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Preparation of cassava starch grafted with polystyrene by suspension polymerization

Kaewta Kaewtatip [a], Varaporn Tanrattanakul [a,b,*]

[a] *Polymer Science Program, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand*
[b] *Bioplastic Research Unit, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand*

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Abstract

Cassava starch grafted with polystyrene (PS-g-starch) copolymer was synthesized via free-radical polymerization of styrene by using suspension polymerization technique. Potassium persulfate (PPS) was used as an initiator and water was used as a medium. The graft copolymer was characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, X-ray diffraction and scanning electron microscopy. The sub-micron spherical beads of PS were observed on the surface of starch granules. SEM micrographs showed porous patches of PS adhering on the starch granules after Soxhlet extraction. FTIR spectra also indicated the presence of PS-g-starch copolymer. XRD analysis exhibited insignificant changes in crystalline structure and degree of crystallinity. The effects of starch:styrene weight ratio, amount of PPS, reaction time and reaction temperature on the percentage of grafting – G (%), were investigated. G (%) increased with increasing starch content. Other variables showed their own individual optimal values. The optimum condition yielding 31.47% of G (%) was derived when the component ratio was 1:3 and reaction temperature and time were 50 °C and 2 h, respectively. Graft copolymerization did not change granular shape and crystallinity of starch. This study demonstrated the capability of polymerization of styrene monomer on the granular starch without emulsifier and the synthesis of graft copolymer without gelatinization of starch.

Keywords: Cassava starch; Polystyrene; Biodegradable polymer; Graft copolymer; Bioplastic

1. Introduction

In the last three decades, there has been tremendous interest in bioplastic and biodegradable polymers. In the beginning, there were many attempts to use starch as a bio-filler in thermoplastic polymers. Starch is used as a filler because it is a natural polymer, abundant, inexpensive and a renewable resource. Starch is degraded by microorganisms and is suitable for blending with bioplastics and biodegradable polymers. Unfortunately, the mechanical properties of thermoplastic polymer/starch blends are very poor due to the incompatibility and hydrophilic nature of starch. As a result, graft copolymerization of thermoplastic polymer onto starch has been widely studied.

Graft copolymerization can be performed by irradiation or free-radical graft copolymerization. Graft copolymerization of polystyrene onto starch has been previously reported. Bagley, Fanta, Burr, Doane, and Russell (1977) prepared starch graft copolymers with styrene, methyl methacrylate, methyl acrylate, and butyl acrylate. Preparation of starch grafted with polystyrene (PS-g-starch copolymer) using ^{60}Co irradiation has been reported (Fanta, Burr, Doane, & Russell, 2003; Henderson & Rudin, 1981; Henderson & Rudin, 2003a; Kiatkamjornwong, Sonsuk, Wittayapichet, Prasassarakich, & Vejjanukroh, 1999).

It is well established that potassium persulfate (PPS), ceric ammonium nitrate, manganic pyrophosphate, potassium permanganate, benzoyl peroxide and redox couples such as ferrous ammonium sulfate – hydrogen peroxide

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[*] Corresponding author. Address: Polymer Science Program, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand. Tel.: +66 8973 54720; fax: +66 7444 6925.
E-mail address: varaporn.t@psu.ac.th (V. Tanrattanakul).

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are effective for grafting vinyl monomers onto starch via freeradical graft copolymerization (Graaf & Janssen, 2000; Pimpan & Thothong, 2006). Graaf and Janssen (2000) prepared PS-g-starch copolymer by reactive extrusion. They used benzoyl peroxide and PPS as the thermal initiators. Cho and Lee (2002) prepared PS-g-starch copolymer by emulsion polymerization. The aqueous solution consisted of corn starch, styrene monomer, PPS, emulsifier and chain transfer agent. The gelatinized sago starch grafted with PS was prepared by using ceric ammonium nitrate in aqueous solution (Janarthanan, Yunus, & Ahmad, 2003). Although both ceric ammonium nitrate (cerium (IV)) and PPS could be used for preparation of PS-g-starch copolymer, PPS may be better because it can initiate homopolymerization of styrene directly but cerium (IV) cannot.

Trimnell, Stout, Doane, and Russell (2003) used hydrogen peroxide as the initiator for grafting PS onto the thiolated starch. The acryloylated potato starch was grafted with PS using PPS in aqueous solution (Fang, Fowler, & Hill, 2005). They employed a two-step process where the starch was modified by acryloyl chloride prior to graft copolymerization. Ammonium persulfate has been used as the initiator for grafting PS onto starch (Singh & Sharma, 2007). Recently, ozone was used to synthesize starch grafted with poly(styrene-*co*-*n*-butyl acrylate) latexes (De Bruyn et al., 2006). PS-g-starch copolymers have been used for different applications. For example it was used as a compatibilizer of PS/starch blend (Graaf & Janssen, 2004), a filler of PS (Graaf & Janssen, 2004, and Kiatkamjornwong et al., 1999), or used directly as a thermoplastic starch and processed by extrusion (Henderson & Rudin, 2003b).

