

# Synthesis of Superabsorbent Starch-graft-Poly(potassium acrylate-co-acrylamide) and Its Properties

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**ABSTRACT:** The superabsorbent's ability to resist deformation and to resist deswelling under externally applied pressures is important in practical application. For instance, it is used in infant diapers, in soil for agriculture, and in forestry. In this article, we report on the synthesis of a superabsorbent/starch-graft-poly(potassium acrylate-co-acrylamide) by inverse suspension polymerization. The effects of reaction conditions, such as monomeric concentration, ratio of water to oil, reaction temperature, and obtaining spherical resin, were investigated. Experiments showed

that the superabsorbent has a good compressive strength and keeps the shape of particles after absorbing water. After mixing with soil it does not become sticky, and the loose structure can better retain air. It is fit to retain water in soil. In addition, thermogravimetric analysis revealed the superior thermal stability of the grafted product and its large particle size also reduces risk of air pollution. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1536–1542, 2003

**Key words:** graft copolymers; copolymerization; monomers

## INTRODUCTION

In the past 20 years, superabsorbent polymers (SAP) have achieved a large worldwide market.<sup>1,2</sup> Statistics indicates that the worldwide production of SAP was 6000 tons in 1983 and 450,000 tons in 1996. The production not only increased by almost 80 times, but remained on an increasing rate of 5–10% in recent years.<sup>1,3</sup> Although its production-increasing rate is higher than any other polymer material, the quality and price of this product still leaves a lot to be desired. For instance, unilateral emphasis on SAP's water-absorbing capabilities sacrificed its stability and durability. Not enough attention was paid to the nutrition requirement of the root growth and the influence of air in the soil using it as water retention agent in agriculture. It resulted in the lack of product variety, high price, and so on.<sup>4</sup> Recently, we synthesized a super-water-absorbent that just fit water retention in soil. It possesses higher compressive strength, large particle size, good thermal stability, and low price.

## EXPERIMENTAL

### Materials

The materials used in this study were purchased. Acrylic acid (AA) and trimethylol propane triacrylic

ester (TMPTA) were from Beijing Oriental Chemical Industry Ltd., Beijing, China. Acrylamide (AAm) was from Jiang Xi Agriculture and Science Chemical Industry Ltd., Nan Chang, China. Starch was from Lang Fang Plant of Starch, He Bei Lang Fang, China. It was treated with  $\text{CH}_3(\text{CH}_2)_3\text{OH}$  before use, a capacity of resisting enzymatic degradation was obtained. Other materials were reagent grade chemicals from Tianjin Plant of Agents, Tianjin, China. Deionized water was used in the polymerization system.

### Inverse suspension polymerization

Copolymerization was carried out in a four-necked, round-bottomed flask with stirrer, thermometer, and nitrogen gas inlet. About 120 mL cyclohexane and the surfactant mixed with Span60 and Span20 for stabilizing the suspension were added. It was used at a concentration of 4%(w/w) of the continuous phase. The mixture was heated in a water bath, which was stirred until the complex surfactant was dissolved into continuous phase.

An acrylic acid aqueous solution was neutralized by a potassium hydroxide aqueous solution, and the degree of neutralization was 75%. It was mixed with starch of resisting enzymatic degradation, acrylamide aqueous solution, TMPTA, and ammonium persulfate-co-N,N,N',N'-tetramethyl ethylene diamine (APS-TMEDA) aqueous solution. The initiator at a concentration of 0.4% (w/w) of the total monomers was used. The obtained mixture was added into the oil phase under stirring. The dispersion lasted for 20 min, and

