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Preparation of cassava starch-graft-polyacrylamide superabsorbents and associated composites by reactive blending

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ABSTRACT

Cassava starch-*g*-polyacrylamide (PAM) was successfully prepared by a reactive batch processing using a specially designed batch reactor resulting in a superabsorbent polymer (SAP) with water absorption of 605 g/g being obtained under the optimized reaction conditions. The occurrence of a graft copolymer was confirmed by FT-IR spectra, where it was found to exhibit all characteristic bands of both starch and acrylamide (AM) units. SEM micrographs of the starch granules showed an irregular shape and varied particle sizes with a smooth surface, while the graft copolymers had a coarse porous structure and broad network. Various types of inorganic filler were added to the graft copolymer to prepare the SAP composites (SAPC). It was found that the SAPC with bentonite clay exhibited the highest water absorption of approximately 730 g/g. Conversely, the incorporation of silica to the graft copolymer gave a significantly lower water absorption capability than the copolymer alone.

1. Introduction

Biodegradable polymers have drawn considerable attention in both academia and industry due to the problem of environmental pollution caused by the disposal of synthetic polymer waste. Therefore, the development of biodegradable polymers has been one of the main areas of current interest. One of the simple practical approaches to prepare biodegradable polymers is to blend polymers with various types of starch. Since Thailand is one of the world's largest exporters of cassava products it, therefore, has a great opportunity to search for a reliable process to use cassava starch by modifying its molecular structure to produce biodegradable products, such as superabsorbent polymers (SAPs) (Lanthong, Nuisin, & Kiatkamjornwong, 2006). SAPs are a lightly crosslinked network of hydrophilic polymer chains that can absorb and retain a large quantity of aqueous fluids, and where the absorbed fluids are hardly removed even under pressure (Zhang, Li, & Wang, 2006). Most of the current SAPs are synthetic polymers that have a poor biodegradability leading to environmental problems with their disposal. The development of starch-based SAPs could potentially be used to solve this problem. Potential applications of starch-based SAPs are fairly diverse and include personal care products, fire-fighting gels, agricultural uses, and so forth (Willett & Finkenstadt, 2006). Starch-based SAPs are developed by grafting starch with unsaturated hydrophilic monomers, such as acrylic, acrylamide (AM) (Athawale & Lele, 1998; Karadağ, Üzüm, & Saraydin, 2005; Lanthong et al., 2006; Mostafa, 1995; Willett & Finkenstadt, 2006; Zhang et al., 2006) and ε-caprolactone (Chen et al., 2005), and can be formed by radical chain copolymerization via chemical initiation (Athawale & Lele, 2000; Chen, Park, & Park, 1999) or by the use of γ-ray irradiation (Caykara, Bozkaya, & Kantoğlu, 2003; Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002).

Although reactive extrusion has been used as a continuous process (Carr, Kim, Yoon, & Stanley, 1992; Willett & Finkenstadt, 2006; Yoon, Carr, & Bagley, 1992), processing of most starch-based graft copolymers is typically done in a batch process, but this consumes a large amount of water (Fanta, 1996; Weaver et al., 1977). Starch-*g*-polyacrylamide (PAM) has been successfully prepared before using a co-rotating twin screw extruder (Finkenstadt & Willett, 2005; Willett & Finkenstadt, 2003), but the maximum water absorption capacity of the SAPs obtained using this process was relatively low at only approximately 300 times their dry weight in water (Carr et al., 1992).

In this work, a specially designed batch reactor was built and used to prepare starch-*g*-PAM based SAPs via reactive processing with low quantities of water. This was aimed to enhance the water retention capability of the saponified starch-*g*-PAM SAP obtained and also to improve some other important properties (see below). The influence of the reaction time, temperature, concentration of

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the initiator and the molar ratio of starch:AM on the conversion, graft efficiency, graft content and water absorbency were investigated. SAP composites (SAPC) of the starch-*g*-PAM with silica, bentonite clay and China clay were also prepared and their water absorption was tested.

2. Experimental

2.1. Materials

The cassava starch used as the polymer substrate was obtained from Siam Starch (1966) Co., Ltd., Rayong, Thailand. AM, used as a grafting monomer, was manufactured by Fluka (Buchs, Switzerland). Potassium persulfate (KPS), used as a free radical initiator, was manufactured by Asia Pacific Specialty Chemicals Ltd. (Seven Hills, Australia). Hydroquinone, used as a free radical scavenger, was manufactured by Merck (Darmstadt, Germany). *N*,*N*′-Methylenebisacrylamide (*N*,*N*′-MBA), used as a crosslinker, was manufactured by Fluka (Buchs, Switzerland). For the preparation of SAPCs, Ultrasil VN 3 GR silica obtained from Evonik Degussa GmbH (Essen, Germany), bentonite clay, grade SAC-1, manufactured by Thai Nippon Chemical Industry, Co., Ltd. (Samut Sakhon, Thailand) and China clay manufactured by Renuka Minchem Pvt. Ltd. (Udaipur, India) were each mixed in the reactive batch processing.

2.2. Reactive polymerization

Reactive batch processing was performed using an in-house specially designed and built batch reactor with a capacity of approx-

