Pilot-Scale Production of Highly Water Absorbing Polymer From Native Cassava Starch by Hydrogen Peroxide-Ascorbic Acid Initiation

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Pilot-scale production of hydrolyzed cassava starch-*g*-poly(acrylic acid) superabsorbents was successfully prepared from our bench-scale experiments developed recently. A specially-designed reactor of 10.6-l capacity can accommodate the production of the superabsorbent by 15 times the bench capacity. The resulting superabsorbent can absorb water as high as 320 g/g its dry weight. This research calculates times needed for heat transfer and measures changes in viscosity in each production step to obtain the optimum reaction conditions with reproducibility. Estimation of the production cost for this material is also reported. An industrial production of this superabsorbent is technically feasible.

Key words: Pilot-scale production, hydrolyzed cassava starch-*g*-poly(acrylic acid), bench scale experiment, hydrogen peroxide, ascorbic acid.

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การผลิตพอลิเมอร์ดูดซึมน้ำสูงในระดับนำร่องจากแป้งมันสำปะหลังพื้นเมืองโดยระบบการเริ่มปฏิกิริยาด้วยไฮโดรเจนเพอร์ออกไซด์และกรดแอสคอร์บิก

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การผลิตสารพอลิเมอร์ดูดซึมน้ำสูงของแป้งมันสำปะหลังไฮโดรไลซ์ที่กราฟต์ด้วยพอลิอะคริลิกแอซิดระดับนำร่องได้ประสบความสำเร็จโดยพัฒนาจากการทดลองระดับห้องปฏิบัติการ เครื่องปฏิกรณ์ออกแบบพิเศษความจุ 10.6 ลิตร สามารถรองรับการผลิตสารดูดซึมน้ำสูงได้ 15 เท่าของความจุในห้องปฏิบัติการ สารพอลิเมอร์ดูดซึมน้ำสูงนี้สามารถดูดซึมน้ำสูงได้ถึง 320 ก./ก. ของน้ำหนักสารแห้ง บทความวิจัยนี้ได้คำนวณเวลาที่จำเป็นต่อการถ่ายโอนความร้อนและวัดการเปลี่ยนแปลงของความหนืดในแต่ละขั้นตอนของการขยายส่วนต่างๆ เพื่อให้ได้ภาวะของปฏิกิริยาที่เหมาะที่สุดของการผลิตซ้ำได้ ได้มีการประเมินค่าใช้จ่ายในการผลิตสารดูดซึมน้ำสูง การผลิตระดับอุตสาหกรรมของสารพอลิเมอร์ดูดซึมน้ำสูงมีความเป็นไปได้มากในด้านเทคนิคการผลิต

คำสำคัญ การผลิตแบบขยายส่วน, แป้งมันสำปะหลังไฮโดรไลซ์ที่กราฟต์ด้วยพอลิอะคริลิกแอซิด,
การทดลองระดับห้องปฏิบัติการ, ไฮโดรเจนเพอร์ออกไซด์, กรดแอสคอร์บิก

INTRODUCTION

Native cassava starch has been used as a substrate for graft copolymerization with vinyl monomers to produce highly water absorbing polymers with various water absorption capacities at the laboratory level.(1-8) The bench-scale graft copolymerization of the superabsorbent of hydrolyzed cassava starch-*g*-poly(acrylic acid) or HCSPA has produced interesting features in terms of environmental concerns and promising applications as a soil conditioner. Kiatkamjornwong and Wiwatwarrapan(7) investigated such a graft copolymerization using a hydrogen peroxide-ascorbic acid initiation system from which the superabsorbent of HCSPA with a water absorption value of 234 g/g its dry weight resulted. In their experiment, the glass reaction vessel of 1-liter capacity was used with a teflon propeller and a water bath heating system. Optimal reaction parameters for the concentrations of acrylic acid monomer and hydrogen peroxide initiator, and the polymerizing temperature were found to be 2.95 and 2.2×10^{-1} M and 35°C, respectively.

However, these reaction conditions are only a guideline for the pilot-scale production; we need to design a new reactor, propeller, and a more stable heating system for proper mass transfer and heat transfer. This article thus investigates the appropriate reaction conditions to permit the production at a pilot scale of 15 times the bench scale.