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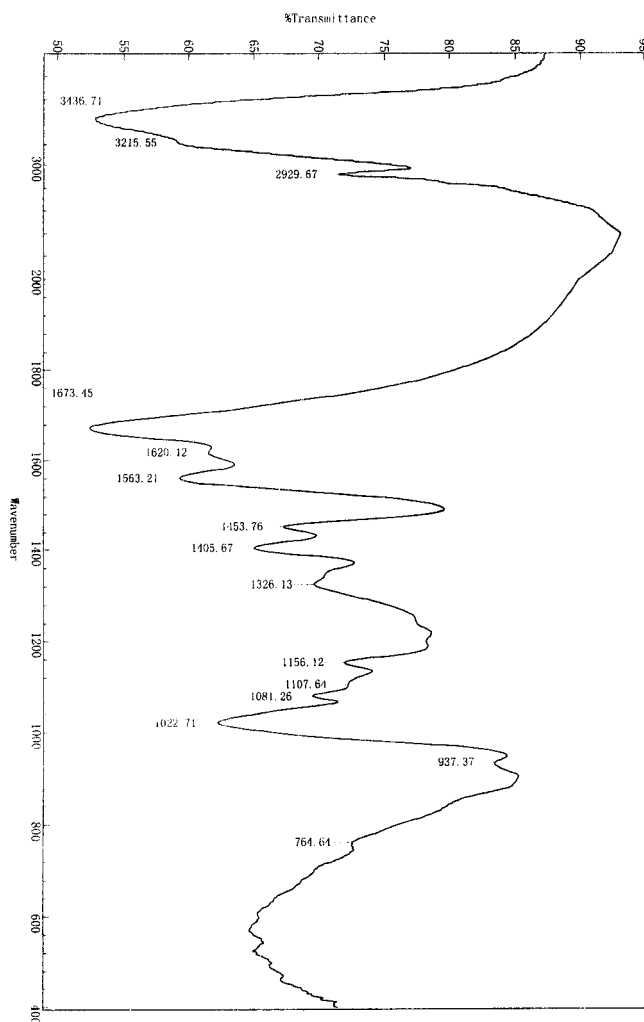


Figure 1 Infrared spectrum of the copolymeric gel.

an water-in-oil system was formed. The pH value of the system was adjusted to 8.0 by adding aqua ammonia. After the reaction was initiated, the stirring rate was raised to 700 rpm and temperature climbed, which increased with conversion. When the temperature could not rise again, the temperature of the water bath was adjusted to 70°C and the reaction lasted for

3 h. After the reaction, the suspension solution was filtered and the product was dried in a vacuum at 50°C. White beads were obtained.

## RESULTS AND DISCUSSION

### Proof of structure of the copolymeric gel

Figure 1 shows the infrared spectrum of the copolymeric gel. The infrared analysis result of the gel in Table I shows that —COOK, —CONH—, —OH, and C—O in starch, characteristic groups exist in the product.

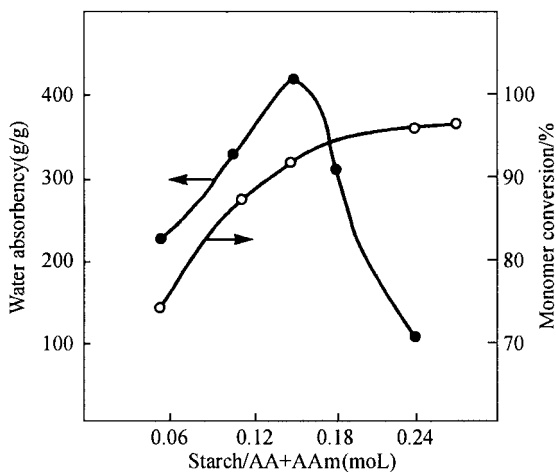
### Effect of total concentration and material mixing ratio

Experiments found that total concentration of starch and monomers is closely related to obtaining spherical resin. Polymeric grain cannot form when total concentration is lower than 50% (w/w). With a total concentration > 55% (w/w), polymerization of monomers occurred before the mixture of aqueous phase was added to organic phase because total concentration of the system was too high. Experiments show that an ideal concentration is 50–55% (w/w).

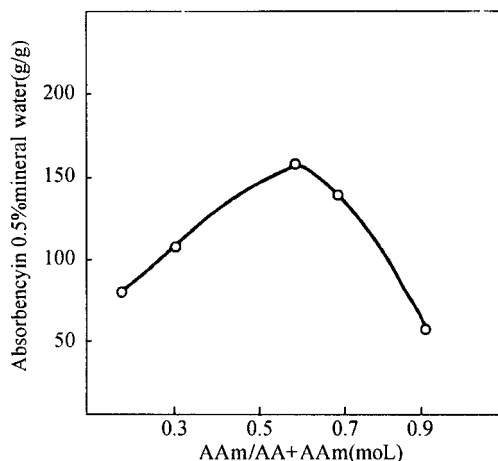
The effect of ratio of three materials on the monomeric conversion and absorbency was investigated. Figure 2(a) and Figure 2(b) show the monomeric conversion and the water absorbency as a function of the copolymeric gels. The monomer conversion and the water absorbency increased with increase of content of starch at the beginning when total concentration and molar ratio of two monomers were constant, and then absorbency decreased and monomer conversion tended to a constant value with further increasing of starch over 0.075 mol (0.25mol AGU/L). It can be seen that starch can promote monomeric conversion, and a molar ratio of starch to two monomers has the best value. The water absorbency in salt solution increased with an increase of molar ratio of AAM to AA for the gels when the content of starch was kept a constant (0.075 mol) and total concentration was 55%. The wa-

TABLE I  
Infrared Analysis Result of the Sample

Group	Type of vibration	Wavenumber (cm <sup>-1</sup> ) (analysis value)	Wavenumber (cm <sup>-1</sup> ) (value in ref)
—CONH <sub>2</sub>	C=O stretching	1673.45	1690–1660
	N—H stretching	3436.71	3500–3300
—COOK, —COOH	C=O stretching	1563.21	1610–1550
	C—O stretching	1156.12	1250–1100
	—OH stretching	3215.55	3400–3200
C—O	C—O stretching in starch	1022.71	1250–1020
		1081.26	
		1107.64	



(a)

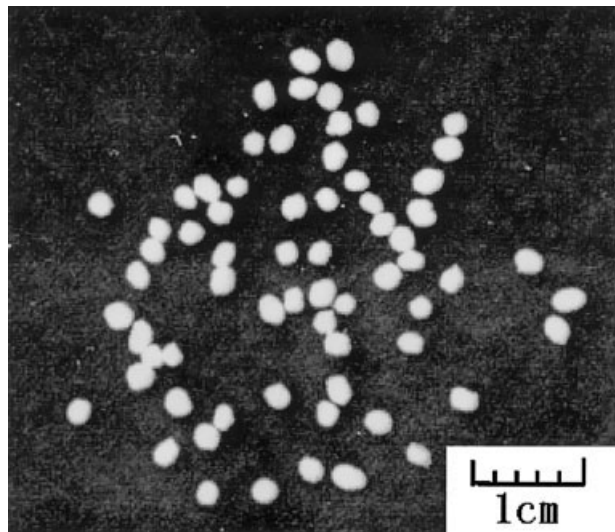


(b)

**Figure 2** (a) Effect of molar ratio of starch to the monomers on monomer conversion and water absorbency. AA : AAm = 0.17 : 0.25 (mol); total concentration, 55 wt %; water:oil = 1 : 1.5 (v/v). (b) Effect of molar ratio of AAm to AA on water absorbency in mineral water. Total concentration, 55% (w/w); starch = 0.075 mol AGU; water : oil = 1 : 1.5 (v/v).

ter absorbency in salt solution decreased for the gels when molar ratio of AAm to AA was higher than 0.25:0.17. This phenomena is explained by the hydrophilic group ( $-\text{COOH}$ ) decreased along with increase of the content of AAm in the gels.

In general, monomeric concentration in the polymerization is one of the key parameters affecting both the properties of the polymer and the economics of the process. Higher monomer concentration in the mixture generally affords a gel that is tough and has a large particle size. We measured the average diameter of the resin, and it was 1.5 mm (see Fig. 3). In addition, the surface of the polymeric gel is rugged by scanning electron microscopy (SEM) observation (see Fig. 4). It seems to be composed of fine particles. Holes exist

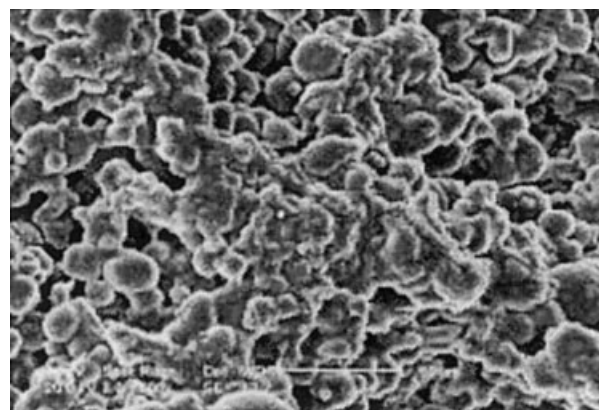


**Figure 3** Particle size of copolymeric gel.

between these fine particles, so water can be absorbed easily by the resin because it has a higher specific surface area.<sup>5</sup> The characteristics of surface morphology is very significant on water absorbency, especially for large particle sizes of superwater-absorbent.