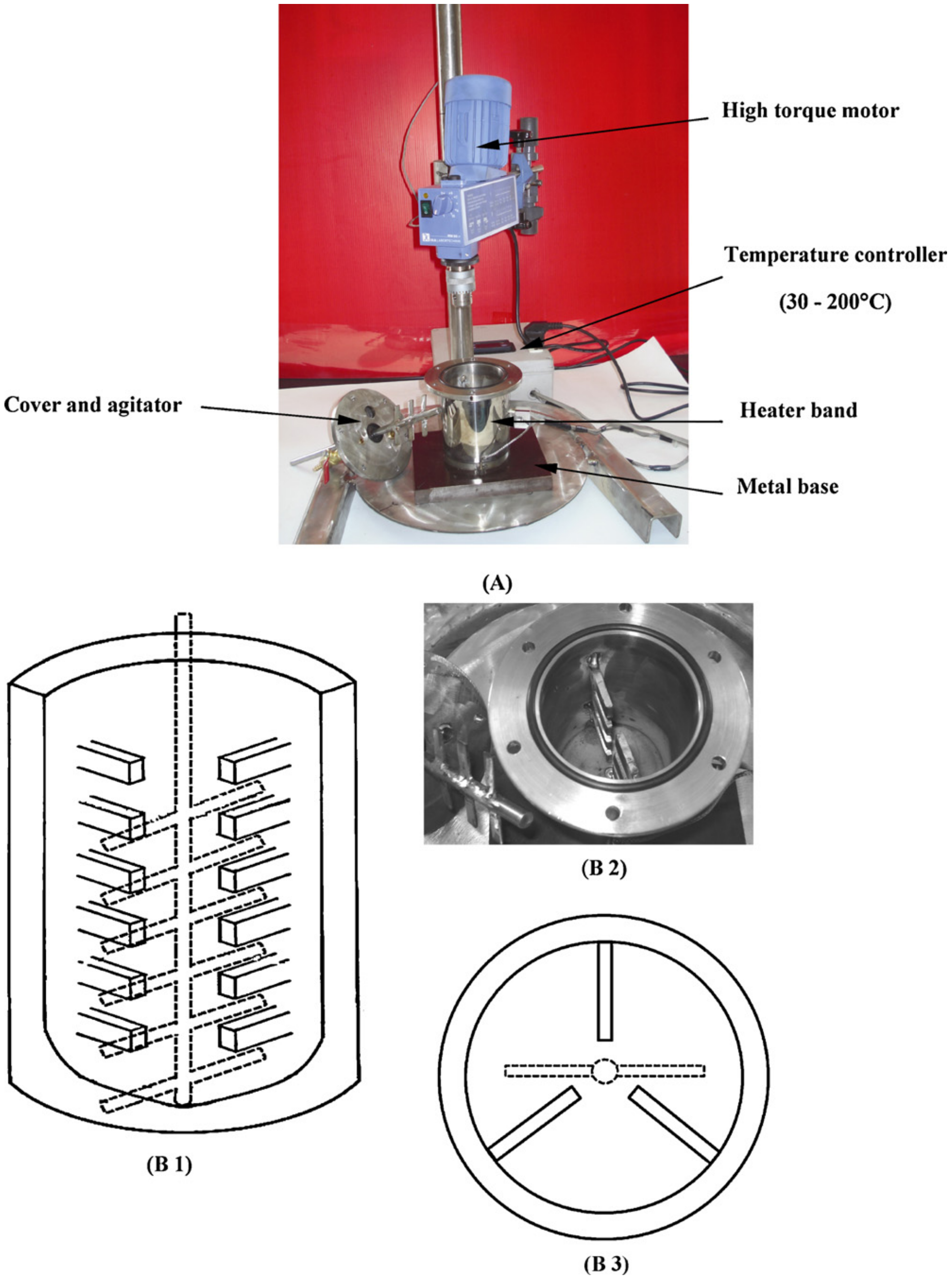


Fig. 1. Components of a specially designed batch reactor. A: Batch reactor, and B: specially designed mixing elements showing (B1) side view of total stirring blades, (B2) top view of the reactor stirring blades, and (B3) top view of total stirring blades.

Table 1
Relationship of the Reynolds number and mixing speed.

Reynolds number	Mixing speed
<10	Low speed for laminar flow
$10 < N_{\text{rev}} < 10^4$	Medium speed for transition
$>10^4$	High speed for turbulent flow

imately 1 L, as shown in Fig. 1. It is a stainless steel reactor with a specially designed internal geometry containing an agitator. A programmable heating element surrounded the outside cylinder of the reactor, and a stainless steel cover for the inlet and outlet of nitrogen gas was also built. A high torque motor with a maximum torque of 3000 N cm (RW 47D High-Viscosity Mechanical Overhead Stirrer powered by a 3 × 230 V, 60 Hz, 570 W, IKA, Staufen Germany) was fitted to an in-house made specially designed agitator to cause a thorough mixing of the highly viscous material during the graft copolymerization.

Graft copolymerization was begun by drying cassava starch in a hot air oven for at least 4 h at 60 °C before incorporating it into the batch reactor. Nitrogen gas was purged thoroughly into the reactor and stirred for at least 1 min to eliminate oxygen gas. Distilled water and cassava starch was added at a 1:1 (w/w) ratio and stirred at 60 °C for 20 min to form the gelatinized starch. The temperature of the mix was then increased to 80 °C and stirred for 2 min before incorporating 3.70 mM KPS initiator and then stirring continuously for another 30 min. An aqueous solution of 23.81% (w/w) AM was then added drop wise to the reactor with a continual stirring for the indicated time intervals (a range of 110–260 min). The actual concentration of the starch was also 23.81% (w/w) of the total mass, i.e., starch:AM = 1:1 by weight. The reactor is capable of handling gelatinized starch at this mixture ratio with the small amount of water because the high torque motor is used. In this part of experiment, no crosslinker was incorporated for characterization purposes. Then, the ungrafted homopolymer (PAM) was soluble in ethanol/water whereas the starch grafted PAM was insoluble.

The reaction and newly synthesized product was then quenched by adding 0.5% (w/w) of hydroquinone in ethanol and left overnight to remove the un-reacted monomer. The solid products were finally collected by filtration and dried.

2.3. *Saponification*

To enhance the water absorbing capability of the resultant SAP, 40 g of the graft copolymer was transferred to a flask containing 100 mL of 1 mol/L of sodium hydroxide solution and 100 mL of distilled water and the content was saponified at 90 °C for 2 h. The final concentration of the graft copolymer in NaOH solution was 16.67% (w/w) of the total mass, i.e., 40 g of the graft copolymer in 240 g of the mixture. The pH of the saponified products was then adjusted to 7 by the addition of a 1 M HCl solution and the graft copolymer was coagulated and precipitated by the rapid addition of an excess amount of methanol. The solid saponified copolymer was then filtered and washed thoroughly to remove the ungrafted starch as well as the un-reacted monomer. The thoroughly washed products were then dried in a vacuum oven at 60 °C until the weight of the polymer was constant. They were then ground and filtered through an 80-mesh screen to leave the powdery SAP.