EXPERIMENTAL

Materials

Cassava starch was obtained from Thai Wah Co., Ltd., Thailand. Acrylic acid was obtained from Siam Resin & Chemical Co., Ltd., Thailand. Methanol was of commercial grade. Hydrogen peroxide (35%), L(+)-ascorbic acid, calcium oxide, and potassium hydroxide were of analytical grade.

PROCEDURE

Figure 1 shows a diagram of the production system. Graft copolymerizations of cassava starch and acrylic acid were carried out as a batchwise process in a cylindrical stainless steel reactor with an inside diameter of about 22 cm, 32 cm height and a capacity of 10.6 l, stirred by a horseshoe shaped paddle. The cylindrical stainless steel reactor had a jacket, which contained the oil and heaters shown as No. 1 in Figure 1. The heated oil in a jacket was measured by the thermocouple (No. 2), and heat was dissipated by gently bubbling air into the hot oil (No. 3). An adjustable stirrer (No. 4) installed in a reactor was adjusted when the graft copolymerization was started. The nitrogen gas (No. 5) was purged in a reactor for all experiments.

Native cassava starch, 10% W/V, was gelatinized at 80°C with a stirring rate of 150 rpm for 1 h. An amount of 7.5 g of CaO and 3 g of ascorbic acid was added to the reaction paste with a stirring rate of 200 rpm. A mixed solution of 2.42 M acrylic acid and 7.4×10^{-2} M of hydrogen peroxide was added into the solid paste. The total graft copolymerization time was 4 h. The newly synthesized graft copolymer was saponified with KOH solution for 1 h and it was transferred to a precipitating stainless-steel tank (No. 6) with an inside diameter of 35 cm and a height of 45 cm. It was cooled down to room temperature. The synthesized product is a transparent, viscous fluid that was precipitated with MeOH to result in a white viscous solid sedimented at the bottom of the precipitation tank (No. 6). It was then dried at 65°C for 24 h. It was then crushed to become fine particles from which the homopolymer of polyacrylate was separated through an extraction with methanol by soxhlet at 65°C for 24 h. The weight difference before and after the soxhlet extraction is calculated in terms of homopolymer content.

CHARACTERIZATION OF THE HCSPA

The HCSPA (hydrolyzed cassava starch-polyacrylate) was subjected to an IR spectroscopic investigation in a KBr disc.

WATER ABSORPTION OF THE HCSPA

Deionized distilled water (75 g) was added to 0.1 g of dried HCSPA in a 250 cm^3 glass beaker and allowed to stand for 30 min to ensure a complete swelling of the polymer. The fully swollen polymer was filtered through a 100 mesh aluminium screen for 3 h and the drained water was weighed. The amount of water retained by the HCSPA was calculated in terms of grams of dry modified starch.

Figure 1. Diagram of the batch production system: (1) stainless steel reactor, (2) temperature control system consisting of a thermocouple, a heating coil, and a temperature switch, (3) air-pump, (4) stirring system comprising a motor and a rpm controller, (5) pressurized system, (6) precipitation tank.

RESULTS AND DISCUSSION

The polymerization parameters are shown in Table 1.

The existence of graft copolymers, HCSPA

Figure 2 shows the IR spectrum of hydrolyzed cassava starch-*g*-polyacrylate after the methanol extraction. The peaks at 3,500 cm^{-1} and 1,000-1,200 cm^{-1} are assigned as the peak of amylose that can be matched with those of the native cassava starch in Figure 3. This indicates that graft copolymerization does occur on the cassava starch substrate. Importantly, we found the -C=O- stretching at 1,710 cm^{-1}, and the -C=O- and -C-O- asymmetric and symmetric stretching of carboxylate anions at 1,566 cm^{-1} and 1,408 cm^{-1}, respectively. The latter two peaks show that the poly(acrylic acid) chains grafted onto the cassava starch backbone are hydrolyzed to become the organic salts. As a whole, we confirm that cassava starch is the framework for graft copolymerization of acrylic acid.(8)

