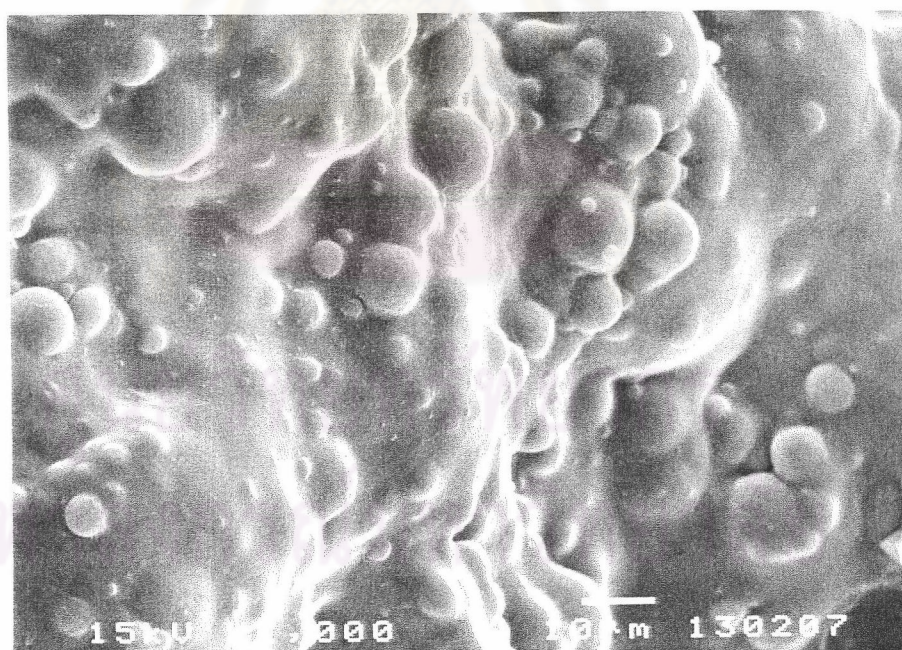


Figure 4.21 Scanning electron micrograph of starch-g-polystyrene copolymer with homopolystyrene.

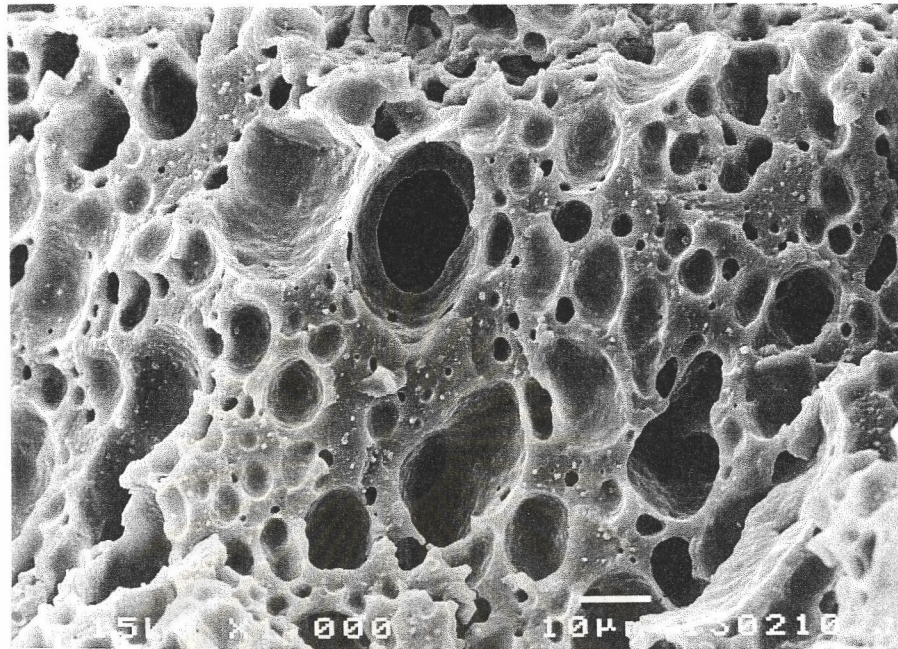


Figure 4.22 Scanning electron micrograph of starch-g-polystyrene copolymer without homopolystyrene.