2.3.1. *Influence of the inorganic filler*

Three types of inorganic filler, namely silica, China clay and bentonite clay, were incorporated in the starch-*g*-PAM copolymer SAP to form SAPCs. The graft copolymer was first prepared using a 1:1 (w/w) ratio of starch:AM at a reaction time and temperature of 140 min and 80 °C with KPS at 1.5 wt% of starch and 0.3 wt% of *N*,*N*′-

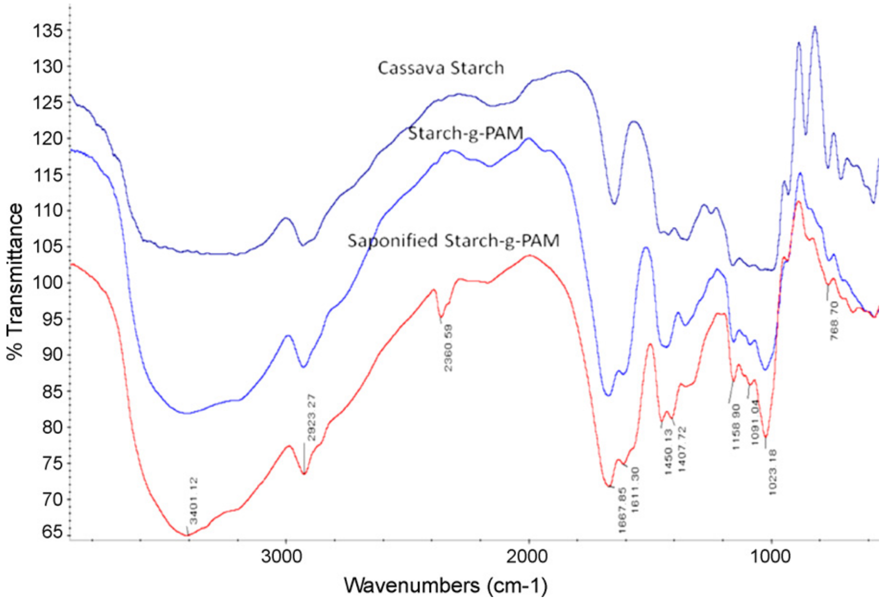
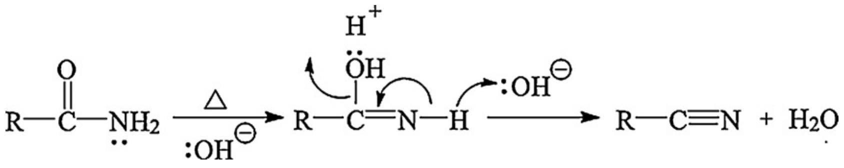


Fig. 2. Representative FT-IR spectra of cassava starch, the starch-g-PAM copolymer and its saponified product.



Scheme 1. Proposed mechanism for the formation of nitrile group from dehydration of amide group by alkaline hydrolysis at 90 °C.

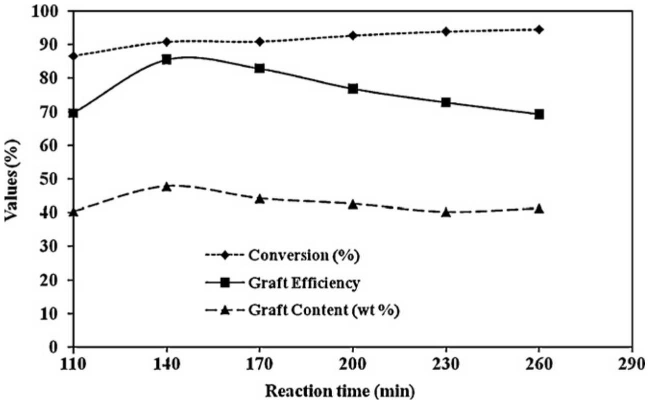


Fig. 3. Relationship between the level of conversion, graft efficiency and graft content of the saponified starch-*g*-PAM copolymer SAP against the reaction time employed for the copolymer formation.

MBA under a stirring speed of 300 rpm. The fillers were filtered through a 325-mesh stainless steel screen before incorporating in the reaction mixture at a loading level of 10 wt% of graft copolymer.

2.4. Water absorbency

The powdery SAP (0.1 g) was immersed in distilled water (250 mL) for 24 h at ambient temperature (25–30 °C) to reach an equilibrium swelling. The residual water was removed by filtration through an 80-mesh stainless steel screen with the water absorbed polymer left on the screen for at least 1 h to drain off the additional unabsorbed water. During this period, the screen was gently shaken with an alternate lined angle of 15–20° to ensure that most of the un-absorbed water was separated. The un-absorbed water which was held in the free spaces among the SAP particles, due to variation in particle sizes, by capillary force must be excluded. The water absorption was determined by weighing the swollen graft copolymer and its dried polymer in Eq. (1) as follows:

$$\text{water absorbency}\,(\text{g/g}) = \frac{W_1 - W_0}{W_0}, \tag{1}$$

where W_0 is the weight of the dried SAP and W_1 is the weight of the swollen sample.

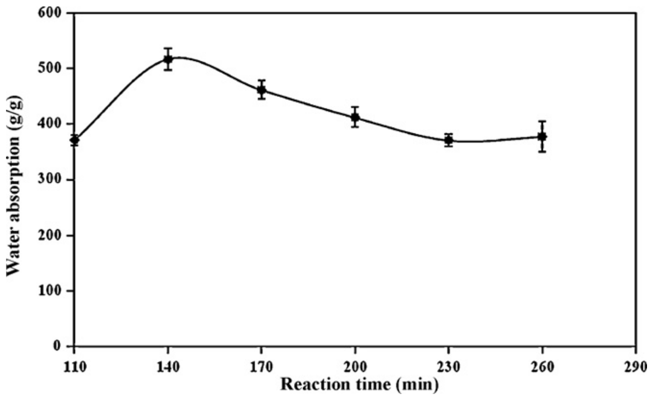


Fig. 4. Relationship between the reaction time used for the starch-*g*-PAM copolymer SAP formation and the resultant water absorption obtained by the SAP. Data are shown as the mean ± 1 S.D. and are derived from 3 replicate samples.