Microscopic observation of the HCSPA

Morphologies of the native cassava starch and HCSPA were investigated by the SEM technique as shown in Figure 4. Cassava starch has an oval shape with one end dented, and the surface is curved inwards. The general morphology is dented and the starch has a circular shape on the surfaces. The HCSPA superabsorbent is irregular with wide spread porosity on the surface. The HCSPA superabsorbent having 320 g/g absorption gives much more pores spreading out on the polymer than that with 54 g/g absorption. The pore and porosity is responsible for water absorption due to hydrogen bonding formation with the carboxylate anions.(7)

Effect of Hydrogen Peroxide Concentration on Water Absorption of HCSPA

When the concentration of H_2O_2 was increased from 4.4×10^{-2} M to 7.4×10^{-2} M, the water absorption value increased from 108 g/g to 205 g/g. When the concentration of H_2O_2 was further increased to 1.03×10^{-1} M and 1.48×10^{-1} M, the water absorption was nearly constant as shown in Figure 5. It should be always borne in mind that homopolymer formation occurs at the expense of graft copolymerization. When increasing the initiator concentration, more radicals were produced which could encounter among them in the aqueous phase to give more polyacrylate. The amount of homopolymer increased from 4.1 to 6.8% with an increase of H_2O_2 concentration of 7.4×10^{-2} M to 1.03×10^{-1} M.

Table 1. Polymerization parameters.

Reaction parameter	**Value**
Hydrogen peroxide concentration, M	4.4×10^{-2} - 1.48×10^{-1}
Ascorbic acid concentration , g	2 - 5
Acrylic acid concentration, M	1.32 - 2.96
Stirring rate of gelatinization, rpm	150 - 200
Stirring rate of graft copolymerization, rpm	200 - 250
Polymerization time, h	4 - 5
Polymerization temperature, °C	30 - 65

wave number, cm^{-1}

Figure 2. IR spectrum of HCSPA.

wave number, cm^{-1}

Figure 3. IR spectrum of native cassava starch.

(a)

(b)

(c)

Figure 4. Morphologies of cassava starch and HCSPAs: (a) the native cassava starch, (b) the HCSPA with 320 g/g absorption, (c) the HCSPA with 54 g/g absorption.

Effect of Ascorbic Acid Concentration on Water Absorption of the HCSPA

Ascorbic acid (AA) is a co-initiator to hydrogen peroxide. Its incorporation is essential for the redox initiation. Figure 6 presents the effect of AA on water absorption. When increasing the AA concentration from 2 to 3 g, the water absorption increases from 57 g/g to 205 g/g. If the concentration AA is higher than 3 g, its water absorption is 133 g/g. At high AA concentrations, more $AH^{\bullet}$ (anhydroascorbic acid radicals) and $OH^{\bullet}$ (hydroxy radicals) were produced. Both radicals can recombine to form H^+ and OH^-, which is inactive to graft copolymerization. Additionally, the $AH^{\bullet}$ can further terminate with the growing polymer radicals to yield the homopolymer. (9)

Effect of Acrylic Acid Concentration on Water Absorption of the HCSPA

Figure 7 shows the effect of acrylic acid concentration on water absorption of the HCSPA. Increasing the acrylic acid concentration from 1.32 M to 2.42 M, the water absorption increases from 48 g/g to 320 g/g, and the percentage of homopolymer formation is from 2.3 to 4.5. With more increases in acrylic acid concentration to 2.96 M, the water absorption value goes down to 80 g/g with an increase in polyacrylate of 5.4%. At higher acrylic acid contents, more monomer radicals resulted, and they can encounter in the aqueous phase to preferentially recombine rather than diffusing to the viscous starch backbone or starch radicals to obtain graft copolymers. (8)

Effect of Stirring Rate for Gelatinization to Graft Copolymerization

Figure 8 depicts the effect of the stirring ratio for gelatinization to graft copolymerization, which indicates that the optimum stirring rate ratio to give the highest water absorption of 205 g/g is 150 rpm (for gelatinization) to 200 rpm (for graft copolymerization). The stirring rate produces forces to convey all the materials to react in the stirring tank and allow the materials to exchange/dissipate heat to the wall of the tank. Better mass transfer and heat transfer resulted

at 200 rpm than at 250 rpm (graft copolymerization). At the higher stirring rate, the materials are disseminated to the wall of the tank rather than to the center of the tank. More reactions occur at the wall area in which a poor mass and heat transfer due to localization resulted to decompose hydrogen peroxide. That means there was a wastage of initiator and less effective graft copolymerization consequently resulted.

