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Preparation of starch-g-polystyrene copolymer by emulsion polymerization

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Abstract

Styrene was graft copolymerized onto native corn starch by emulsion polymerization, using potassium persulfate (KPS) as an initiator, sodium dodecylbenzenesulfonate (SDBS) as an emulsifier, and tetraethylthiuram disulfide (TETDS) as a chain transfer agent. As the reaction time and the emulsifier concentration increased, graft percent (GP) was increased. With the increase of TETDS concentration, GP was decreased. When the corn starch was pre-heated in water, or when the reaction mixture was post-reacted at 80°C, higher GP values were obtained. The molecular weight of the grafted polystyrene showed a certain relationship with the variation of GP. The particle size of the starch in the grafted starch was reduced by pre-heating or by post-reaction heating. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Corn starch; Styrene; Emulsion polymerization; Graft copolymer

1. Introduction

Modification of starch is increasingly being studied and starch is used for applications in which synthetic polymers have traditionally been the materials of choice (Wurzburg, 1987; Whistler, 1984; Willett, 1994; George, Sullivan & Park, 1994; Kim, Chin, Yoon, Lee, Kim & Jung, 1998). The main impetus for this activity is due to the fact that starch is both biodegradable and a renewable resource. In many studies starch and its derivatives are used as biodegradable fillers for various synthetic polymers. For this purpose, graft polymerization of thermoplastic polymers onto starch is an excellent method for preparing composites of starch with synthetic polymers (Wurzburg, 1987; Whistler, 1984).

It is known that starch generates graft copolymers with many vinyl monomers. Active vinyl monomers such as acrylates, methacrylates, or acrylonitriles were easily graft polymerized onto starch by various initiation methods. These monomers can be graft polymerized onto starch when the latter is in a range of different states—granular form, slurry, gelatinized, or modified form.

Graft copolymerization of styrene onto starch, however, has not been studied extensively compared to other monomers. Kargin, Koslov, Plate & Konoreva, 1959a; Kargin, Plate & Reibinder, 1959b reported that styrene can be graft copolymerized onto oxidized starch. Mino and Kaizerman (1958) reported that cerium(IV) initiation could not give a graft copolymer of granular starch with styrene, but a graft copolymer could be obtained when styrene is mixed with an active monomer such as methyl methacrylate (MMA) or acrylonitrile. Fanta, 1973; Fanta, Burr, Doane & Russell, 1971 reported that styrene can be graft copolymerized by cobalt-60 irradiation of starch–styrene mixture. They also reported that starch-g-polystyrene can be obtained by persulfate initiation in the slurry state. So far, however, it is known to be difficult to prepare styrene graft copolymer with granular starch by free radical initiation. Simple solution grafting polymerization does not yield graft copolymer (Cho, Lee, Woo, Choi & Hwang, 1997).

Previously we reported (Lee & Cho, 1998) that MMA can be graft copolymerized onto corn starch by emulsion polymerization. In this report we graft copolymerized styrene onto corn starch by the same procedure. Grafting behavior such as percent conversion, graft efficiency (GE), and graft percent (GP) were studied, by varying the concentration of tetraethylthiuram disulfide (TETDS), initiator, and emulsifier. Because it is known (Lim, Jane, Rajagopalan & Seib, 1992) that the particle size of the starch greatly influences the mechanical properties of a starch filled polymer composites, particle size reduction was attempted by pre-heating of starch granule or by post-reaction heating of the starch-g-polystyrene.