To the best of our knowledge, there is no report of cassava starch grafted with PS via suspension polymerization using PPS as the initiator. One research group has used gamma radiation (Kiatkamjornwong et al., 1999) and another PPS under emulsion polymerization (Cho & Lee, 2002) to make grafted starch. The latter group reported that no PS was obtained when no emulsifier was used and the redox initiation system failed unless the starch was gelatinized. The utilization of PPS as the initiator in other systems has been reported. For instance, poly(methyl methacrylate) grafted sago starch (Qudsieh et al., 2004; Razi, Qudsieh, Yunus, Ahmad, & Rahman, 2001), and poly(acrylamide) grafted with potato starch (Singh, Tiwari, Pandey, & Singh, 2006) have been reported. Cho & Lee, 2002 stated that although PS-g-starch copolymer has been prepared by persulfate initiation in the slurry state it is difficult to prepare styrene graft copolymer with granular starch by freeradical polymerization. Simple solution grafting polymerization did not yield graft copolymer. This may be due to the different reaction conditions. It is difficult to polymerize styrene with the water-soluble initiator. However, it is necessary to employ the water-soluble initiator for starch graft copolymerization because water is the medium used in making a starch slurry.

The objective of this study was to synthesize PS-g-starch copolymer by using PPS as the initiator. This study showed the success of graft copolymerization between granular cassava starch and polystyrene via the suspension polymerization. The PS-g-starch copolymer derived from this study will be used as a thermoplastic starch and compatibilizer for PS/starch blends. Based on these applications, it was not necessary to extract or digest ungrafted starch from the graft copolymer.

2. Experimental

2.1. Materials

Cassava starch was kindly supplied by GSL General Starch Ltd., Thailand. It is a native, granular starch and had standard specification as follows: maximum moisture content = 12.2%, maximum ash = 0.07%, fiber content = 0.10%, pH 5.6, SO_2 content = 21.59 ppm, maximum viscosity = 630 Brabender units, and sieve test = 99.61% after passing through 100 mesh. The starch was dried at 100 °C for 48 h in an oven and kept in a desiccator prior to using. Styrene monomer (from Fluka) was used after inhibitor was extracted with 5% sodium hydroxide aqueous solution and distilled water sequentially. The inhibitor-free styrene was dried with anhydrous calcium chloride and stored at 4 °C. Potassium persulfate, toluene and methanol (from Fisher chemicals) were used as received.

2.2. Preparation of PS-g-starch copolymer

Dried starch and distilled water were mixed in a three-neck flask under nitrogen atmosphere and stirred at reaction temperature for 30 min to obtain homogeneous slurry. After adding PPS for 10 min, styrene monomer was added. Water was 100 ml while the total amount of starch and styrene monomer was 10 g. Graft copolymerization was carried out at various conditions. The graft copolymerization parameters included starch:styrene ratios (1:3, 1:1 and 3:1 by weight), PPS content (0.2–1.2 g), reaction time (1–5 h) and reaction temperature (30–60 °C). The nitrogen atmosphere and agitation at 420 rpm of slurry were maintained throughout the experiment. After the reaction time was over, the slurry was dropped into methanol. The precipitate was filtered, washed with methanol, dried in an oven at 50 °C until a constant weight was achieved and kept in a desiccator. The "controlled starch" was prepared under identical experimental condition as described earlier except the addition of styrene monomer. In order to test reproducibility of graft copolymerization, three runs of polymerization were carried out for all samples.

Soxhlet extraction with toluene was applied to the precipitate for removing polystyrene homopolymer. The extraction was done at 120 °C for 10 h. The extracted solution was dropped into methanol which is a non-solvent of PS, if no precipitation was observed, complete extraction was confirmed. The PS-g-starch copolymer was dried in a vacuum oven at 60 °C until a constant weight and kept in the desiccator. To substantiate the validity of Soxhlet extraction technique, the same extraction technique was applied to a polymer blend of starch and polystyrene homopolymer. The product prior to Soxhlet extraction was called as "non-extracted product", and the product after extraction was called as "un-extractable product".

In order to verify the polymerization of styrene monomer with PPS by the suspension polymerization technique, the reaction was carried out under identical reaction condition except the presence of starch. Styrene monomer (7.5 g), PPS (0.4 g) and distilled water (100 g) were mixed together and stirred at 420 rpm. Reaction time and temperature were 2 h and 50 °C, respectively. The mixture was precipitated in methanol. The precipitate was filtered and dried before characterizing similar to the PS-g-starch copolymer.

2.3. Characterization of PS-g-starch copolymer

The products before and after Soxhlet extraction were weighed and characterized by various techniques. The percentage of grafting, G (%), and yield of graft copolymerization, Y (%), were calculated from Eqs. (1) and (2), respectively:

$$G(\%) = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

$$Y(\%) = \frac{w_2 - w_1}{w_3} \times 100 \quad (2)$$

where w_1 was the original weight of cassava starch, w_2 was the weight of un-extractable products (after Soxhlet extraction), and w_3 was weight of styrene monomer. Because w_2 represented to the weight of starch and PS grafted on starch; therefore, the differences in w_2 and w_1 could be equal to the weight of PS grafted on starch granules. The calculation of G (%) and Y (%) was similar to that reported by Singh et al. (2006) and Fang et al. (2005). The G (%) and Y (%) were reported in terms of an average value and standard deviation derived from triplicated polymerization.

The Fourier Transform Infrared Spectrometer BRUKER® EQUINOX 55 was used to determine the presence of PS in the graft copolymer. The dried powder samples were mixed with potassium bromide and pressed into disc shape. The samples were scanned at a frequency range of 4000–400 cm^{-1} with 128 consecutive scans in a 4 cm^{-1} resolution. A scanning election microscope (JEOL® JSM-5800LV) was used to observe the presence of PS on starch granules. The samples were coated with gold prior to observation. Thermal properties were evaluated by thermogravimetric analysis (PerkinElmer® TGA 7) and differential scanning calorimetry (PerkinElmer® DSC 7). TGA analysis was operated at a heating rate of 10 °C/min from 50 to 950 °C under nitrogen atmosphere. DSC analysis of starch and graft copolymers was conducted on the second heating of a heating–cooling–heating cycle with a heating rate of 5 °C/min. The first and the second heating scans were operated from 25 to 180 °C and 25–500 °C, respectively, under nitrogen atmosphere in order to ensure that there was no influence of the thermal history and moisture. Semi-crystalline structure of starch granules was detected by using a wide angle X-ray diffractometer (Phillips® PW1830).

3. Results and discussion

3.1. Suspension polymerization of polystyrene

The mixture became turbid after reaction time was over. This was due to very fine particles of PS were dispersed in the water. These particles were filtered and dried at 100 °C for 24 h. SEM micrographs of PS micro-particles are shown in Fig. 1a and b. Fig. 1a shows agglomerates of very fine PS particles which smaller than 200 μm. At higher magnification (Fig. 1b) a number of sub-micron spherical PS particles are observed. Practically, it is difficult to polymerize styrene monomer with water-soluble initiator under suspension polymerization. Comparing to another work (Pimpan & Thothong, 2006), benzoyl peroxide, monomer

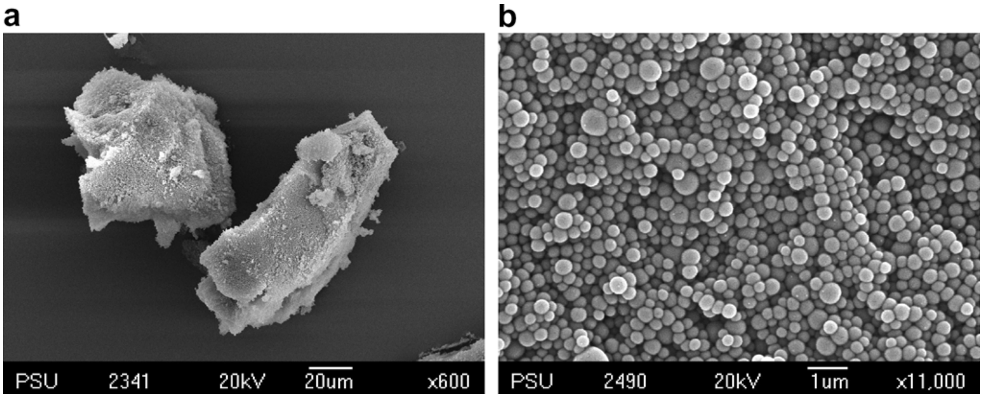

Fig. 1. SEM micrographs of PS polymerized by suspension polymerization using PPS as the initiator. (a) agglomerates of PS; (b) sub-micron spherical particles of PS.

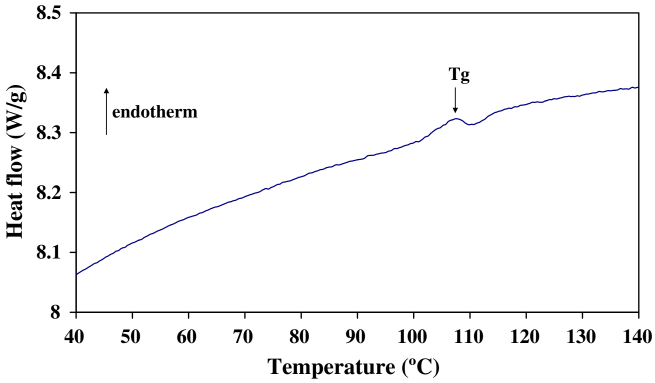

Fig. 2. DSC thermogram of PS polymerized by suspension polymerization using PPS as the initiator showing T_g at 107.5 °C.

soluble initiator, was employed to polymerize poly(methyl methacrylate) (PMMA). The PMMA particles obtained were about 50 μm in diameter whereas the PS particles in the present study were <0.5 μm. The glass transition temperature of these PS particles was 107.5 °C (Fig. 2). This experiment confirmed that suspension polymerization of styrene monomer with PPS was successful. As a result, graft copolymerization between PS and starch could be carried out in the present system. The present result is contrast to the previous result which was unable to polymerize PS without emulsifier (Cho & Lee, 2002).