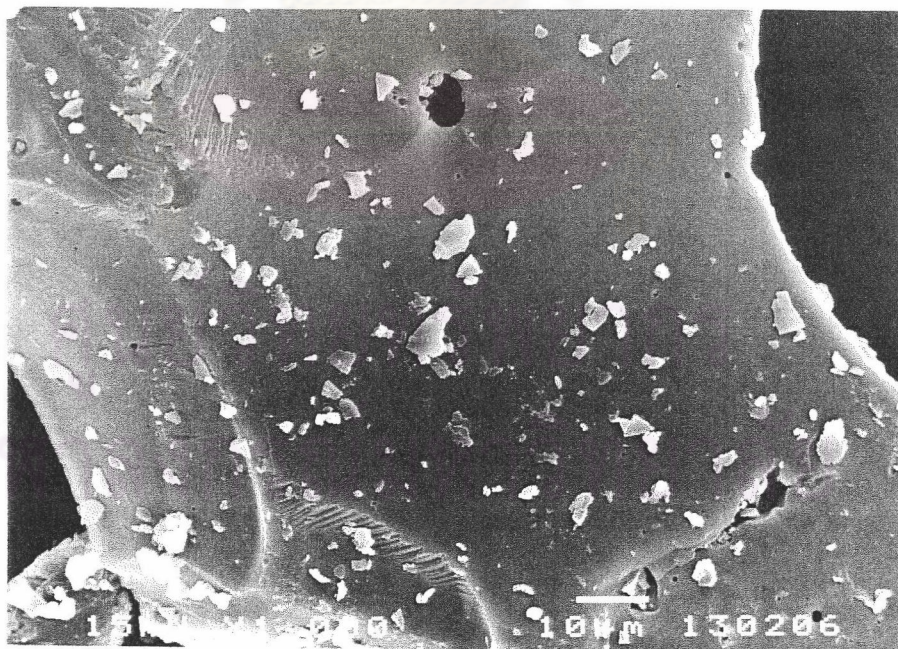


Figure 4.23 Scanning electron micrograph of grafted polystyrene.

From Figure 4.21, it can be seen that the micrograph of starch-*g*-polystyrene with homopolystyrene shows smooth spherical beads embedding in smooth surface. On the other hand, the micrograph of starch-*g*-polystyrene without homopolystyrene shows smooth surface consisting of many holes with different sizes as shown in Figure 4.22. Therefore, it can be concluded that the beads found in Figure 4.21 are homopolystyrene beads. The formation of the spherical beads was achieved since the process used for grafting can produce the conditions for suspension polymerization of homopolystyrene as previously reported by Eduardo, Phillip and Archie [69]. Due to stirring and hydrophobic characteristic of styrene monomer, the monomer droplets are formed and since benzoyl peroxide is soluble in these droplets, polymerization of styrene monomer in these droplets occurs. Consequently, the spherical beads of homopolystyrene are obtained. Figure 4.23 shows the surface of grafted polystyrene being smooth similar to the surface of polystyrene reference (Figure 4.20).

4.4.6 Solubility Behavior

The results of solubility test are given in Tables 4.11 - 4.15. It was found that starch-*g*-polystyrene copolymer shows higher tendency to be soluble in solvents which can solubilize starch than in solvents which can solubilize polystyrene. This suggests that starch-*g*-polystyrene copolymer has higher hydrophilic characteristic than polystyrene but lower hydrophilic characteristic than starch. This phenomenon is expected to be observed since polystyrene molecules which are hydrophobic were grafted onto starch backbone.