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Table 1
Influence of reaction time on starch-g-polystyrene polymerization. Starch 29 g, styrene 20 g, KPS 0.06 g, TETDS 0.02 g, SDBS 1.0 g, $NaHCO_3$ 0.2 g, H_2O 100 g, reaction temp 63°C

Time (h)	1	2	3	4	5	8
PS yield (%)	11	20	39	50	52	66
GE (%)	6	7	26	26	29	24
GP (%)	0.5	1	10	13	16	17

2. Experimental

2.1. Materials

Corn starch (from Jenex Incorporated., Korea) was used after drying under vacuum at 60°C for 1 day. Styrene (from Aldrich Chemicals) was used after passing over activated alumina column. Potassium persulfate (KPS, from Shinyo Chemicals) and tetraethylthiuram disulfide (TETDS, from Aldrich Chemicals) were used after recrystallization from methanol. Sodium dodecylbenzenesulfonate (SDBS, from Aldrich Chemicals), aluminum sulfate (from Aldrich Chemicals), and other chemicals were used as received.

2.2. Preparation and characterization of polymers

Emulsion polymerization was carried out in a 250 ml four-neck flask equipped with a mechanical stirrer and a condenser. Dried corn starch (20.0 g), distilled water (100.0 g), styrene (20.0 g), and $NaHCO_3$ (0.2 g) were charged into the flask, and sparged with a slow stream of nitrogen for 15 min at room temperature with stirring. KPS (60 mg) and TETDS (20 mg) were added, and sparged further with a slow stream of nitrogen for 10 min. Finally SDBS (1.00 g) was added and the polymerization was conducted at 63°C (bath temperature 70°C). A nitrogen atmosphere was maintained throughout the reaction.

Reaction products were precipitated by the addition of 10–20 ml of 2.5% aluminum sulfate aqueous solution, poured into ~500 ml of methanol, filtered, and then dried under vacuum at 60°C. Percent conversion of styrene to polystyrene were calculated from the gain in weight of the starch product. Polystyrene homopolymer in the dried polymer product was isolated by Soxhlet extraction with chloroform for 24 h (Fanta, 1973; Fanta et al., 1971).

Polystyrene grafts were separated (Gao, Tian, Yu & Duan, 1994) from the chloroform extracted graft copolymer (starch-g-PS) by oxidation of starch; 2 g of starch-g-PS was suspended and stirred in 100 ml of glacial acetic acid at 90–100°C for 1 h. Then 2 ml of perchloric acid (60%) was added dropwise and stirred for 2 min. The reaction mixture was poured into cold water. Obtained product was separated by filtration, washed with water, dried under vacuum, and accurately weighed. Percent conversion, graft efficiency (GE), and graft percent (GP) were calculated from the following equations (Fanta, 1973; Fanta et al., 1971).

$$\%\text{Yield} = \frac{\text{Weight of styrene polymerized}}{\text{Weight of styrene monomer}} \times 100(\%)$$

$$\text{Graft Efficiency (GE)} = \frac{\text{Weight of grafted PS}}{\text{Weight of PS polymerized}} \times 100(\%)$$

$$\text{Graft Percent (GP)} = \frac{\text{Weight of grafted PS}}{\text{Weight of total starch}} \times 100(\%)$$

$$\text{Graft Frequency (GF)} = \frac{W_s/162}{W_g/M_n}$$

W_s:	Weight of starch
W_g:	Weight of grafted PS
M_n:	Number average molecular weight of grafted polymer

Molecular weight of polystyrene graft was determined by size exclusion chromatography equipped with RI detector calibrated with polystyrene standards using THF as an eluent. For the measurement, the polystyrene graft was purified by dissolving in chloroform and precipitating into methanol. Scanning electron micrographs of polystyrene grafted starch were obtained with Jeol JSM 35-CF.