2.4.1. Characterization

The nitrogen contents were measured using a Kjeldahl digestion unit consisting of Kjeldatherm block digestion units (702001 KBL 20S), a programmable distillation unit with a titration unit (Vapodest 45s) and a scrubber unit, all manufactured by Gerhardt (Königswinter, Germany). Details for the determination of nitrogen content were as described elsewhere (McGill & Figueiredo, 1993). The conversion, graft content and graft efficiency were each calculated using the following equations (2)–(4) (Willett & Finkenstadt, 2003):

$$\text{conversion} = \frac{100N_{crud}}{N_f}, \tag{2}$$

$$\text{graft content} = \frac{100N_i}{19.72}, \tag{3}$$

$$\text{graft efficiency} = \frac{100(1-f)N_i}{(1-f)N_i + fN_s}, \tag{4}$$

where N_{crud} is the nitrogen content (wt%) of the newly synthesized (crude) product. N_f is the theoretical nitrogen content based on the feeding amount of the monomer. N_i is the nitrogen content of the EtOH/H_2O-insoluble fraction and f is the weight of the soluble fraction in the EtOH/H_2O. The nitrogen content of the PAM was 19.72 wt% by the above method. Graft efficiency is based on the amount of monomer polymerized, and is equal to the ratio

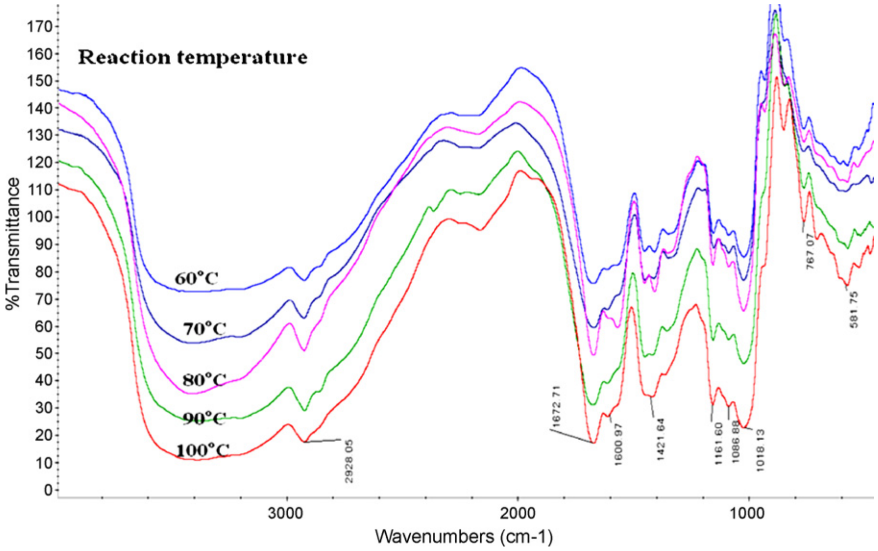


Fig. 5. Representative FT-IR spectra of the purified starch-*g*-PAM copolymer prepared at the indicated five different reaction temperatures.

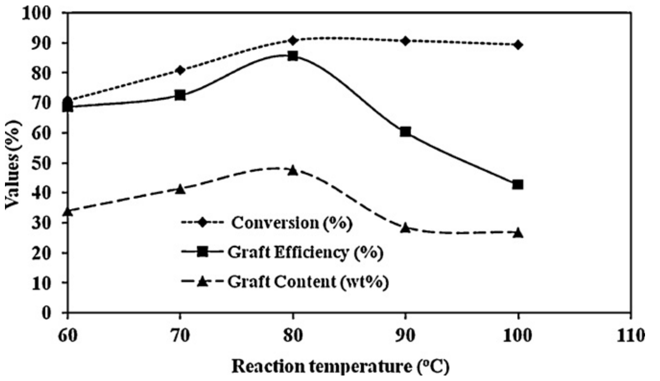


Fig. 6. Relationship between the reaction temperature used to form the starch-*g*-PAM copolymer SAP and the level of conversion, graft efficiency and graft content of the obtained SAP.

of the insoluble amount of PAM to the total amount of PAM (the insoluble and soluble parts). It should be mentioned that GE was calculated only in the reaction system without incorporation of the crosslinking agent.

2.4.1.1. Morphology of SAP and SAPC. The SAP and SAPC samples were dried at 105 °C for 2 h to eliminate moisture. They were cooled in a desiccator, and coated with gold and characterized using a scanning electron microscopy (JOEL SEM, JSM-5200, Tokyo, Japan) at 15 kV.

3. Results and discussion

Based on the specially designed reactor (Fig. 1), the mixing speeds for the polymerization reaction can be controlled based on the relationship between the Reynolds number of the reactor and the mixing speed of the reaction mixture (Table 1). The Reynolds number (N_{Re}) equation is shown in Eq. (5):

$$N_{Re} = \frac{\rho n D^2}{\mu}, \qquad (5)$$

where D is the diameter of the propeller (0.31 in), n is the speed of the propeller (300 rpm), ρ is the initial density of the starch (1.50 g/cm^3) and μ is the initial viscosity of the starch (0.018 Pa s). Based on Eq. (5), the specially designed reactor has a Reynolds number of 224.7 and it is possible to state that the reactor is capable of handling viscous dispersion and thus it can mix the reaction mixture by the transition mode at a medium speed (see Table 1).

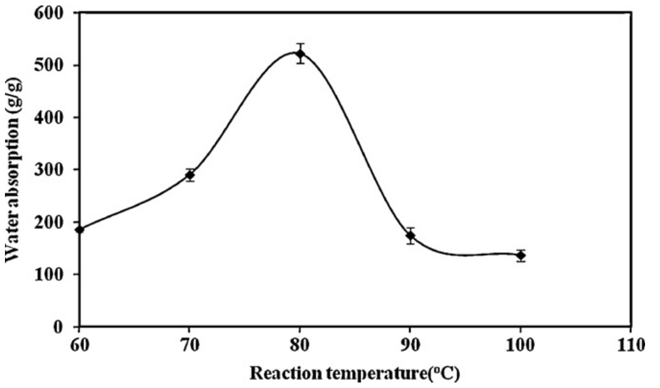


Fig. 7. Relationship between the reaction temperature used to form the starch-*g*-PAM copolymer SAP and the level of water absorption of the obtained SAP. Data are shown as the mean ± 1 S.D. and are derived from 3 replicate sample.

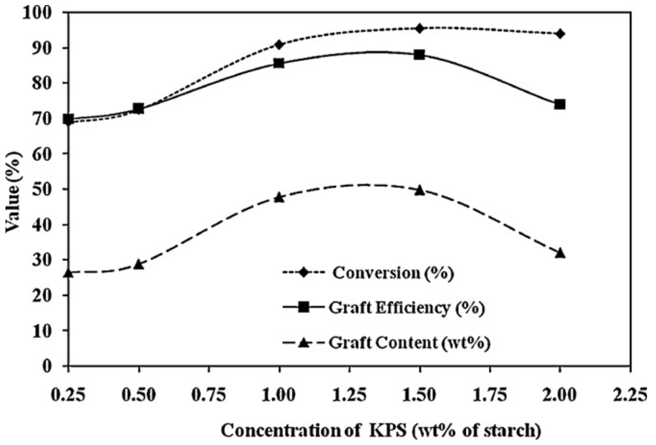


Fig. 8. Relationship between the KPS concentration used to form the starch-*g*-PAM copolymer SAP and the level of conversion, graft efficiency and graft content of the obtained SAP.