Furthermore, this solubility test was also used to determine the formation of crosslinked starch that would occur during grafting process. As previously proposed, crosslinked starch can be obtained from combination termination of two starch-*g*-polystyrene radicals. Normally, the crosslinked molecules cannot be dissolved in any solvent. In this research, starch-*g*-polystyrene copolymer was completely soluble in solvent such as DMSO; therefore, this suggests that no crosslinked starch was formed in grafting process.

Table 4.11 Solubility behavior of polymers in water

	Room tempera- ture (°C)	50 (°C)	60 (°C)	70 (°C)	80 (°C)	90 (°C)	100 (°C)
Starch powder	SW-4	SW-5	SW-5	SL-3	SL-3	SL-4	-
Starch gel	SL-4	SL-4	SL-5	SL-5	SL-5	SL-5	SL-5
Polystyrene reference	X	X	X	X	X	X	X
StOH-g-St ^{#1}	SW-2	SW-2	SW-2	SW-3	SW-3	SW-3	-
StOH-g-St ^{#2}	SW-2	SW-2	SW-3	SW-3	SW-4	SW-4	-
Grafted polystyrene	X	X	X	X	X	X	X

#₁ : starch-g-polystyrene copolymer with homopolystyrene

#₂ : starch-g-polystyrene copolymer without homopolystyrene

SW = swell, SL = soluble, X = not soluble or swell

5 = very good, 4 = good, 3 = moderate, 2 = poor, 1 = very poor

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.12 Solubility behavior of polymers in dimethyl sulfoxide (DMSO)

	Room temperature (°C)	50 (°C)	60 (°C)	70 (°C)	80 (°C)	90 (°C)	100 (°C)
Starch powder	SW-4	SL-2	SL-3	SL-4	SL-5	SL-5	-
Starch gel	SW-5	SL-2	SL-3	SL-4	SL-5	SL-5	-
Polystyrene reference	X	SL-3	SL-3	SL-4	SL-5	SL-5	-
StOH-g-St ^{#1}	SW-3	SW-4	SW-5	SL-1	SL-2	SL-3	-
StOH-g-St ^{#2}	SW-3	SW-4	SL-1	SL-2	SL-3	SL-4	-
Grafted polystyrene	X	SL-3	SL-3	SL-4	SL-5	SL-5	-

#₁ : starch-g-polystyrene copolymer with homopolystyrene

#₂ : starch-g-polystyrene copolymer without homopolystyrene

SW = swell, SL = soluble, X = not soluble or swell

5 = very good, 4 = good, 3 = moderate, 2 = poor, 1 = very poor

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.13 Solubility behavior of polymers in chloroform

	Room temperature (°C)	50 (°C)	60 (°C)	70 (°C)	80 (°C)	90 (°C)	100 (°C)
Starch powder	X	X	-	-	-	-	-
Starch gel	X	X	-	-	-	-	-
Polystyrene reference	SL-4	SL-5	-	-	-	-	-
StOH-g-St ^{#1}	SW-1	SW-1	-	-	-	-	-
StOH-g-St ^{#2}	X	X	-	-	-	-	-
X Grafted polystyrene	SL-5	SL-5	-	-	-	-	-

#₁ : starch-g-polystyrene copolymer with homopolystyrene

#₂ : starch-g-polystyrene copolymer without homopolystyrene

SW = swell, SL = soluble, X = not soluble or swell

5 = very good, 4 = good, 3 = moderate, 2 = poor, 1 = very poor

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.14 Solubility behavior of polymers in tetrahydrofuran (THF)

	Room temperature (°C)	50 (°C)	60 (°C)	70 (°C)	80 (°C)	90 (°C)	100 (°C)
Starch powder	X	X	X	-	-	-	-
Starch gel	X	X	X	-	-	-	-
Polystyrene reference	SL-5	SL-5	-	-	-	-	-
StOH-g-St ^{#1}	SW-1	SW-2	SW-2	-	-	-	-
StOH-g-St ^{#2}	X	X	X	-	-	-	-
Grafted polystyrene	SL-5	SL-5	-	-	-	-	-