3.2. Graft copolymerization on native starch granules

It is well established that the free-radical water-soluble initiators, including PPS, are dissociated in water and attract the OH group of starch causing free-radicals on the starch molecules and these free-radicals will attract the double bonds of vinyl monomers resulting in graft copolymer. Based on the results described in Section 3.1, PPS was able to initiate free-radicals on styrene monomer without the presence of surfactant and starch. Therefore, it is believed that synthesis of PS-g-starch copolymer under the present system is capable. Although PPS is water-soluble, radical formation on a starch chain and styrene monomer were simultaneously occurred due to sulfate ions ($S_2O_8^{2-}$) and finally the starch radicals reacted with a growing PS chain. The graft copolymerization occurred only at the interface between starch granule and PS phase. The evidence of this phenomenon was proved by SEM analysis and will discuss later. In practice the starch graft copolymer was performed in a slurry reactor with gelatinized starch or granular starch including the present study. Therefore, factors studied always include initiator concentration, monomer concentration, reaction time and temperature. In the present study, various conditions were chosen for graft copolymerization and compared grating efficiency in terms of the percentage of grafting – G (%), and yield of graft copolymerization – Y (%). Table 1 represents G (%) and Y (%) of various samples polymerized in 0.2 g of PPS and 100 g of water for 2 h. The G (%) indicates the amount of polystyrene grafted on starch granules and the Y (%) indicates yielding of polymerization of PS grafted on starch granules. In the starch-rich and styrene-rich systems both values show similar tendency, higher G (%) value showed higher Y (%) value. In the system containing 50:50 starch:styrene, both values were identical. Undoubtedly, the values of G (%) and Y (%) are not the same number due to different meaning. In the present study, G (%) was a criterion of grafting reaction. As evident from Table 1, the results indicate that the amount of cassava starch and styrene monomer showed significant effects on G (%), the styrene-rich system was preferable. The highest styrene content (7.5 g) offered the highest G (%). The G (%) increasing with monomer concentration and the optimal condition obtained from the monomer-rich system were reported by others (Fang et al., 2005; Pimpan & Thothong, 2006). The more styrene monomer the more polymerization; therefore, there was more opportunity for graft copolymerization. In general, there will be an optimum monomer concentration for each system. The too low concentration leads to decrease in active sites on the growing chains and the too high concentration leads to more homopolymerization (Qudsieh et al., 2004; Singh & Sharma, 2007).

Table 1
Effect of starch:styrene ratio and reaction temperature on the percentage of grafting, G (%), and yield of graft copolymerization, Y (%), of samples polymerized for 2 h with 100 g of water and 0.2 g of PPS

Starch (g)	Styrene (g)	Temperature (°C)	G (%)	Y (%)
2.5	7.5	30	1.07 ± 0.23	0.36 ± 0.08
2.5	7.5	40	9.33 ± 1.01	3.11 ± 0.34
2.5	7.5	50	15.07 ± 1.01	5.02 ± 0.33
2.5	7.5	60	2.67 ± 0.61	0.89 ± 0.20
5.0	5.0	30	2.60 ± 0.40	2.60 ± 0.40
5.0	5.0	40	5.40 ± 0.40	5.40 ± 0.40
5.0	5.0	50	8.80 ± 0.92	8.80 ± 0.92
5.0	5.0	60	4.67 ± 0.99	4.67 ± 0.99
7.5	2.5	30	5.07 ± 0.48	15.20 ± 1.44
7.5	2.5	40	5.96 ± 0.87	17.87 ± 2.60
7.5	2.5	50	7.20 ± 0.87	21.60 ± 2.62
7.5	2.5	60	2.40 ± 0.27	7.20 ± 0.80

Reaction temperature also played an important role on graft copolymerization. The G (%) increased with increasing reaction temperature up to 50 °C then decreased at 60 °C. The maximum G (%), 15.07%, was achieved when the reaction temperature was 50 °C. Undoubtedly, every polymerization system has its own optimum reaction temperature. Similar result was reported, the maximum grafting efficiency in graft copolymerization of starch and PMMA with PPS was at 50 °C (Qudsieh et al., 2004). Singh and Sharma (2007) also showed the optimum temperature in preparation of PS-g-starch copolymer. It is well established that the rate of decomposition of initiator increased with increasing reaction temperature, leading to more free-radicals. Increase in temperature also increased the molecular mobility and rate of diffusion of monomer. Consequently grafting reaction was promoted. Decrease in grafting after the optimum temperature was attributed to premature termination of growing chains and grafted chains as well as chain transfer reactions. It should be noted that the present study used very low reaction temperature. The gelatinization temperature of cassava starch is 62–73 °C (Taggare, 2004). For that reason, the crystallinity and starch granules of PS-g-starch should be similar to the native starch. These were proved by XRD and SEM analysis as discussed later.

To optimize PPS content, the 1:3 weight ratio of starch:styrene was polymerized at 50 °C for 2 h by using PPS in the range of 0.2–1.2 g. The experimental results are listed in Table 2. The G (%) and Y (%) increased after increasing PPS content from 0.2 to 0.4 g. Further increases in PPS content ($\geqslant$0.6 g), both values decreased. The maximum G (%), 31.47%, and Y (%), 10.49%, were obtained from the system containing 0.4 g of PPS. More PPS content may promote homopolymerization of styrene. The incidence of an optimum PPS content in polymerization has been reported (Qudsieh et al., 2004; Singh et al., 2006). The former group stated that the decrease of G (%) after the optimum may be due to an increase in the number of starch radicals terminated prior to monomer addition and an increase in homopolymer formation. The latter group mentioned that the decrease of G (%) may be due to accumulation of a large number of free-radicals resulting into premature termination of the growing chains and the grafting.