Effect of Polymerization Time on Water Absorption of HCSPA

As mentioned earlier, the graft copolymerization time of this system was 4 h with a water absorption value of 205 g/g. Basically, graft copolymerization of acrylic acid onto cassava starch backbone is an exothermic reaction, which undergoes auto-acceleration. When the polymerization commences, the viscosity of the reaction paste increases accordingly. Polymerization of acrylic acid through diffusion control is rather difficult. The assigned amount of acrylic acid and hydrogen peroxide to polymerize need about 4 h to complete the addition of this mixed solution. Whenever the above-mentioned addition and polymerization times are longer than 4 h, the water absorption decreases rapidly to ca. 55 g/g as shown in Figure 9. Based on our calculation of heat transfer, the times needed for heat transfer from the heated oil through the stainless steel tank to the reacting mixture in the tank for gelatinization and graft copolymerization are approximately 6 s. This time indicates that the stainless steel has a low thermal resistivity, which it implies that there is no obstruction for heat transfer of the system. Likewise, the time required for the heating coil to transfer heat to the gelatinized starch is 9.2 min. In the experiment, it takes 1 h to obtain a complete gelatinization. The calculated heat transfer of the heated coil to the graft copolymerization needs only 1.2 min, but four-hour grafting is used to control heat and the reaction viscosity to rise from 50 Pa.s to 97 Pa.s. This is the reason for the need of slow addition of the acrylic acid and hydrogen peroxide mixture to the reaction paste.

Effect of Polymerization Temperature on Water Absorption of the HCSPA

Figure 10 shows the effect of the grafting temperature on the water absorption of the HCSPA. When increasing the grafting temperature from 30°C to 45°C, the water absorption increases from 111 g/g to 320 g/g. When increasing the grafting temperature even higher than 45°C, the water absorption decreases to 21 g/g. This is attributed to the following reasons. At high temperatures, the decomposition rate of hydrogen peroxide to water and oxygen becomes very high. The oxygen molecules oxidize ascorbic acid to yield dehydroascorbic acid that is an inert component for graft copolymerization.

Additionally, the oxygen molecule is a strong inhibitor that stops radical chain polymerization. The acrylic acid radicals in the aqueous phase can recombine to produce poly (acrylic acid). At a 45°C polymerization temperature, 4.5% homopolymerization is realized, whereas 5.0% is observed at 65°C.

It is worthwhile to mention that the homopolymer of acrylic acid with a relatively low water absorption value can be used as a flocculant, thickener for textile printing, paper additives, and so on.(10)

Effect of Viscosity Change on Polymerization

After 1 h of polymerization, a viscosity increase from 50 Pa.s to 97 Pa.s was observed. Afterwards, the viscosity decreases gradually all the way to 10.5 Pa.s at the end of the 4-h polymerization time. At the first hour of the reaction, the viscosity increases to 97 Pa.s as the reaction mixture becomes thicker as polymerization proceeds. As the reaction proceeds, auto-acceleration occurs and increases the reaction temperature steadily, which reduces the system viscosity as a result of the destructive gel network. The information of viscosity change is of prime importance, because it is needed for the large reactor design of industrial-scale production. (9)

Relationship Between the Contents of Homopolymer and Graft Copolymer on Water Absorption

The relationship between the contents of homopolymer and graft copolymer on water absorption is shown in Table 2. The graft copolymer content is calculated based on homopolymerization occurring at the expense of graft copolymerization.

$$\%\ \text{graft copolymer} = 100 - \%\ \text{homopolymer} \qquad (1)$$

Theoretically, graft copolymerization of vinyl monomer onto starch is always accompanied by homopolymer formation. In general, the rate of graft copolymerization decreases with monomer and initiator concentrations in the swollen phase; the rate of consumption of the monomer is higher because homopolymerization is usually high at high temperatures.(7) The experimental data show that a high amount of homopolymer is consequently produced, leading to a low water absorption value. On the other hand, for some data, the graft copolymer concentration increases while the water absorption decreases. The result can be explained in terms of the sampling technique. An amount of 10 g of the product from the batch of about 1 kg was removed for the determination of the homopolymer, because its content was determined by a soxhlet extraction of a laboratory scale. The mixture removed might not be homogeneous enough to represent the whole batch; therefore, deviate data could result.

Figure 9. Effect of polymerization time on water absorption of HCSPA in deionized distilled water.

Figure 10. Effect of polymerization temperature on water absorption of HCSPA in deionized distilled water.

Table 2. Relationship between the Content of Homopolymer and Graft Copolymer on Water Absorption.

Parameter	Homopolymer content, %	Graft Copolymer content, %	Water absorption, g/g
Hydrogen peroxide concentration, M			
4.4×10^{-2}	4.8	95.2	108±4.50
7.4×10^{-2}	4.1	95.9	205±3.06
1.03×10^{-1}	6.8	93.2	54±2.63
1.48×10^{-1}	7.1	92.9	59±1.55
Ascorbic acid concentration, g			
2	2.7	97.3	57±4.58
3	4.1	95.9	205±3.06
4	5.4	94.6	133±3.95
5	6.8	93.2	135±4.95
Acrylic acid concentration, M			
1.32	2.3	97.7	48±1.75
1.88	2.5	97.5	50±5.13
2.42	4.5	95.5	320±6.24
2.96	5.4	94.6	80±4.51
Stirring rate for gelatinization to graft copolymerization			
150 : 250	6.4	93.6	148±5.49
150 : 200	4.1	95.9	205±3.06
200 : 250	5.7	94.3	52±6.76
Polymerization time, h			
4	4.1	95.9	205±3.06
4.5	4.8	95.2	57±6.11
4.75	4.7	95.3	59±3.26
5	5.1	95.9	51±2.65
Polymerization temperature, °C			
30	3.3	96.7	111±4.58
35	4.1	95.9	205±3.06
45	4.5	95.5	320±6.24
55	5.0	95.0	230±3.61
65	6.8	93.2	21±4.73

Estimation of the Production Cost

A preliminary cost estimation for producing highly water absorbing polymer from native cassava starch indicates the promising feasibility of the production scale of this polymer. For such a batch reactor with a capacity of 1 kg/batch of the product, the cost is about ฿141.35/kg as shown in Table 3 provided that the product contains 5% moisture.

Table 3. Estimated Production Cost of Powdery Highly Water Absorbing Polymer for a 1 kg/batch Capacity.

Items	**Cost**		
Raw materials	**Quantity used, g**	**Raw material prices, ฿/kg**	**Production cost, ฿/kg**
Cassava starch	450	13	5.85
Calcium oxide	7.5	550	4.1
Ascorbic acid	3	1,800	5.4
Hydrogen peroxide	10	850	8.5
Potassium hydroxide	740	30	22.2
Acrylic acid	900	60	54
Methanol*	600	19	11.4
Deionized distillated water	6,000	4	24
Electric cost			5.9
	Total estimated cost		141.35

* Based on 5% loss

Costs are reported as of early 1997 and cost items included in the estimated production cost are raw materials (commercial grade) and electricity costs.

The present investigation has achieved a set of superabsorbents with various water absorption values for different applications. The optimum reaction conditions for soil conditioner type superabsorbent(5,10) with 320 g/g of water absorption were described.

CONCLUSIONS

A cylindrical stainless steel reactor of 10.6-l capacity, stirred by a horseshoe paddle, was used to synthesize the highly water absorbing polymer from native cassava starch. The superabsorbents can absorb water from 21 to 320 g/g dry weight. The water absorption of HCSPA depends on the hydrogen peroxide concentration, ascorbic acid concentration, acrylic acid concentration, stirring rate for gelatinization, stirring rate for graft copolymerization, polymerization time, and polymerization temperature. The maximum water absorption of HCSPA was 320 g/g dry weight when the optimum parameters were used. This research gives the reaction viscosity in the graft copolymerization to rise from 50 Pa.s to 97 Pa.s, and the percentage of homopolymer formation is from 2.3 to 7.1. Estimation of the production cost for a batch reactor with a capacity of 1 kg/batch of the product is about ฿141.35 per kg.

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