#₁ : starch-g-polystyrene copolymer with homopolystyrene

#₂ : starch-g-polystyrene copolymer without homopolystyrene

SW = swell, SL = soluble, X = not soluble or swell

5 = very good, 4 = good, 3 = moderate, 2 = poor, 1 = very poor

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.15 Solubility behavior of polymers in benzene

	Room temperature (°C)	50 (°C)	60 (°C)	70 (°C)	80 (°C)	90 (°C)	100 (°C)
Starch powder	X	X	X	X	-	-	-
Starch gel	X	X	X	X	-	-	-
Polystyrene reference	SW-1	SW-2	SL-1	SL-2	-	-	-
StOH-g-St ^{#1}	X	X	X	X	-	-	-
StOH-g-St ^{#2}	X	SW-1	SW-2	SL-1	-	-	-
Grafted polystyrene	SW-1	SW-2	SL-1	SL-2	-	-	-

#₁ : starch-g-polystyrene copolymer with homopolystyrene

#₂ : starch-g-polystyrene copolymer without homopolystyrene

SW = swell, SL = soluble, X = not soluble or swell

5 = very good, 4 = good, 3 = moderate, 2 = poor, 1 = very poor

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.4.7 Moisture Absorption

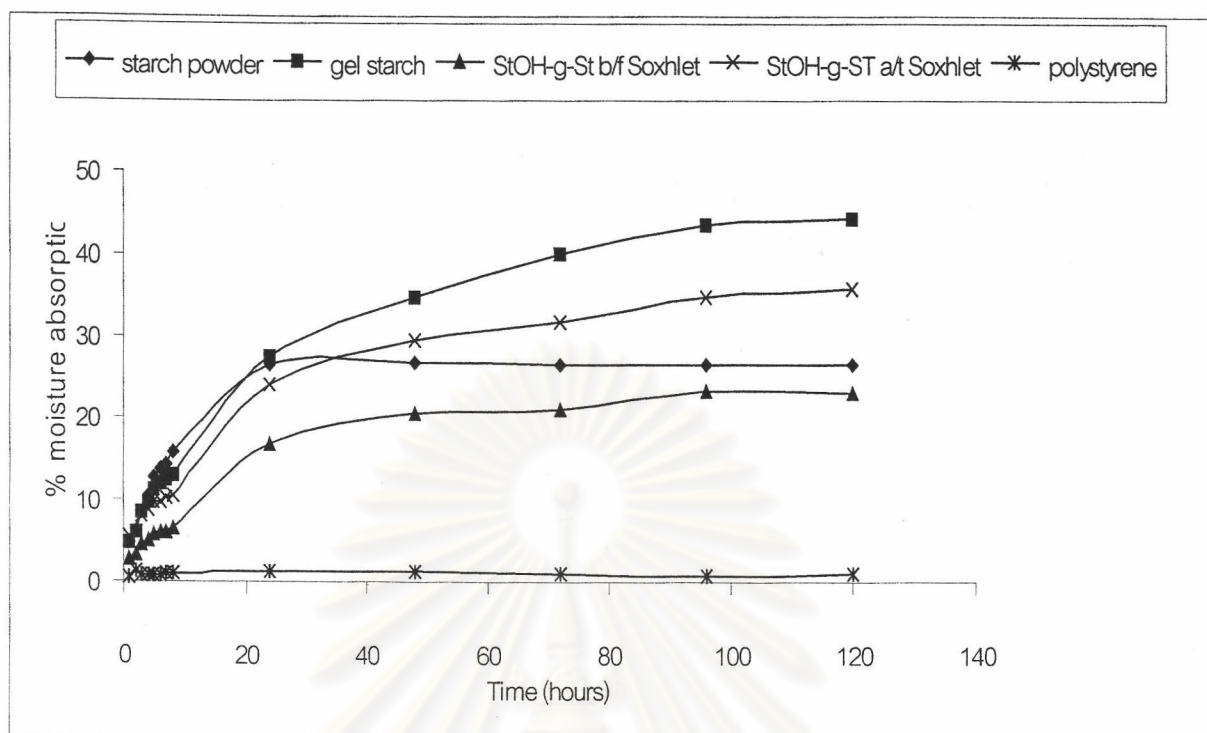


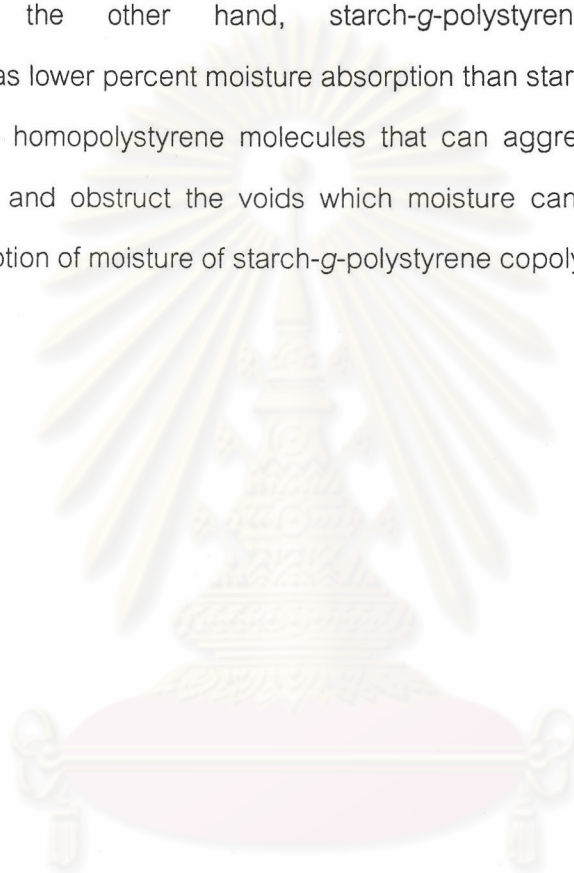
Figure 4.24 Moisture absorption of polymers.

A plot of percent moisture absorption as a function of time is exhibited in Figure 4.25. Because of its hydrophilic nature, starch can absorb high amount of moisture from atmosphere. An absorption rate is very high at first and then it slowly increases until it reaches equilibrium. However, it can be seen that starch gel can absorb more moisture than starch powder. This is because starch molecules in gel form are more expandable and has more free hydroxyl groups than those in powder form; therefore, it is easier for water molecules to penetrate and form hydrogen bonds with hydroxyl groups of starch backbone in gel form than in powder form.

Unlike starch, polystyrene has very low percent moisture absorption due to its hydrophobic characteristic. This suggests that starch-*g*-polystyrene copolymer is expected to have percent moisture absorption in between those of starch and polystyrene. However, it was found that starch-*g*-polystyrene copolymer had higher percent moisture absorption than starch powder. Although starch-*g*-polystyrene copolymer consists of hydrophobic molecules of grafted polystyrene which cannot form

hydrogen bonds with water molecules but the presence of grafted polystyrene disturbs molecular packing and hydrogen bonding between starch molecules. As a result, there are more voids and more hydroxyl groups on starch backbone in copolymer than in starch powder for water molecules to diffuse through and to form hydrogen bonds with, respectively.

On the other hand, starch-g-polystyrene copolymer with homopolystyrene has lower percent moisture absorption than starch powder. This is due to the presence of homopolystyrene molecules that can aggregate between grafted polystyrene chains and obstruct the voids which moisture can diffuse through. This prevents the absorption of moisture of starch-g-polystyrene copolymer.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย