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Agar 그래프트 폴리아크릴산 겔의 흡수능 최적화

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Optimization of the Water Absorption by Crosslinked Agar-*g*-Poly(acrylic acid)

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Abstract: Crosslinked agar-*g*-poly(acrylic acid) (x-agar-*g*-PAA) superabsorbent with a water absorbency (Q_{H_2O}) of approximately 660 g/g was synthesized by the copolymerization of agar with an acrylic acid monomer. KPS and MBA were used as the initiator and crosslinker, respectively. Grafting was performed in air. Infrared spectroscopy was used to identify the product of copolymerization. The optimum conditions to synthesize the x-agar-*g*-PAA superabsorbent were 0.1 g of agar, 0.1 g of the KPS initiator, for 15 min; 50% AA monomer, 0.005 g of the MBA crosslinker, for a propagation time of 5 min; and 1 M NaOH for 15 min to allow for saponification. The reaction temperature was 80 ℃.

Keywords: crosslinked agar-*g*-poly(acrylic acid), water absorbency, solution polymerization.

Introduction

Superabsorbent hydrogels are granular solid materials that have high affinity to absorb and retain distilled water 500~3000 times their weight and 100~500 times their weight in saline solution.[1] Chemically, these gels consist of lightly 3D crosslinked and partially saponified hydrophilic polymers. Well known examples are polyacrylic acid,[2] acrylonitrile,[3] polyacrylamide,[4] and poly(acrylic-*co*-acrylamide).[5] Recent awareness on sustainable production has resulted in intensified research of superabsorbent hydrogels made from natural polymer fillers, such as, starch,[6] cellulose,[7] chitosan,[8] gelatin,[9] carrageenan,[10] and other hydroxyl-rich natural polymers.[11]

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Previous investigations used synthesis methods that include free radical polymerization,[12] microwave radiation,[13] and γ-irradiation.[14] These products have been widely applied in sanitary napkins and disposable diapers,[15] agricultural soil moist,[16,17] and biomedical materials.[18] To the best of our knowledge, the grafting of polyacrylic acid on the surface of agar by solution polymerization to be applied as superabsorbent has not been made.

Previous research has been focused on the effect of the polymerization factors: concentration of initiator,[19] concentration of monomer,[20] crosslinker content,[4] reaction temperature,[21] saponification degree,[22] and reaction volume[19] on the water absorbency (Q_{H_2O}) of polysaccharide superabsorbent synthesized under N_2 atmosphere. Free radical polymerization is mostly done under inert N_2 atmosphere because

oxygen interferes with the polymerization by reacting with radical sites to produce a less reactive radical.[1,11] Pourjavadi and Zohuriaan-Mehr,[23] however, have demonstrated polymerization in oxygen atmosphere without nitrogen gas purging. They used an excess of initiator and showed that oxygen in the air was first consumed, followed by generating free radical for the polymerization process. The study of polymerization factors of agar in solution polymerization under air atmosphere to be applied as superabsorbent has also not been performed.

Agar is a natural polymer that is extracted from seaweed. Chemically, it is a polymer of agarobiose, a disaccharide consisting of 1,3-β-D-galactose and 1,4-α-3,6-anhydro-*L*-galactose of ~390 units per chain, Figure 1.[24] It is an unbranched polysaccharide that gelatinizes in water at about 45 ℃.[20] The native agar molecule itself can absorb water.[25]

There are a few leading research groups who have been studying agar grafting. Prasad *et al.*[26] studied the grafting mechanism of agar-*g*-polyvinylpyrrolidone in the presence of potassium persulfate (KPS) that yielded a Q_{H_2O} of 8.5 g/g. Athawale investigated solution polymerization of agar-*g*-methacrylic acid[19] and agar-*g*-methacrylamide with ceric ammonium nitrate as the initiator.[20] A more recent work has been reported by Meena's group on grafting agar and sodium alginate blend (agar/Na-Alg) with acrylamide (AAm) to obtain a copolymer agar/Na-Alg-graft-PAAm.[27] For pharmaceutical application, agar was grafted to acrylamide (agar-*g*-PAAm) and hydroxyethyl methacrylate (agar-*g*-PHEMA) to be used in retard release of sodium from Diclofenac tablets.[28]

In this paper, a simple method of solution grafting copolymerization of agar with acrylic acid (AA) monomer is presented. The polymerization process was done without purging nitrogen in air atmosphere. KPS was used as initiator and *N,N*-methylene bisacrylamide (MBA) as crosslinker to obtain crosslinked agar-*g*-poly(acrylic acid) (x-agar-*g*-PAA) superabsorbent hydrogels. The polymerization factors studied include: agar content, initiation time, KPS content, percent acrylic acid (%AA), MBA content, reaction temperature, saponification time, and concentration of NaOH ([NaOH]).

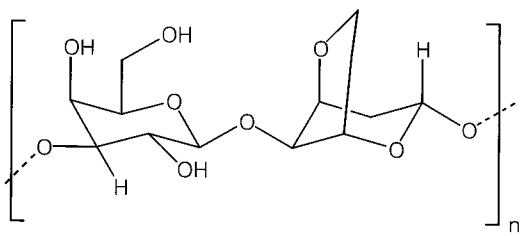


Figure 1. Structure of natural agar repeating unit (n≈390).

Experimental

Materials. The agar was purchased from Pearl Mermaid (Bangkok, Thailand) and stored in a desiccator prior to grafting. Analytical grade of potassium persulfate (KPS) initiator and *N,N*-methylene bisacrylamide (MBA) crosslinker were purchased from Fluka Chemicals. Analytical grade of NaOH was supplied by Labscan Asia Co. Ltd. Industrial grade acrylic acid (AA) was purchased from Sumika Chemical Analysis Service, Co. Ltd. (Singapore). Chemicals above were used without further purification.

Crude methanol was purchased from Bang Trading 1992 Co., Ltd. (Thailand) and was distilled before use.

Investigating Grafting Factors. The (0-0.5 g) agar and (0-0.3 g) KPS were dissolved in 5 mL of distilled water in a 50 mL test tube and stirred in a water bath for varying initiation time (0-30 min). Then a well mixed mixture of 5 mL (40-100%) AA monomer, (0-0.035 g) MBA crosslinker, and 5 mL distilled water were added to the previous mixture of agar and KPS. The slurry gelled within 2 min; but was stirred for 5 min to keep the polymerization time constant for all conditions. The gel was then cut into small pieces using a blender. Saponification was done using (0-5 M) NaOH for 0-30 min. The reaction temperatures were varied from 60-100 ℃ for both the polymerization and saponification procedures. Homopolymer was removed by washing 3 times with 200 mL distilled water. To de-water the product, the sample was stirred in a mixture of distilled methanol and distilled water (90 : 10) for 10 min at room temperature. The gel was then cut into small pieces again and dried in an oven at 65 ℃ overnight. Table 1 summarized the parameters being varied and those that were kept constant during grafting. All experiments were done in triplicate repeats.

Product Analysis Using Infrared Spectroscopy. The product was characterized using a Perkin Elmer Spectrum GX Fourier Transform Infrared Spectrometer. The 2 mg of samples were mixed with 150 mg of KBr pellets. It was scanned at a frequency range of 4000-370 cm^{-1} with 16 scans in a 4 cm^{-1} resolution.

Samples consisted of x-agar-*g*-PAA, native agar, cross-linked PAA (x-PAA) homopolymer, and physically mixed agar+x-PAA homopolymer for comparison. The physically mixed agar+x-PAA was prepared using 0.2 agar and 1.8 mg x-PAA homopolymer. This was done to keep the ratio of agar and PAA equivalent to the theoretical x-agar-*g*-PAA sample of about 1:12.5.

Water Absorbency (Q_{H_2O}) Measurement. After the x-agar-*g*-PAA was obtained, the sample was dried overnight in an oven at 65 ℃ and stored in a dessicator until the water

Table 1. Parameters of Grafting Conditions

Parameters	Varied	Constant
Agar content(g)	0, 0.01, 0.05, 0.1, 0.2, 0.5	0.1
Initiation time(min)	0, 5, 10, 15, 20, 30	15
KPS content(g)	0, 0.01, 0.05, 0.1, 0.2, 0.3	0.1
%AA	40, 50, 70, 90, 100	50
MBA content(g)	0, 0.001, 0.005, 0.01, 0.025, 0.035	0.005
Reaction temperature(℃)	60, 70, 80, 90, 100	80
Saponification time(min)	0, 5, 10, 15, 20, 30	15
Concentration of NaOH(M)	0, 1, 2, 3, 5	2

absorbency was measured. Dried sample (0.1 g, m_1) was immersed in 100 mL distilled water for 1 h and 6 h (the equilibrium water uptake). The excess water was drained-off with a household sieve until water ceased to drip. The sample was then placed on a filter paper above 20 plies of newspaper for 5 min to remove excess water on the gel surface. Then the weight of the gel and the absorbed water (m_2) was measured. The water absorbency, Q_{H_2O}, in grams of water per gram of sample was determined at room temperature. Equation 1 was applied.

$$Q_{H_2O} = \frac{\text{mass of wter absorbed}}{\text{mass of dry sample}} = \frac{m_2 - m_1}{m_1} \quad \text{(Equation 1)}$$

where m_1 is the mass of dry sample; and m_2 is the mass of dry sample plus water-absorbed by the sample.

Results and Discussion

IR Spectral Analysis. Evidence of grafting on the polysaccharide grafted polymer had been obtained by infrared spectroscopy (IR).[13,23] IR spectra of agar, x-PAA homopolymer, physically mixed agar+x-PAA homopolymer, and x-agar-*g*-PAA are shown in Figure 2.

The characteristic absorption peaks of native agar were observed at 3435, 1054, 999, and 930 cm^{-1} (Figure 2(a)). The absorption peak at 3435 cm^{-1} is attributed to -OH stretching of the hydroxyl group on agar. The absorption peak at 1054 cm^{-1} are due to the glycosidic bonding.[29] The absorption peaks at around 999 and 930 cm^{-1} represent the -C-O-C bending of 3,6-anhydro-β-galactose skeletal on agar.

The characteristic absorption peaks of x-PAA homopolymer were observed at 3436, 1561, 1411, and 1169 cm^{-1} (Figure 2(b)). The absorption peaks at 3436 cm^{-1} are due to -OH stretching of acrylic acid group in the polymer chain. The absorption peak at 1561 cm^{-1} represents the C=O stretching in carboxylate anion. The absorption peak at 1411 cm^{-1} is attributed to the $-CH_2-$ bending vibrations of -CH-CO- group in the polymer chain. The peak at 1169 cm^{-1} corresponds to the C-O stretching coupled with O-H in-plane bending of the carboxyl group in polyacrylic acid group.

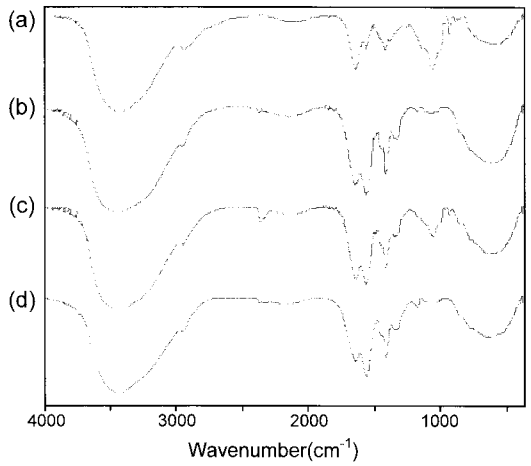


Figure 2. IR spectra of (a) agar, (b) x-PAA homopolymer, (c) physically mixed agar+x-PAA homopolymer, and (d) x-agar-*g*-PAA.

As a qualitative comparison of IR spectrum to identify grafting of PAA on agar (x-agar-*g*-PAA), the spectrum of a physically mixed agar+x-PAA homopolymer spectrum was attributed with peaks at 3435, 1561, 1412, 1054, 999, and 929 cm^{-1} (Figure 2(c)). In comparison, x-agar-*g*-PAA showed absorption peaks at 3435, 1560, 1411, and 1171 cm^{-1} (Figure 2(d)). The absorption peaks at 3435 cm^{-1} showed insignificant difference as both agar and acrylic acid have -OH stretching. The presence of carboxylate group in the x-agar-*g*-PAA was confirmed by the appearance of the strong absorption bands at 1560, 1411, and 1171 cm^{-1}. The disappearance of the peaks at 1054, 999, and 929 cm^{-1} that is attributed to the glycosidic bonding[29] in the physically mixed agar+x-PAA homopolymer also suggested that agar structure was modified after the polymerization process for the x-agar-*g*-PAA.

Polymerization Factors that Affect Q_{H_2O}.

Agar Content: The key to free radical polymerization grafting

on a natural polymer is to form radical sites on the natural polymer backbone. The natural polymer is required to have hydroxyl group that would act as the site to initiate free radical. Agar is one of the natural polymer candidates that can be use for grafting. Result in Figure 3(a) showed the effect of agar contents (0, 0.01, 0.05, 0.1, 0.2, and 0.5 g) on the Q_{H_2O} of x-agar-*g*-PAA. The Q_{H_2O} of x-agar-*g*-PAA increased with increasing agar content until achieving

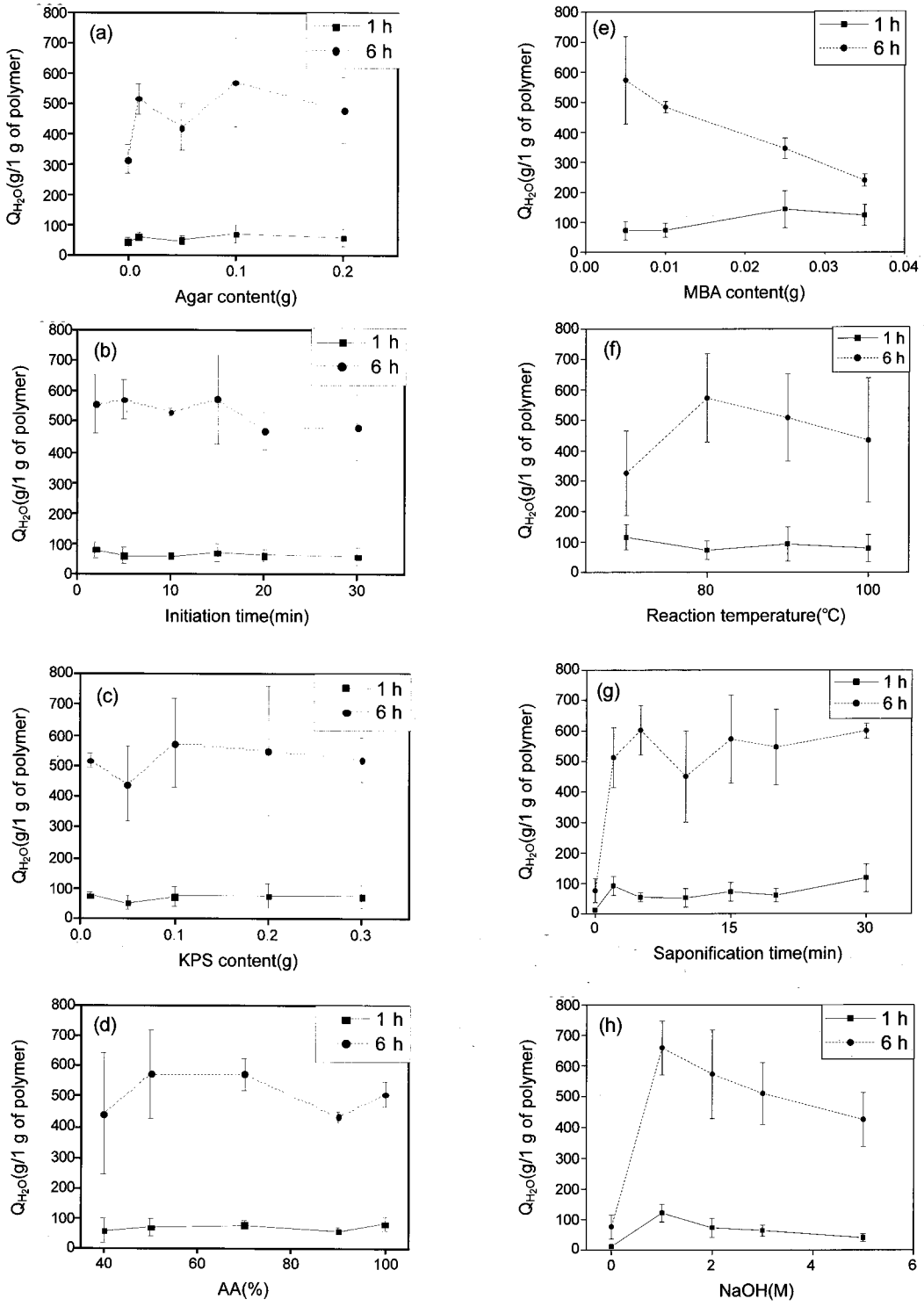


Figure 3. Effect of (a) agar content, (b) initiation time, (c) KPS content, (d) %AA, (e) MBA content, (f) reaction temperature, (g) saponification time, and (h) concentration of NaOH on the Q_{H_2O} at 1 h (■) and 6 h (●).

the maximum Q_{H_2O} of about 570±145 g/g using 0.1 g of agar.

The Q_{H_2O} for 0 g of agar was least among other conditions because the product only had x-PAA chains and PAA homopolymer in the gel structure (IR results not shown). PAA homopolymer was wash-off during the washing process.[6] And the x-PAA alone had low Q_{H_2O}. Q_{H_2O} of the superabsorbent hydrogel was improved when agar was introduced into the polymer network. The initial increase (<0.1 g of agar) in Q_{H_2O} resulted from the ability of the native agar itself in absorbing water.[25] The optimum agar content was about 0.1 g because the product had highest water-absorbing properties. Further increase of agar decreased Q_{H_2O}, because the increase of agar was observed to increase the viscosity of the system and hinders the movement of agar molecule in reacting with free radical initiator (>0.1 g of agar).[30] In the condition of 0.5 g of agar, the agar gelatinized already in absence of the acrylic acid monomer solution. Gelation of agar is caused by intermolecular folding of agarobiose chains forming hydrogen bonded double helices. The helices joining together make junction zones resulting in an immobilized 3D network.[31] The gelatinized agar was unsuitable for further solution polymerization with the acrylic acid; and the Q_{H_2O} was not measurable.