3.1. *Influence of reaction time*

The total time from the start of stirring, to mix the starch with water, until the end of the stirring is termed the reaction time. In this work, the reaction time was varied at 110, 140, 170, 200, 230 and 260 min, with a fixed 1:1 (w/w) ratio of starch:AM, KPS at 1 wt% of starch, a reaction temperature of 80 °C with a stirring speed of 300 rpm.

Fig. 2 shows the representative FT-IR spectra of the cassava starch, the purified starch-*g*-PAM and its saponified product. The broad absorption bands in the region of wave number 3550–3200 cm^{-1}, which represent the O–H stretching vibration, are clearly seen, and the medium absorption peak at 2923 cm^{-1} represents the C–H stretching vibration. Furthermore, the triplet peaks with a strong absorption at 1156, 1051 and 1023 cm^{-1} indicate the presence of the C–O–C stretching vibration. The IR spectrum of the starch-*g*-PAM copolymer gives all the absorption bands of cassava starch plus, additionally, the absorption peaks at 3401, 1667 and 1611 cm^{-1}, which indicate the N–H stretching, C=O stretching and N–H bending of the amide groups, respectively. Therefore, these are the characteristics of the –CONH$_2$ groups in the grafted PAM. Furthermore, the peak at 1407 cm^{-1} that represents –C–N stretching, and that at 766–710 cm^{-1} that represents the weak band of N–H out of plane bending, all are also characteristic bands of the amide grafted onto the cassava starch backbone. After the saponification, the following absorption peaks were observed

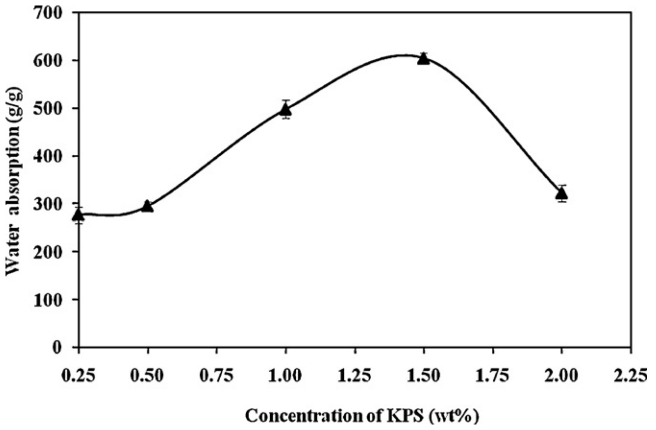


Fig. 9. Relationship between the KPS concentration used to form the starch-*g*-PAM copolymer SAP and the level of water absorption of the obtained SAP. Data are shown as the mean ± 1 S.D. and are derived from 3 replicate samples.

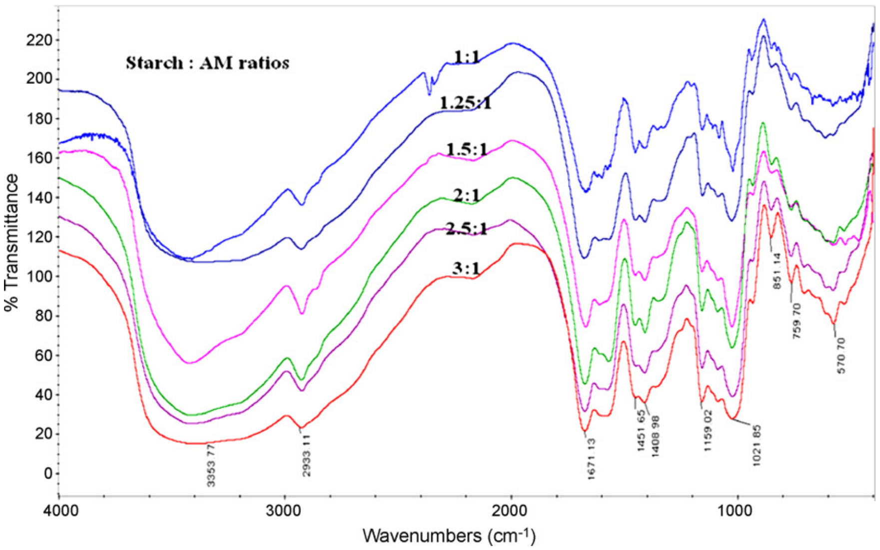


Fig. 10. Representative FT-IR spectra of the purified starch-g-PAM copolymer prepared from six different (w/w) ratios of starch:AM.

that confirm the occurrence of PAM; the N–H stretching of O=C–NH (amide band), the C=O stretching, the N–H bending at 1450 cm^{-1} for the –C–N stretching and a relatively intense and sharp peak at 2360 cm^{-1} which is the –C≡N (nitrile or cyanyl) peak, an intermediate peak from the saponification in alkaline solution of the amide group converted to the nitrile or cyanyl group. Although an amide is considered a neutral functional group, it is both weak acid and weak basic, and amide is hydrolyzed by strong acid or strong base. Even though $POCl_3$ is widely used as a dehydrating agent to convert O=C–NH (amide) to R–C≡N (nitrile or cyanyl) (Wade, 1991) it is possible that heat generated at the saponification condition can act as a dehydrating agent to dehydrate acrylamide moiety to nitrile moiety for the SAP prepared from high content of acrylamide (starch:AM = 1:1). This is because the two hydrogen atoms of the amino group can be abstracted by the hydroxide anion under heat. The carbonyl oxygen of acrylamide moiety is simultaneously protonated to become the hydroxyl group as a leaving group which can promote the formation of the nitrile or cyanyl group as shown in Scheme 1.

It is further observed (see the effect of starch:AM ratio) that at the higher starch:AM ratios, this peak (2360 cm^{-1} peak) disappeared because more starch active sites were available for AM grafting.

Fig. 3 shows the influence of the reaction time on the conversion from monomer to polymer, graft efficiency and graft content (based on Eqs. (2)–(4)). The conversion level slightly increased with increasing reaction time from ~88% at 100 min to a maximum value of approximately 95% at a reaction time of 260 min (the longest reaction time). On the other hand, the graft efficiency and graft content initially increased more significantly as the reaction time was increased from 110 to 140 min (70–85% and 40–50%, respectively), and then decreased with longer reaction times. The decrease in graft efficiency with longer reaction times was slightly more marked for graft content but nevertheless the maximum graft efficiency and content were both attained at a reaction time of 140 min. This might be attributed to a higher level of PAM homopolymer formation with reaction times of longer than 140 min. Furthermore, there is a possibility that the crosslinked PAM can be simply degraded by mechanical shear into lower molecular weight fragments during a prolonged reaction time. Regardless, the graft copolymer prepared with a reaction time of 140 min incorporated the highest grafted PAM, content and this corresponded to the highest water absorption capability of the saponified graft copolymer (Fig. 4) which was also obtained from a reaction time of 140 min at ca. 520 g/g). Increasing the reaction time above 140 min caused a decreased water absorption capability, and this is also likely to be due to a lower amount of the grafted PAM which becomes saponified and so more hydrophilic in nature.

Given that reaction times over 140 min only slightly increased the level of conversion but markedly reduced that of the graft efficiency, graft content and water absorbance, a reaction time of 140 min was selected for further investigation.

3.2. *Influence of the reaction temperature*

Fig. 5 shows the representative FT-IR spectra of the purified starch-g-PAM copolymer prepared from five different reaction temperatures (60, 70, 80, 90 and 100 °C) with a fixed reaction time of 140 min, a starch:AM (w/w) ratio of 1, KPS at 1% (w/w) and a stirring speed of 300 rpm. The characteristic bands of cassava starch and amide groups are present, similar to those observed for the purified starch-g-PAM copolymer in Fig. 2, which confirms the formation of a cassava starch-g-PAM copolymer. The influence of the reaction temperature upon the graft efficiency, graft con-

Table 2
Properties of the cassava starch-*g*-PAM copolymer SAP derived from various (w/w) ratios of starch:AM.

Starch:AM (w/w) ratio	Conversion (%)	Graft efficiency (%)	Graft content (wt%)	Absorbency in DI water (g/g)
1:1	90.9 ± 1.5	85.6 ± 2.1	47.8 ± 1.7	606 ± 10.2
1.25:1	86.7 ± 1.8	80.6 ± 3.5	44.0 ± 3.7	479 ± 9.8
1.5:1	76.4 ± 2.1	76.7 ± 3.9	31.3 ± 3.1	407 ± 11.1
2:1	73.2 ± 3.2	71.1 ± 2.7	28.3 ± 4.7	349 ± 9.7
2.5:1	61.7 ± 3.8	55.6 ± 3.9	23.1 ± 3.1	222 ± 8.9
3:1	48.2 ± 2.7	39.4 ± 4.1	16.8 ± 2.9	132 ± 10.4

The experiment was carried out in triplicate and the data was presented within ±1 S.D.

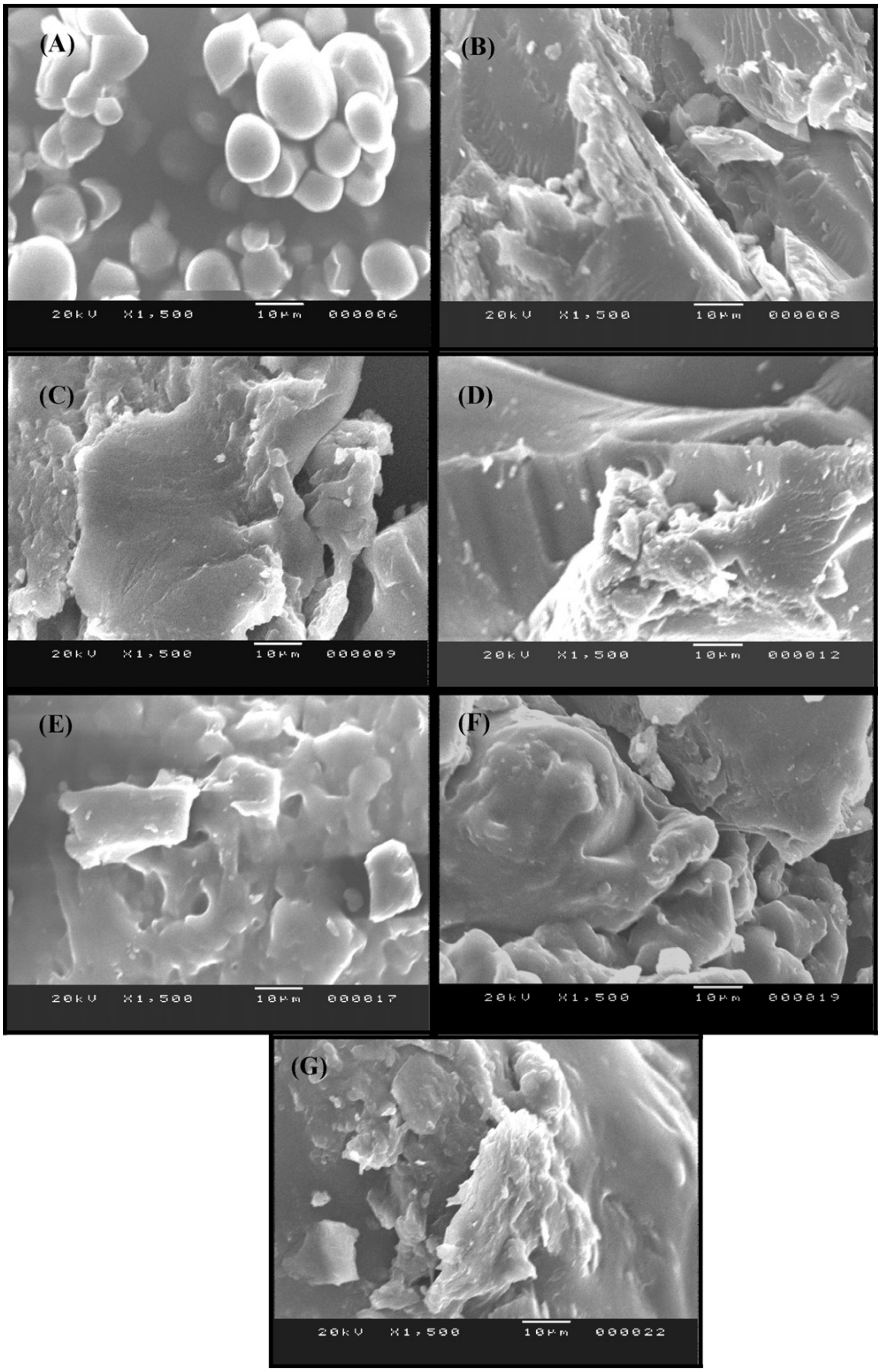


Fig. 11. Representative SEM micrographs of (A) cassava starch, and the purified starch-*g*-PAM copolymer SAP prepared from starch:AM (w/w) ratios of (B) 1:1, (C) 1.25:1, (D) 1.5:1, (E) 2:1, (F) 2.50:1 and (G) 3:1.