The reaction time was determined in the range of 1–5 h by using the reaction conditions giving G (%) = 31.47% in Table 2. The results were tabulated in Table 3. It was found that the reaction temperature of 2 h yielded the highest G (%). All conditions used in Table 3, except the reaction time of 5 h, provided high grafting reaction, and both values of G (%) and Y (%) were higher than those listed in Tables 1 and 2. In the present study longer reaction time was favorable to homopolymerization of styrene. Because graft copolymerization performed only on the surface of the starch granules; consequently, the rate of graft copolymerization was controlled by the surface of starch granules covering with PS growing chains. Once the starch surface was fully covered with PS, no more new PS could attach on the starch. As a result, longer reaction time generated more PS homopolymer. This optimum reaction time was in the same range as reported by Qudsieh et al. (2004) but Pimpan and Thothong (2006) reported slight effect of reaction time on grafting efficiency. The latter group used 80 °C for grafting reaction whereas the former group and the present study used 50 °C. The former group stated that the decrease of G (%) after the maximum was due to the solution viscosity increased with reaction time resulting in the reduction of reactive sites exposed to the vinyl monomer.

Table 2
Effect of PPS content on the percentage of grafting, G (%), and yield of graft copolymerization, Y (%), of samples polymerized at 50 °C for 2 h with 100 g of water, 2.5 g of starch and 7.5 g of styrene

PPS (g)	G (%)	Y (%)
0.2	15.07 ± 1.01	5.02 ± 0.33
0.4	31.47 ± 1.40	10.49 ± 0.47
0.6	12.53 ± 1.22	4.18 ± 0.41
0.8	6.93 ± 0.83	2.31 ± 0.28
1.0	8.00 ± 0.80	2.67 ± 0.27
1.2	13.07 ± 0.61	4.53 ± 0.20

Table 3
Effect of reaction time on the percentage of grafting, G (%), and yield of graft copolymerization, Y (%), of samples polymerized at 50 °C with 100 g of water, 2.5 g of starch, 7.5 g of styrene, and 0.4 g of PPS

Reaction time (h)	G (%)	Y (%)
1	21.07 ± 1.80	7.02 ± 0.60
2	31.47 ± 1.40	10.49 ± 0.47
3	17.60 ± 0.80	5.87 ± 0.27
4	20.40 ± 1.20	6.80 ± 0.40
5	7.07 ± 0.83	2.36 ± 0.28

To determine validation of graft copolymerization technique, the experiments were performed three replicates for each value. The standard deviations of G (%) and Y (%) shown in Tables 1–3 were in the acceptable range. Most of the standard deviations were less than 1%. The experimental results substantiated the reliability of grafting reaction in the present study.

3.3. Characterization of PS-g-starch copolymer

FTIR spectra of virgin materials and graft copolymer are represented in Fig. 3, and FTIR assignment of cassava starch and PS are listed in Table 4. FTIR assignment of starch had been reported by many research groups (Athawale & Lele, 2000; Ezekiel, Rana, Singh, & Singh, 2007; Mano, Koniarova, & Reis, 2003; Park, Im, Kim, & Kim, 2000). The cassava starch (Fig. 3a) and PS (Fig. 3b) showed the characteristic peaks as described in Table 4.

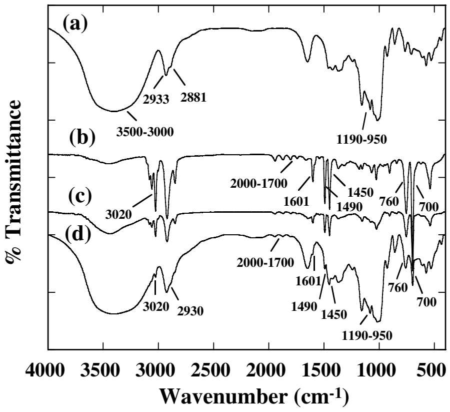

Fig. 3. FTIR spectrum of cassava starch (a), PS (b), PS-g-starch before Soxhlet extraction (c) and PS-g-starch after Soxhlet extraction with G (%) = 22.80% (d).

Table 4
FTIR assignment of cassava starch and polystyrene

Wavenumber (cm^{-1})	Assignment
Cassava starch	
3600–3000	O–H stretching
2933 and 2881	C–H stretching of CH_2
1190–950	C–O stretching
Polystyrene	
3020, 1601, 1490, 760 and 700	C–H stretching of aromatic ring
2920 and 2850	C–H stretching of CH_2
2000–1660	C=C in aromatic ring