Initiation Time: KPS is a water-soluble free radical initiator that requires thermal decomposition to form sulfate radicals. The sulfate radicals then abduct hydrogen atom from the -OH group of the agar backbone to form agar radicals, Figure 4.[5] From previous research, KPS has been shown to form sulfate anion radicals at 90 ℃ within 30 sec using microwave radiation.[26] Figure 3(b) showed the effect of various initiation times (0, 2, 5, 10, 15, 20, and 30 min) on the Q_{H_2O}. It took less than 5 min for the dissociation of KPS in solution polymerization, but dissociation in solution took longer time than by microwave radiation. Two main reasons that were accounted for the longer initiation time was the heating up of KPS that was prepared in a solution that requires heat transfer rather than the direct heating of the microwave radiation. Secondly, because the reaction was done without nitrogen purging, oxygen in the system will first compete for the initiator. Only after all the oxygen was used up, the initiator would begin to react with agar.[23]

KPS Initiator Content: Varying the KPS content, varied the amount of free radicals in the polymerization process that could generate agar radicals. Figure 3(c) illustrated the effect of KPS content (0, 0.01, 0.05, 0.1, 0.2, and 0.3 g) on the Q_{H_2O} of x-agar-*g*-PAA. Maximum Q_{H_2O} was achieved when 0.1 g of KPS was used. The maximum Q_{H_2O} was 570±145 g/g. For this polymerization condition, 0.1 g of KPS was rather high compared to the work by Huang and *co*-worker[32] who studied the synthesis of maleoylchitosan-*g*-PAA using KPS as an initiator in N_2 atmosphere. This is because in our condition an excess of the initiator was required for the initiator consumption by oxygen in the system as well.[23] With less than 0.1 g of KPS, low Q_{H_2O} was observed. And with excess of KPS, excess radicals were generated that resulted in homopolymerization of grafting monomer and in self-termination of the initiator itself.[33,34] Homopolymer of PAA was observed to have been washed-off with distilled water during the washing process.[6] This resulted in a lower yield of x-agar-*g*-PAA (<10%) when compared to other conditions (~70%).

Percent AA Monomer: Another essential factor of synthesizing hydrogels was to graft hydrophillic polymer chains onto the agar backbone. Figure 3(d) showed the effect of %AA (40, 50, 70, 90, and 100%) on the Q_{H_2O}. The Q_{H_2O} initially increased with increasing %AA until reaching a plateau value of Q_{H_2O} at 50% AA.

In keeping all other parameters constant, except lesser monomer being available in the system, the lower Q_{H_2O} observed with 40% AA must resulted from the shorter chains of grafted PAA[35] compared to other conditions. With 40%AA, the chains were too short for absorbing water.[35] Longer chains of grafted PAA were expected to absorb water better (≈ 50% AA).[16] But further increase of %AA slightly decreased Q_{H_2O}, due to the increased viscosity of the polymerizing system that terminates the reaction (>50% AA).[6,36,37]

MBA Crosslinker Content: The hydrogels structure that can retain large amounts of water must have sufficient crosslink sites between the PAA chains. The crosslinker is required to have terminally active double bonds that could connect free radicals in the grafted-PAA chains. The effect of variation in MBA content (0, 0.001, 0.005, 0.01, 0.025, and 0.035 g) on the Q_{H_2O} was studied (Figure 3(e)). Increase of MBA content initially increases Q_{H_2O} up to 0.005 g of MBA. Higher MBA content sharply decreased the Q_{H_2O} of x-agar-*g*-PAA. With low MBA (<0.005 g), gel structure was not formed. Q_{H_2O} was not measurable. A similar phenomenon was observed by Liu *et al.*[8] and Wu *et al.*.[36] Optimum MBA content of 0.005 g was explained by the optimum degree of crosslinking that allow the gel network to expand during water absorption. And when the crosslinker content was too high, Q_{H_2O} decreased because too much crosslinked points restrict polymer network from expanding when water was absorbed. This result agreed with most natural polymer-based superabsorbent research.[5,37-39] From Flory's water absorbency equation, higher crosslinker content resulted in lower Q_{H_2O}.[40]

The trend of Q_{H_2O} for 1 h soaking differs from that of 6 h.

For 6 h soaking, we observed the maximum Q_{H_2O} with the use 0.005 g of MBA. But for 1 h soaking, a maximum is not reached but seems to increase with increasing crosslinker. This is because, for 1 h soaking, the grafted-PAA chains have not expanded to their maximum. High crosslinker content might be preferable for applications that require fast absorbency.

Reaction Temperature: Reaction temperature can greatly influence the synthesis process of hydrogels. The process required a suitable temperature for the decomposition of KPS,[21,39,41] the breakdown of the double bond of AA,[41] and the diffusion of NaOH into the hydrogels during saponification.[42] The rate of polymerization increased with the increase of reaction temperature.[5] The effect of increasing reaction temperatures (60, 70, 80, 90, and 100 ℃) on the Q_{H_2O} was reported in Figure 3(f). Dissociation of KPS started at approximately 60 ℃;[5] however, at 60 ℃, the product was not in gelled state because active radicals from KPS were consumed by oxygen in the system.[23] The product at 60 ℃ had a sol-gel state in water. Q_{H_2O} data cannot be measured. For 70 ℃, amount of KPS dissociation increases[5] resulting in the increase in the yield of x-agar-*g*-PAA and Q_{H_2O} increased. With the increase of the reaction temperature, the resulting Q_{H_2O} of x-agar-*g*-PAA increased until achieving the maximum Q_{H_2O} with 80 ℃ reaction temperature. Higher reaction temperature (>80 ℃) decreased Q_{H_2O}, because although, there was an increase of KPS initiators dissociation, the rate of reaction is also very high at higher temperature resulting in a highly viscous solution that quickly terminates further polymerization of monomer.[5,39] Higher temperature has also been reported to destroy the structure of the agar backbone.[20]

Saponification Time: Another important process to improve the Q_{H_2O} is to increase the osmotic pressure in the PAA structure with ions by the saponification process. The process was performed with the use of NaOH. NaOH reacted with the carboxylic group (-COOH) in the grafted-PAA structure to produce carboxylate group ($-COO^-Na^+$) as shown in Figure 5.[33] The effect of saponification times (0, 2, 5, 10, 15, 20, and 30 min) on Q_{H_2O} of x-agar-*g*-PAA was shown in Figure 3(g). The $-COO^-Na^+$ groups increased with longer saponification time.[36] The Q_{H_2O} of x-agar-*g*-PAA increased with increasing saponification time until achieving the plateau value for Q_{H_2O} of about 600±80 g/g with 5 min saponification time.