tent and level of conversion of monomer to polymers is shown in Fig. 6, where the conversion linearly and significantly increases with increasing temperature within the range of 60–80 °C and then reaches a smooth plateau (or mild decrease) region at reaction temperatures higher than 80 °C. This might be related to the optimum decomposition temperature of KPS at 80 °C, where at temperatures lower than 80 °C the initiator molecules decompose less to give fewer free radicals. On the other hand, at temperatures higher than 80 °C too high a rate of free radical generation is attained which then recombine and so reduce the efficiency of the initiator. The graft efficiency and graft content also increased with increasing reaction temperatures up to 80 °C, and thereafter at higher temperatures an abrupt decrease in the graft efficiency and graft content was observed (Fig. 6). This is attributed to the increasing rate of graft copolymerization in reaction temperatures in the range of 60–80 °C, but at higher temperatures a greater rate of PAM homopolymer formation occurred at the expense of the graft copolymerization. In addition, chain transfer at higher temperatures is likely to significantly reduce the extent of graft copolymerization. These results correlated well with the water absorption ability of the saponified starch-*g*-PAM copolymer based SAP at various reaction temperatures, where the maximum water absorption was obtained in the saponified starch-*g*-PAM copolymer prepared at 80 °C (Fig. 7). This is because the graft copolymer contains the highest grafted PAM that thereafter was hydrolyzed by the saponification process to result in the presence of the more hydrophilic carboxamide and carboxylic acid groups and therefore a greater level of water absorption.

3.3. Influence of the concentration of potassium persulfate initiator

The conversion level, graft efficiency and graft content of the starch-*g*-PAM copolymer prepared using KPS at five different concentrations (0.25, 0.50, 1.00, 1.50 and 2.00 wt% of the cassava starch), with a fixed starch:monomer (w/w) ratio of 1, a 140 min reaction time at 80 °C and a stirring speed of 300 rpm is summarized in Fig. 8. The conversion level obtained increased with increasing KPS concentrations up to a maximum conversion value at 1.50–2.00 wt% KPS. This may be attributed to the increasing availability of reactive free radicals to initiate the polymerization of PAM to form the grafted PAM and PAM homopolymer. Increasing the concentration of KPS from 1.50–2 wt% did not cause any further significant effect upon the conversion level, although a slight numerical decrease was seen. Although an abundant level of free radicals were formed in the system, the amount of monomer available for the reaction was limiting and, therefore, any further excess production of free radicals might recombine.

The graft efficiency and graft content of the starch-*g*-PAM copolymer also increased with increasing KPS concentrations within the range of 0.25–1.00 by 1.50 wt% KPS, with the maximum values observed between 1 and 1.5 wt%. Likewise, the graft efficiency and content both decreased with further increases in the KPS concentration above 1.50 wt% (Fig. 8). The higher concentrations of initiator (KPS) produced a higher grafted PAM level in cassava starch molecules but at 2 wt% the KPS concentration is too high and chain transfer to monomer or homopolymer formation was more pronounced causing lower graft content and graft efficiency (Fig. 8) as well as the lower water absorption capability (Fig. 9). Indeed, as expected, the water absorption of the saponified cassava starch-*g*-PAM copolymer prepared using KPS at 1.50 wt% exhibited the highest water absorption capability (ca. 605 g/g), which is approximately 2–3 times higher than those of the graft copolymers prepared by reactive extrusion reported elsewhere (Willett & Finkenstadt, 2006).

3.4. Influence of the starch:acrylamide ratios

The influence of the starch:AM ratios, at six different (w/w) ratios of 1:1, 1.25:1, 1.5:1, 2:1, 2.5:1 and 3:1, was analyzed using a 140-min reaction time at 80 °C, a stirring speed of 300 rpm and a KPS concentration of 1.5 wt% of the starch.

The FT-IR spectra of the purified starch-*g*-PAM derived from the six different starch:AM (w/w) ratios revealed all the characteristic bands of both cassava starch and PAM (Fig. 10), as shown respectively in Figs. 2 and 5, supporting the formation of a starch-*g*-PAM copolymer in all six different starch:AM (w/w) ratios. The characteristics and properties of these six different starch-*g*-PAM copolymers based SAPs are shown in Table 2, where it is clear that increasing the starch content decreased the level of conversion, graft efficiency, graft content and water absorption of the SAP. This is attributed to the lowering level of the newly formed graft PAM, which plays the main role in water absorption of the polymer. Therefore, a starch:AM (w/w) ratio of 1:1 was selected to prepare the graft copolymer for further studies.

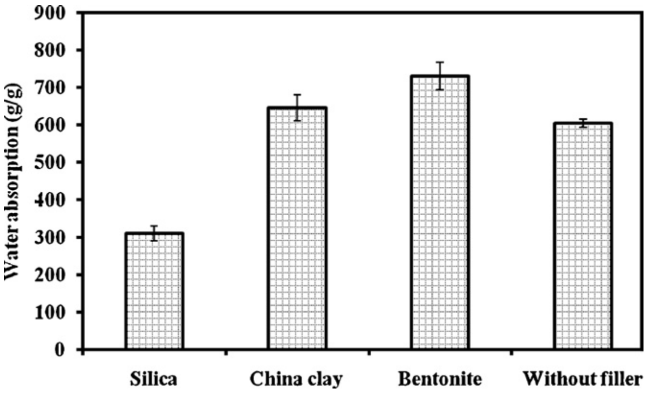


Fig. 12. Water absorption of the saponified starch-*g*-PAM copolymer SAP (without filler) and the derived composite based SAPCs with the indicated inorganic fillers. Data are shown as the mean ± 1 S.D. and are derived from 3 replicate samples.

Representative SEM micrographs of starch and of the starch-*g*-PAM copolymers with different starch:AM (w/w) ratios are illustrated in Fig. 11. Starch granules (Fig. 11(A)) had an irregularly oval shape and a fairly diverse array of particle sizes (in the range of 0.3–1.2 μm in diameter) with a smooth surface. On the other hand, the graft copolymers had a clearly different surface morphology in that the oval particle shape was absent but rather they had a coarse and broad network structure with a rather rough surface. This yields a higher water absorption capability for the copolymer, especially in the case of the SAP derived from a starch:AM (w/w) ratio of 1:1 (Fig. 11(B).