The peak of starch at 1640–1650 cm^{-1} is controversial as had been reported in many articles. Ezekiel et al. (2007) mentioned bending mode of water at 1800–1600 cm^{-1}, while the δ (OH) bend of absorpted water was assigned at the wave number at 1640 cm^{-1} (Athawale & Lele, 2000; Mano et al., 2003; Park et al., 2000) and at 1650 cm^{-1} (Athawale & Lele, 2000). The wavenumber at 1653 cm^{-1} was assigned as a peak of the first overtone of OH bending (Pal, Mal, & Singh, 2005). On the other hand, 1650 cm^{-1} was assigned as COC stretching (Lee, Kweon, Koh, & Lim, 2004). Nevertheless, this peak was not the main characteristic of starch; therefore, discussion of this peak was beyond the scope of this study. The little peak at 3444 cm^{-1} appeared in PS spectrum may be due to the moisture content in the PS. The FTIR spectrum of the product obtained from grafting reaction (non-extracted product) is shown in Fig. 3c. It showed a combination of both PS's and cassava starch's characteristics. The peaks of CH stretching (2933 and 2881 cm^{-1}) and CO stretching (1190–950 cm^{-1}) of starch were not observed; only a broad peak of OH stretching at 3444 cm^{-1} was detected. In contrast, all characteristics of PS were remarkably shown in this spectrum. After Soxhlet extraction, the precipitate (un-extractable product) exhibited the spectrum similar to that of starch and also showed the characteristic peaks of PS: CH stretching of aromatic ring (1601, 1490, 760 and 700 cm^{-1}) and C=C in aromatic ring (2000–1700 cm^{-1}) as shown in Fig. 3d. Both starch and PS showed CH stretching in CH_2 within the same range of wavenumber; therefore, this assignment was not in consideration. The main characteristics of the precipitate arose from the starch manner due to the non-reacted starch was not extracted. The result indicates that PS-g-starch copolymer was derived in the present system.

TGA thermograms of polymers are shown in Fig. 4. PS showed higher thermal stability than starch; degradation temperature of PS and starch was in the range of 360–465 °C and 275–360 °C respectively. Furthermore, PS showed very little ash (~0%) after thermal degradation, whereas starch showed 20% of ash. The weight loss from 50 to 110 °C of starch could be the result of water evaporation and has been reported by others (Janarthanan et al., 2003; Kiatkamjornwong et al., 1999). The product without extraction of PS homopolymer (the non-extracted product) showed two-step degradation process including the characteristics of both PS and starch (Fig. 4c). The first step was higher than the degradation temperature of starch but lower than that of PS. The second step was in the degradation temperature of PS. Remarkably, the major percentage of weight loss derived mainly from PS homopolymer. After Soxhlet extraction, TGA thermograms of the graft copolymers (the un-extractable product) also showed the two-step degradation process (Fig. 4d–f); however, the starch characteristics played a major role in the thermograms. This was because the PS homopolymer was completely extracted and the starch remains became the major component of the graft copolymer. The evidence of PS-g-starch copolymer was only exhibited at the temperature range of 320–450 °C similarly to the non-extracted product. The degree of weight loss at this temperature range increased with increasing G (%). The TGA results confirmed the achievement of graft copolymerization in the present study and also indicated the increase in thermal stability of starch with PS-g-starch copolymer.

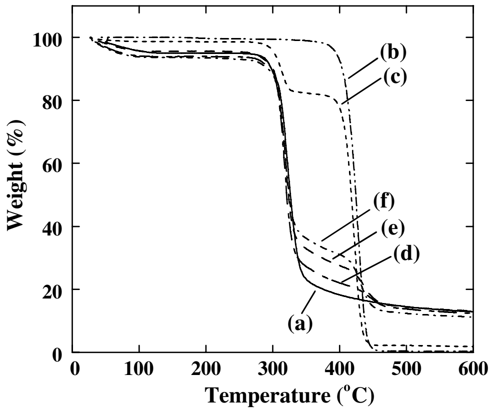

Fig. 4. TGA thermogram of cassava starch (a), PS (b), the non-extracted product with G (%) = 22.80% (c), the un-extractable product with G (%) = 14% (d), 22.80% (e) and 32.8% (f).

DSC traces of starch, PS and graft copolymers are demonstrated in Fig. 5. In general DSC thermograms of starch

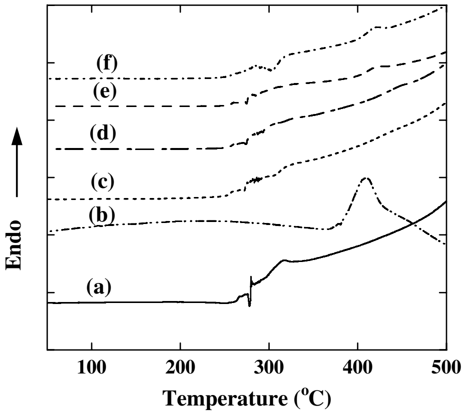

Fig. 5. DSC thermogram of cassava starch (a), PS (b), the non-extracted product with G (%) = 22.80% (c), the un-extractable product with G (%) = 14% (d), 22.80% (e), and 32.8% (f).

obtained from the first heating scan will show a broad endothermic peak at 100 °C. Some researchers reported the crystalline melting temperature in native starch. Hamdan, Hashim, ahmad, and Embong (2000) mentioned that the peak between 50 and 150 °C was due to the melting of the amylopectin fraction in sago starch, while Ge, Xu, Meng, and Li (2005) believed that the endothermic peak at 126.9 °C was due to the crystalline melting which was formed between residue water and molecular chains of starch via hydrogen bondings. Mano et al. (2003) assumed that it may be due to water adsorption occurring above room temperature during heating scan. There is no conclusion for these explanations at this moment although all native starch shows this peak. However, this broad peak will not be observed on the second heating scan as shown in Fig. 5a. A sharp exothermic peak at 275 °C on DSC thermogram of starch agreed with its TGA thermogram, the starting decomposition temperature. PS showed thermal oxidation at 400 °C (Fig. 5b) correspondingly to TGA result. DSC trace of the product before and after Soxhlet extraction (Fig. 5c–f) looked similar to that of starch. Thermal oxidation of the starch phase in the graft copolymer occurred at higher temperature (>275 °C) as increasing G (%).