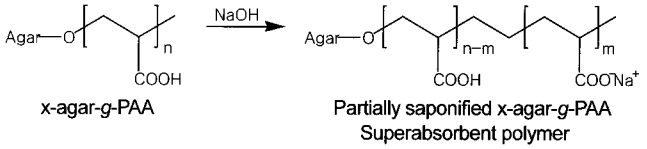
According to Flory's theory,[40] the fixed charges on polymer network of superabsorbent was related to hydrophilicity of the charges, electrostatic repulsion between charges on the polymer backbone, and osmotic pressure

$$K_2S_2O_8 \xrightarrow[30\ s]{90\ ^\circ C} 2SO_4^{\bullet -} + 2K^+$$

$$Agar-OH + SO_4^{\bullet -} \rightarrow Agar-O^{\bullet} + HSO_4^-$$

agar radical

Figure 4. Mechanism of agar radical formation.



x-agar-*g*-PAA

Partially saponified x-agar-*g*-PAA Superabsorbent polymer

Figure 5. Saponification process of x-agar-*g*-PAA.

between the polymer network and the surrounding water. Consequently, the types and amount of hydrophilic groups on polymeric network would greatly affect the water absorbency behavior. Without Na^+ (0 min saponification), there is no osmotic drive to draw water into the hydrogel. The Q_{H_2O} at 6 h was only ~80 g/g, the water absorption was only due to the hydrophilic effect of the carboxylic side chains. In addition, hydrogen bonding between carboxylic groups results in strong intermolecular structures that restricted to the chain expansion of the x-agar-*g*-PAA in absorbing water.[38] With appropriate Na^+ content, there is sufficient osmotic drive to draw water into the hydrogel.[5] After swollen by water, the net charge repulsion of grafted PAA chains is enhanced due to high ionic intermolecular force that can maximize chains expansion[38] and resulted in higher Q_{H_2O} (≥ 5 min).[36] Longer saponification time does not significantly increase the Q_{H_2O} of x-agar-*g*-PAA because the diffusion for Na^+ into the hydrogel has already reached equilibrium.

NaOH Concentration: Figure 3(h) showed the effect of [NaOH] (0, 1, 2, 3, and 5 M) on the Q_{H_2O}. Na^+ content increased with the increasing concentration of NaOH.[36] The Q_{H_2O} of x-agar-*g*-PAA increased with increasing [NaOH] until reaching the maximum Q_{H_2O} of about 660±90 g/g with 1 M NaOH. With 0 M NaOH, Q_{H_2O} was only ~80 g/g, this was because without Na^+ there was no osmotic drive to draw water into the hydrogel. With sufficient osmotic drive to draw water into the hydrogel with appropriate Na^+ content and an enhanced net charge repulsion of grafted PAA chains can increase chains expansion when absorbing water. Too much Na^+ ion (≈ 5 M NaOH) can decrease the effectiveness of anion-anion repulsion of $-COO^-$ because of charge attraction between $-COO^-$ and Na^+ thus reducing the expansion of grafted PAA chains; and Q_{H_2O} decreased.[36,39,43,44] The optimum ratio of acrylic acid and sodium polyacrylate

in the synthesis of acrylic-based superabsorbent had been studied.[6,39,45]

Conclusions

In conclusion, the conditions to synthesize x-agar-*g*-PAA superabsorbent by solution polymerization with 0.1 g of agar was to use 0.1 g of KPS initiator with 15 min initiation time; 50% AA monomer and 0.005 g of MBA crosslinker with 5 min propagation time; and 1 M NaOH with 15 min saponification time. The reaction temperature should be kept at 80 ℃. The best Q_{H_2O} of x-agar-*g*-PAA superabsorbent was 660±90 g/g.

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