3. Results and discussion

3.1. Hypothesis for the surface grafting reaction

As the polymerization time progressed, %conversion increased as shown in Table 1. GE increased and showed maximum at 5 h and a subsequent decrease. GP also increased as the polymerization time increased but after 5 h it stayed at almost same value. It appears that GP value has an attainable limit. Because the grafting reaction occurs at the surface of the starch particle, one can imagine that GP reaches a maximum value once the whole surface area of the particle is covered with polystyrene grafts. If this is likely, then the process can be schematically shown as in Fig. 1. Assuming that there are a fixed number of grafting sites available on the particle surface. Once all the available grafting sites have reacted, i.e., once the whole area of the particle surface is covered with polystyrene grafts, then GP

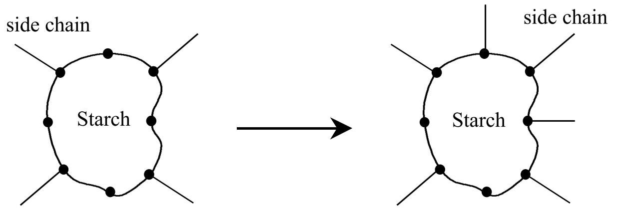

Fig. 1. A schematic picture of grafting reaction on the surface of starch particle.

Table 2
Influence of TETDS concentration on starch-g-polystyrene polymerization. Starch 20 g, styrene 20 g, KPS 0.06 g, TETDS 0.02 g, $NaHCO_3$ 0.2 g, H_2O 100 g, reaction time 5 h, reaction temp 63°C

TETDS (g)	0	0.005	0.010	0.015
PS yield (%)	70	71	50	43
GE (%)	66	27	27	23
GP (%)	46	19	14	8
GF	4492	3744	3860	–
M_w of homo PS	991,000	654,000	481,000	185,700
M_w of PS grafts	1,346,000	634,000	366,000	190,400

value will be determined by the average molecular weight of the grafted polystyrene. In order to test this hypothesis, the molecular weight of polystyrene graft was controlled by the use of chain transfer agent, TETDS, as in Table 2. As the TETDS concentration increased, %conversion, GE, and GP values decreased. When the molecular weight of the polystyrene graft was measured, M_w of polystyrene graft showed a good correlation with GP value as in Fig. 2. Here, M_w was used instead of M_n because GP measures by weight. Graft frequency estimated by M_n showed almost the same values reported in Table 2.

Starch granule used in this experiment showed a very smooth surface (Fig. 3a). After grafting the granule surface was covered with polystyrene (Fig. 3b). Because the reaction system is heterogeneous, uniform coverage of the granule surface is not guaranteed, and also the surface may be covered with the polymer without a grafting reaction taking place. Fig. 3b shows the polystyrene grafted starch after Soxhlet extraction. Irregular crater-like shapes were formed due to extraction. From the SEM study it appears that gelatinization of corn starch granules does not occur under the polymerization condition of 63°C. Corn starch gelatinizes in excess water at 62–73°C (Schoch & Maywald, 1956). In a control experiment we observed that starch granule swells slightly but do not gelatinize under similar condition at 63°C.

All homo polystyrene was extracted during the extraction experiment for 24 h. Extracted polystyrene was assumed to be composed of ungrafted homo polystyrene. Molecular weight determination showed that extracted polystyrene and grafted polystyrene have almost same molecular weight for a given TETDS concentration.

3.2. Interpretation of emulsion polymerization

The polymerization system of this graft copolymerization is a heterogeneous which contains starch granules of a relatively large size (~10 μm). Because this system is different from a typical emulsion polymerization, it is very hard to figure out a proper mechanistic pathway for the grafting.

In this system initiator is dissociated in the aqueous phase, but the grafting has to occur at the surface of starch particle. An oxy radical may be formed at the starch surface by a reaction between a primary radical and an hydroxyl group located at starch surface. One possible hypothesis is that grafting occurs by the polymerization of styrene onto oxy radicals. In this situation, more initiator will produce more oxy radicals at the starch surface, and it will result in more grafts per starch particle. Mehrotra and Ranby (1978) reported that graft frequency increased and molecular weight was reduced when more initiating radicals formed at the starch surface by redox initiation with manganic pyrophosphate, in slurry state. A similar observation was made for the graft polymerization of acrylonitrile onto starch

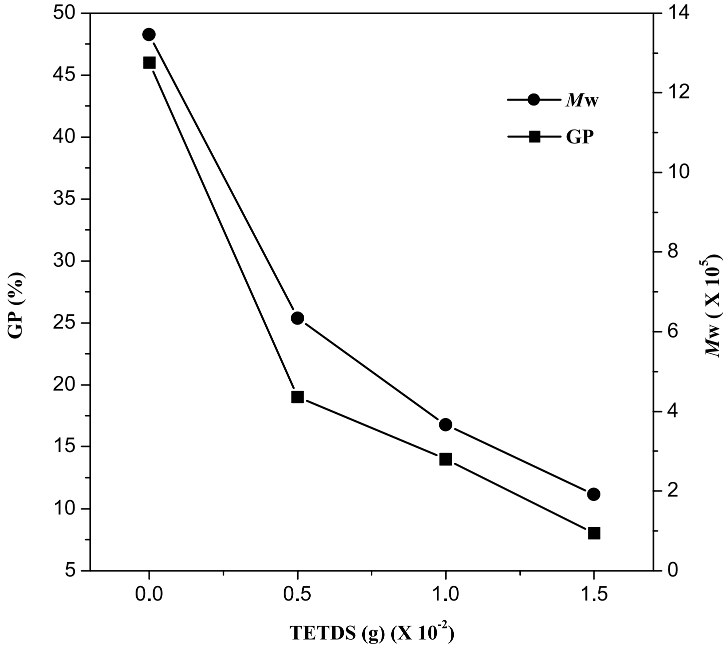

Fig. 2. GP and M_w versus TETDS concentration in starch-g-polystyrene polymerization.

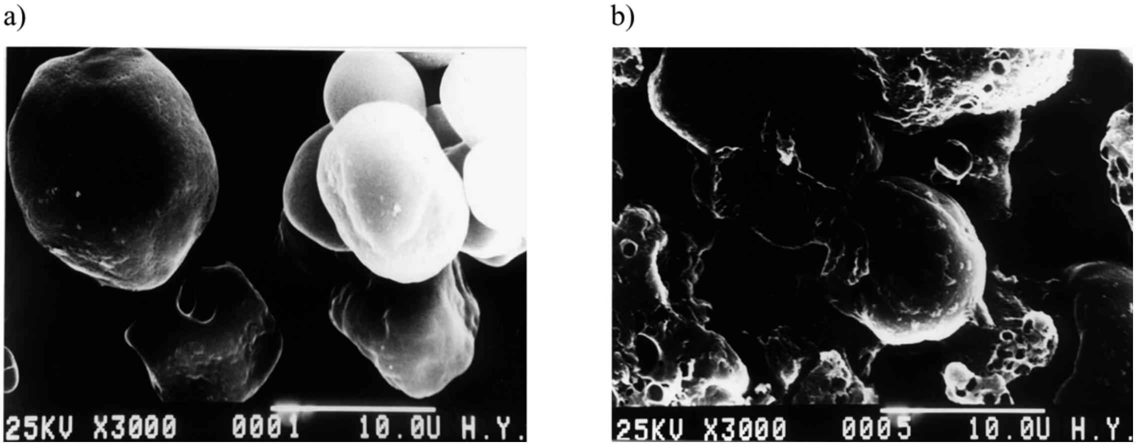

Fig. 3. Scanning electron micrographs of starch-g-polystyrene copolymers, (a) unmodified granule corn starch, (b) styrene grafted corn starch after extraction, polymerization time 8 h, GP 17%.

Table 3
Influence of KPS concentration on starch-g-polystyrene polymerization. Starch 20 g, TETDS 0.02 g, SDBS 1.0 g, $NaHCO_3$ 0.2 g, H_2O 100 g, reaction time 3 h.

KPS (g)	0.01	0.03	0.05	0.07	0.10
PS yield (%)	22	39	43	44	54
GE (%)	0	26	26	21	16
GP (%)	0	10	9	9	9
M_w of PS grafts	–	443,000	478,000	566,000	428,000

Table 4
Influence of SDBS concentration on starch-g-polystyrene polymerization. Starch 20 g, styrene 20 g KPS 0.06 g, TETDS 0.02 g, $NaHCO_3$ 0.2 g, H_2O 100 g, reaction time 3 h.

SDBS (g)	0	0.6	1.0	1.4	1.8
PS yield (%)	0	33	39	46	51
GE (%)	0	23	26	33	63
GP (%)	0	8	10	14	34
M_w of PS grafts	–	436,000	443,000	380,000	233,000

Table 5
Influence of pre-heating time on starch-g-polystyrene polymerization. Starch 20 g, styrene 20 g, KPS 0.06 g, TETDS 0.02 g, SDBS 1.0 g, $NaHCO_3$ 0.2 g, H_2O 100 g, polymerization time 3 h.

Time (h)	0	0.5	1	1.5	2
PS yield (%)	39	39	39	39	38
GE (%)	25	67	72	68	77
GP (%)	10	26	29	27	27

Table 6
Influence of pre-reaction heating time on starch-g-polystyrene polymerization. Starch 20 g, styrene 20 g, KPS 0.06 g, TETDS 0.02 g, SDBS 1.0 g, $NaHCO_3$ 0.2 g, H_2O 100 g, polymerization time 2 h.

Time (h)	0	0.5	1.0	1.5	3.0
PS Yield (%)	39	69	77	88	93
GE (%)	25	49	59	37	29
GP (%)	10	33	45	33	27

initiated by ceric(IV) redox initiator (Bazuaye, Okieimen & Said, 1989). Molecular weight reduction is also expected in a traditional emulsion polymerization theory. Smith-Ewart theory (Gardon, 1982) shows that the increased initiator concentration does not change either the number of micelles or the rate of polymerization at Stage II, but the chain length of a polymer is reduced. As in Table 3 when the initiator concentration was increased, polymer conversion increased slightly, but GP showed almost same value at the initiator concentration of 0.03–0.10 g, and molecular weight values were also very close to each other. This data shows that increased initiator concentration does not influence the surface grafting reaction.

In this research SDBS was used as an emulsifier. When the SDBS concentration was increased %conversion, GE, and GP increased as in Table 4. When no emulsifier was used, no polymer was obtained. Actually many reported attempts to prepare starch-g-polystyrene by redox initiation failed unless the starch was gelatinized. Increase of %conversion with SDBS concentration is normally expected when one assumes a typical emulsion polymerization behavior. An interesting point of the data in Table 4 is that GP increased with SDBS. In a typical emulsion polymerization, rate of polymerization is expressed as $R_p = k_p[M][P\cdot]$ where $[M]$ is monomer concentration, and $[P\cdot]$ is concentration of active particles. $[P\cdot]$ is usually proportional to the 0.6th power of emulsifier concentration (Gardon, 1982). The degree of polymerization X_n is represented as R_p/R_i (rate of initiation). Therefore increase of emulsifier concentration gives increased GP, and also gives the increase in degree of polymerization. M_w data in Table 4, however, does not support this interpretation. When we recall the