SEM micrographs of the non-extracted product or the product before Soxhlet extraction are shown in Fig. 6a and b. Sub-micron spherical particles of PS covering the starch granules were observed. The PS particles adhered both on the surface of the starch granules and on themselves. The fibrils between PS particles and starch granules are shown in Fig. 6b indicating PS-g-starch copolymer. After Soxhlet extraction, PS patches covering on the starch granules were obtained as demonstrated in Fig. 6c. The number of holes on the patchy PS were the homopolymer particles (“Free PS”) dissolved by toluene during Soxhlet extraction. Similar feature has been observed by others (Chen et al., 2005; Cho & Lee, 2002). SEM micrographs of other un-extractable products are shown in Fig. 7. At low G (%), PS patches still showed many holes (Fig. 7a and b). The hole free patchy PS was obtained from the product with the highest G (%) (Fig. 7c). The morphology of graft copolymer correlated to the value of G (%). The highest G (%) showed denser graft copolymer.

Based on the above characterization, it was shown that PS-g-starch copolymer could be prepared by using suspension polymerization technique. The graft copolymerization was carried out at temperature lower than gelatinized temperature; as such, there was no change in granular shape of starch as determined by SEM. However, the semi-crystalline structure of the starch granules may or may not change after grafting reaction. In order to identify changes in crystallinity, XRD technique was utilized. XRD pattern of the un-extractable product with G (%) = 22.80% looked similar to that of the virgin starch (Fig. 8). Degree of crystallinity obtained from area under the peaks was in the same range, 37% and 39% for the native starch and the un-extractable product with G (%) = 22.80%, respectively. This indicated that the reaction condition did not impact the crystalline phase. Undoubtedly, this is due to the low reaction temperature. If the system employed gelatinized starch, the crystallinity should be lower than the native one.

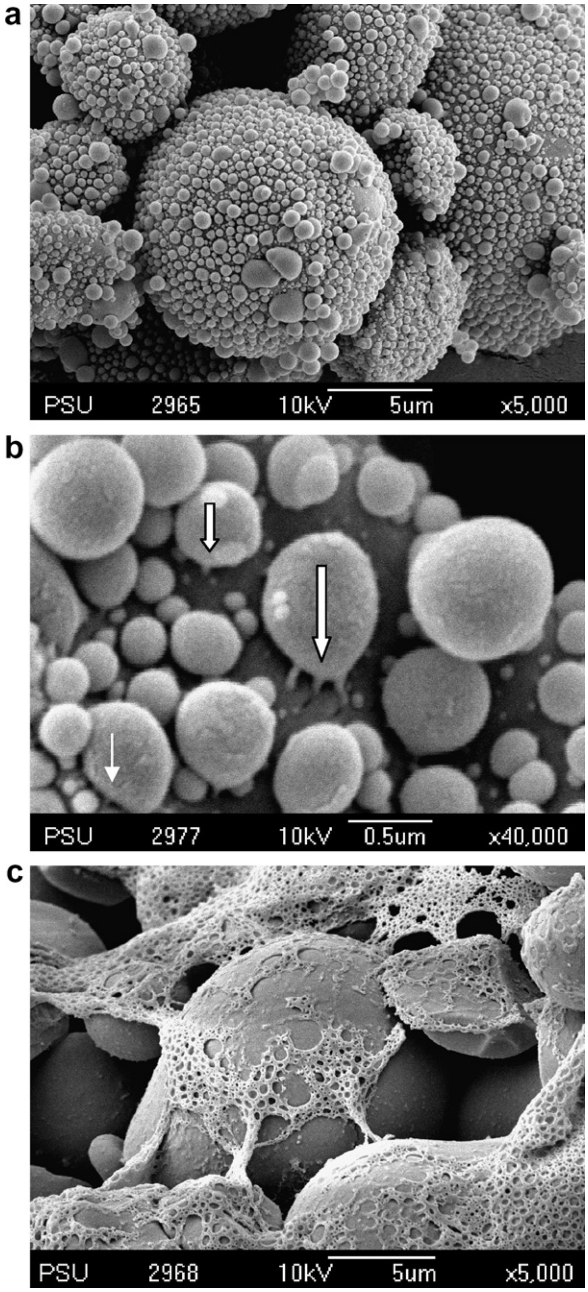

Fig. 6. SEM micrographs of product with G (%) = 22.80%. (a) and (b) the non-extracted product (before Soxhlet extraction); (c) the un-extractable product (after Soxhlet extraction).