3.5. Influence of inorganic fillers

The water absorption of the saponified starch-*g*-PAM copolymer based SAP and the three SAPCs derived from the SAP is shown in Fig. 12, where the water absorption of the bentonite (730 g/g) and China clay (650 g/g) based SAPCs are significantly higher than those of the base SAP, i.e., without filler (606 g/g) or the silica based SAPC (310 g/g). This is because the hydration of bentonite powder is higher than that of China clay and especially silica and also that the bentonite powder dispersed more readily and produced more particulates in water than did either the China clay or the silica. Unfortunately, the incorporation of the silica resulted in a significantly lower water absorption of the resulting SAPC than that of the original starch-*g*-PAM copolymer based SAP. Perhaps this type of silica caused a smooth surface with a low content of coarse pores, a notion that is supported to some extent by the SEM micrographs (Fig. 13(A)). In contrast, the SAPCs formed with bentonite clay (Fig. 13(C)) and China clay (Fig. 13(B)) both showed a more porous surface which allowed a higher water intension capability of the composite.

Bentonite is an aluminium phyllosilicate absorbent and consists mostly of montmorillonite. Both bentonite and China clay are hydrous aluminium phyllosilicates, while silica is a porous silica dioxide. The former two phyllosilicates can both graft and intercalate the polymer chains but the latter cannot. The work (Foungfung, Seetapan, Phattanarudee, & Kiatkamjornwong, 2010) showed that the inclusion of phyllosilicate clay at an appropriate amount in the *in situ* polymerization of the monomer both enhances the superabsorbent polymer strength and gives a higher level of water absorption. The bentonite, after alkaline saponification, becomes

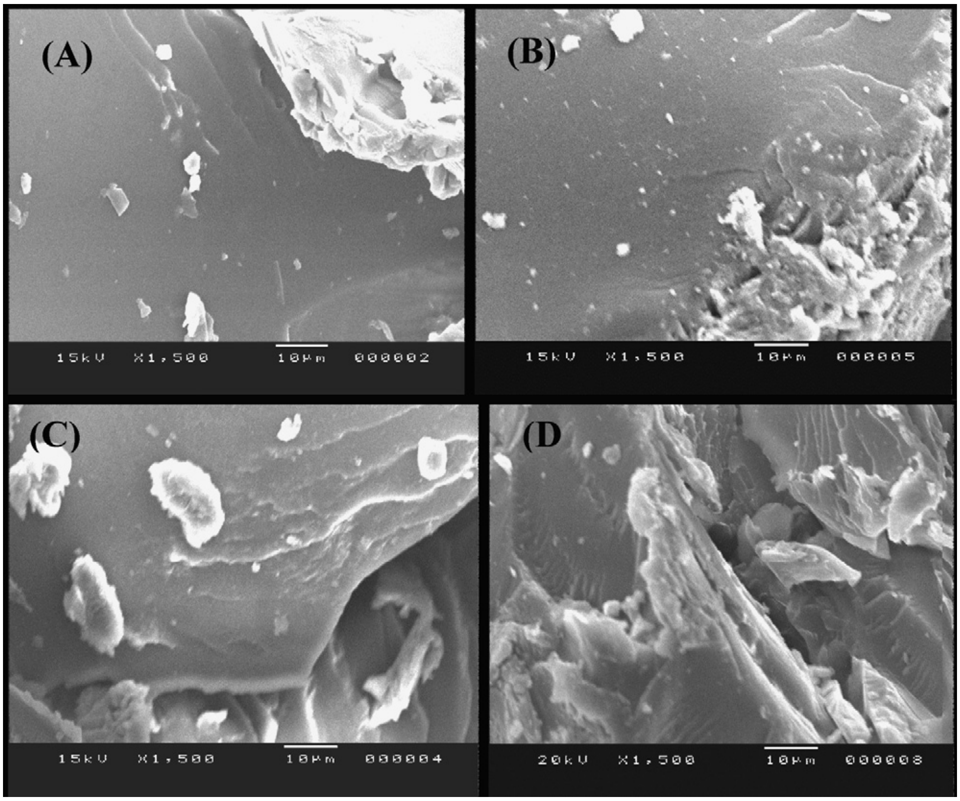


Fig. 13. Representative SEM micrographs of the purified starch-*g*-polyacrylamide composites with (A) silica, (B) China clay, (C) bentonite clay, and (D) without filler.

sodium bentonite which can increase the water absorption more than the kaolinite in the China clay. The *N*,*N*′-MBA crosslinker at 0.3 wt% was used for connecting the acrylamide units to starch or the acrylamide itself. Then the crosslinker could be used to crosslink the ungrafted PAM to be the crosslinked homopolymeric SAPC which can influence water absorption of the whole system. Besides, the clay powder can act as a crosslinking point and plays an important role in the formation of network structure of the SAPC (Wu, Wei, Lin, & Wu, 2003). Likewise, the *N*-MBA crosslinker might also crosslink the active site of the clay with acrylamide monomer or the starch graft PAM SAP (Foungfung et al., 2010; Wu et al., 2003).

4. Conclusions

A high water absorbing copolymer, based on the graft copolymerization of cassava starch and AM, was successfully prepared by reactive batch processing using a specially designed batch reactor. The reactor has a Reynold number of 224.7 and can mix the mixture effectively even at low water content. The highest obtained water absorption capability of the saponified starch-*g*-PAM copolymer was 605 g/g when prepared with a reaction time and temperature of 140 min and 80 °C, a KPS concentration of 1.5 wt% of starch and a starch:AM (w/w) ratio of 1:1. The FT-IR spectra confirmed the formation of saponified starch-*g*-PAM copolymer by exhibiting all the characteristic bands of both starch and AM units. The starch granules, as viewed by SEM, had irregularly oval shaped particles of variable sizes with a smooth surface. However, the graft copolymers exhibited coarse porous structures and a broad network, which may contribute to the higher water absorption capability of the copolymer and the SAPCs over the SAP. The bentonite clay SAPC exhibited the highest water absorption capability (ca. 730 g/g), significantly higher than that of the unfilled graft copolymer SAP (606 g/g). This is due to larger hydration of bentonite powder than those of the China clay and silica.

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