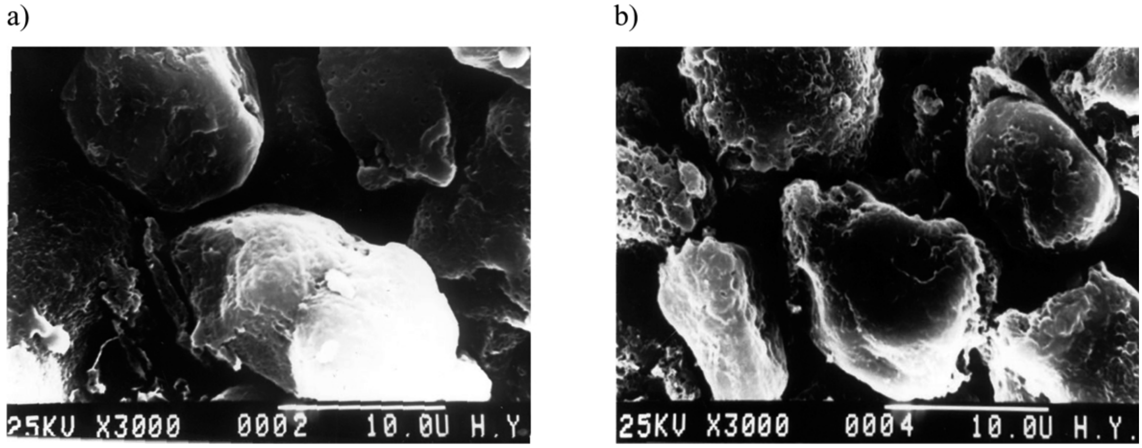

Fig. 4. Scanning electron micrographs of starch-g-polystyrene, (a) pre-heating time 0.5 h, GP 26%, (b) pre-heating time 1.5 h, GP 27%.

data in Table 2, that the molecular weights of homo polystyrene and grafted polystyrene are almost same, it seems certain that a growing chain radical in a micelle reacts with the starch surface via an yet unidentified route.

Another possibility is that a growing chain radical in a micelle has to react with starch. It may be visualized that a growing chain radical in a micelle is adsorbed on the starch surface and attached to an oxy radical at the starch surface.

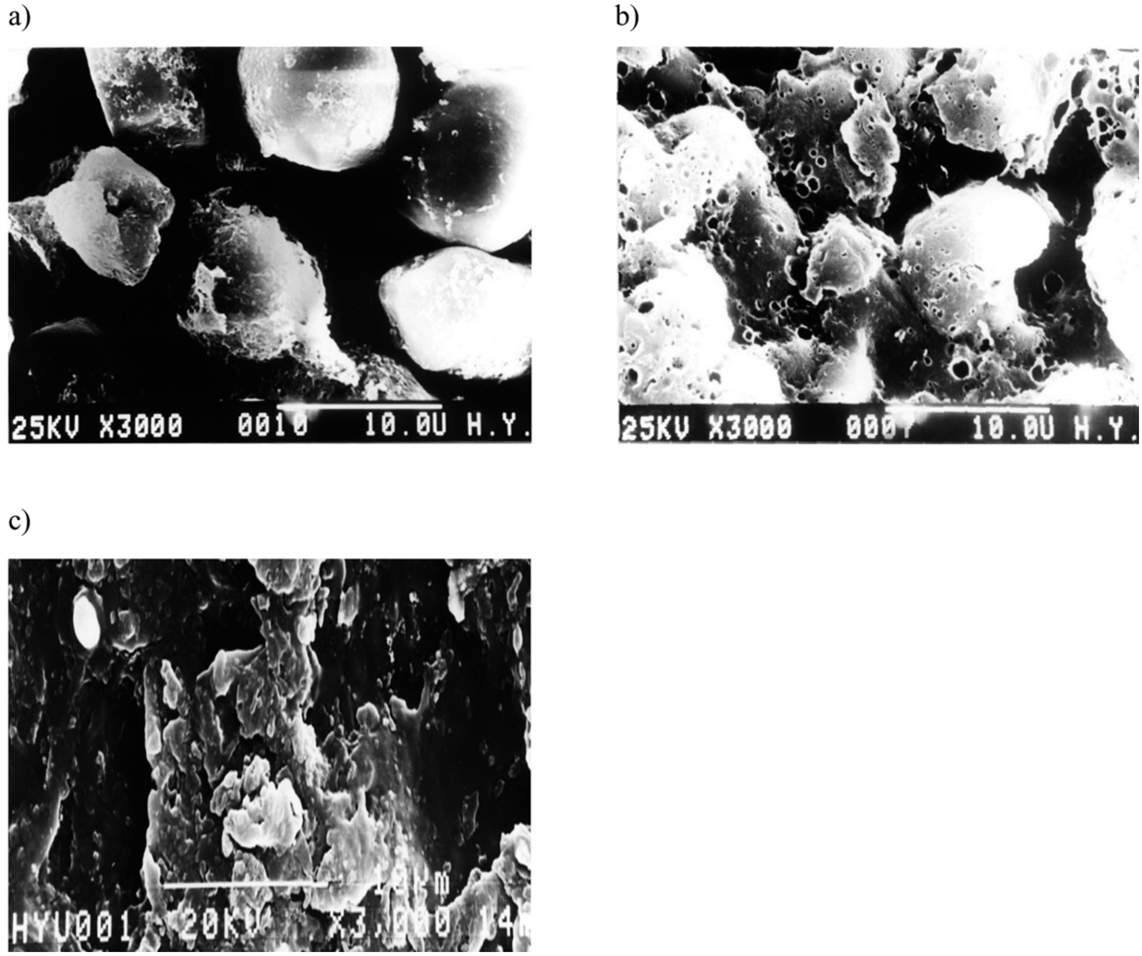

Fig. 5. Scanning electron micrographs of starch-g-polystyrene, (a) untreated, GP 15%, (b) post-reaction heating for 1 h at 80°C, GP 45%, (c) gelatinized starch, stirred at 80°C for 1 h.

3.3. Influence of pre-heating and post-reaction heating on the particle size of corn starch

Starch exists as a granule. When the dispersed starch granules are heated in water, hydrogen bonding inside of the granule is destroyed and gelatinization occurs. Sometimes the gelatinization is beneficial to graft copolymerization, but if the gelatinization becomes complete, then the viscosity of the reaction mixture becomes too high for effective agitation of the reaction mixture. In this experiment a controlled gelatinization or swelling was attempted in order to increase the available surface and thus the GP value. As mentioned earlier a controlled gelatinization was attempted in two ways: by pre-heating, by post reaction heating. For the pre-heating, the starch granules were stirred in water at 70°C before polymerization. As in Table 5, pre-swelled starch showed no differences in %yield but showed increased GP and GE values compared to the none pre-swelled starch. Increased pre-heating time did not show any tendency or differences in GP or GE values. Fig. 4 shows the scanning electron micrographs of starch-g-polystyrenes. Particular size reduction was not so distinctive from the micrographs, but it is possible to see the reduced particle size as the pre-heating time increased from 0.5 h (Fig. 4a) to 1.5 h (Fig. 4b). Perhaps a pre-heating temperature of 70°C was not high enough in this experiment.

For the post-reaction heating, reaction mixture were reacted for 80°C for a predetermined time after polymerization for 2 h at 63°C. As in the Table 6 %conversion increased as the post-reaction heating time increased. This post reaction gave higher %conversion due to the faster decomposition of initiator and the resultant increase of the polymerization reaction rate. GP and GE also increased as the post-reaction heating time increased, but showed maximum values at the post-reaction heating time of 1 h, then decreased. Scanning electron micrographs (Fig. 5) showed that the size of starch granule was ~10 μm before post-reaction heating, and this size was reduced to 3–5 μm after post reaction of 1 h. In another experiment, ungrafted starch granules were gelatinized for 1 h at 80° for comparison. As in Fig. 5c it was found out the starch granules were completely disrupted in the control experiment. From these experiments it is clear that hydrophobic polystyrene grafts gave a controlled gelatinization of the starch granules. The decrease of GP or GE with longer post-reaction heating could be caused by grafts of long-chain polystyrene on a short chain amylose. Such a graft could escape from the swollen granules during heating, and then be solubilized by chloroform when extracting the homo polystyrene.

Acknowledgement

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