3.4. Soxhlet extraction validation

The Soxhlet extraction was the key process to identify the PS-g-starch copolymer. For that reason, it is very important to validate this process. Every extraction was checked with precipitation in the non-solvent as described

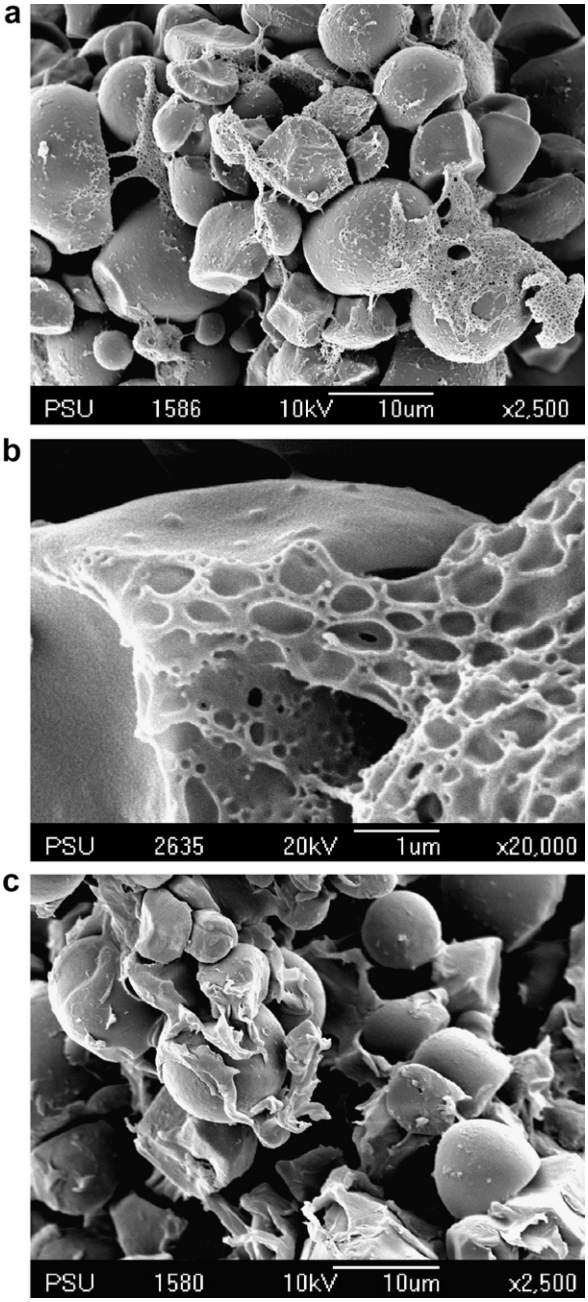

Fig. 7. SEM micrographs of the un-extractable product (after Soxhlet extraction). (a and b) G (%) = 14.00%; (c) G (%) = 32.80%.

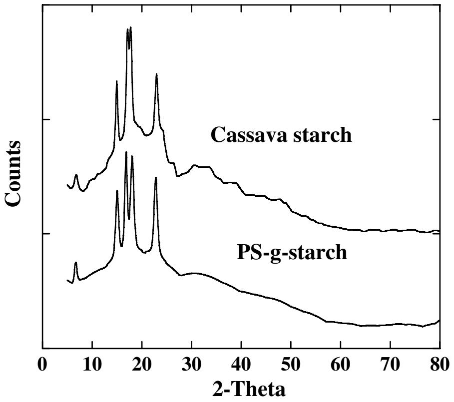

Fig. 8. XRD pattern of the cassava starch and the un-extractable product (after Soxhlet extraction) with G (%) = 22.80%.

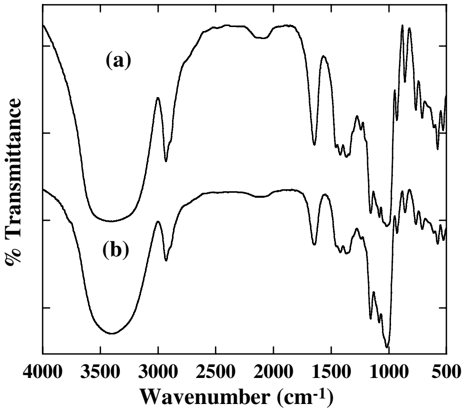

Fig. 9. FTIR spectrum of the virgin cassava starch (a) and the un-extractable product (after Soxhlet extraction) of the starch/PS blend (b).

in Section 2.2. Nonetheless, to confirm this process, blend of starch and PS was prepared and was extracted under the same procedure. The FTIR spectrum of the un-extractable product from the polymer blend was the same as that of virgin starch (Fig. 9). As a result, the process of Soxhlet extraction in the present study was valid.

4. Conclusions

The synthesis of polystyrene grafted cassava starch was carried out from styrene monomer and cassava starch using potassium persulfate as an initiator. The optimum condition giving the maximum percentage of grafting (31.47%) was derived when 2.5 g of cassava starch, 7.5 g of styrene monomer, reaction time of 2 h and reaction temperature of 50 °C were used. The formation of the polystyrene grafted on cassava starch was investigated by FTIR technique. The results obtained from SEM, TGA and DSC confirmed the presence of polystyrene grafted on cassava starch. Morphology of starch granules did not changed after grafting reaction as determined by SEM and XRD. The present study shows that PS-g-starch copolymer could be prepared by suspension polymerization of styrene monomer on the starch granules.

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