#### Effect of crosslinking agent

The crosslinking agent can notably affect characteristic of the superwater-absorbent. This has been reported previously<sup>6</sup>—that is, the higher the content of the crosslinking agent, the lower the water absorbency because the crosslinking density is great and the three-dimensional network is small. Here fraction of the gel portion is the important factor that influences its application. If a water-absorbent resin contains a large amount of the sol portion, the strength of the resin is decreased remarkably when it is in contact with water for a long period of time. The gel portion was mea-



**Figure 4** SEM micrographs of the copolymeric gel on the surface.

**TABLE II**  
Effect of Amount of Crosslinking Agent on Fraction of Gel and Water Absorbency

Amount of crosslinking agent (%)	G × 100	Absorbency (g/g)	
		Deionizing water	0.5% Mineral water
0.02	49	172	61
0.04	76	220	74
0.06	85	385	126
0.08	90	420	150
0.10	90	298	92

Starch:AAM:AA = 0.075:0.25:0.17 (mol); water:oil = 1:1.5 (v/v); the degree of neutralization, 0.75.

sured with methods from ref. 6. Our experiments show that the fraction of the gel portion in water-absorbent resin increased with the increase of the crosslinking agent when the concentration of the crosslinking agent was low. After that the fraction of the gel portion reached a maximum value when the concentration of the crosslinking agent was 0.08% of total amount of monomers, and maintained a constant value (see Table II). In addition, the chemical and physical nature of the crosslinking agent played an important role in determining the property of the manufactured SAP. TMPTA[CH<sub>3</sub>CH<sub>2</sub>C—(CH<sub>2</sub>O—COCH=CH<sub>2</sub>)<sub>3</sub>] is the crosslinking agent of a multifunctional group, and it can form a macromolecular three-dimensional network structure by crosslinking with monomers. This is a “structure of build type.” The reactivity ratios of all of the various double of TMPTA bonds in similar system hve been investigated.<sup>7</sup> Experiments showed that all of the double bonds of TMPTA were incorporated into gel network, and so crosslinking gel with it could have high strength.

### Effect of the ratio of water to oil

To simplify processing techniques, we used cyclohexane as the organic phase. The product easily is separated from the reaction system because its boiling point is low. Even if it is not washed with organic solvent, it can be used directly.

In heterophase polymerization, control of the ratio among water and oil is important for the reaction. The

high ratio of water and oil preserves the heat, and the product will conglutinate and affect its quality. A low ratio will slow down the activity of reaction, and makes the process difficult to complete. Experiments show that the appropriate ratio between water and oil is 1:1.5 (v/v) (see Table III).

### Effect of reaction temperature

The control of temperature in the copolymerization is another important condition. Increase of temperature may lead to several effects on copolymerization such as the initiating system may be easily decomposed, diffusion of monomer increased, and rate of initiation and propagation may be proceed at a much faster rate. But the temperature is too high, reaction rate will be unusually fast, and exploding polymerization may occur. A great quantity of polymerization heat generates during the process. In addition, both rate of termination and chain transfer reaction will be increase at high temperature. However, if the temperature is too low, the three-dimensional network of the copolymers cannot form. Here “program temperature up” was employed. We used a redox couple of the initiator. The reaction was initiated at a low temperature. At that moment, polymerization heat contributes to the temperature increase of the reactants and then the temperature of water bath is elevated progressively. However, its temperature should be 1–2°C lower than the reactants until the temperature of the reactants cannot rise again. The temperature of the water bath was adjusted to 70°C. The levels of residual monomers are low and the molecular weight is high using this method.

### Swelling behavior of the copolymer gel

The gel with different water absorbencies measured by suction method<sup>8</sup> is shown in Table IV. The results show that its absorbency in deionized water was about 420 g/g; it conforms to the requirement of a superabsorbent for agricultural use (200–500 g/g).<sup>9</sup> Absorbency was 150 g/g in 0.5% mineral water. This

**TABLE III**  
Effect of Water/Oil Ratio on the Copolymerization

Water/Oil (v/v)	The stability of copolymerization	Form of the product
1:1.2	The system is not stable	The product is in the form of lump or conglutination
1:1.5	Stable	The product is in the form of granule and even distribution of particles
1:2	Stable	The product is in the form of granule and even distribution of particles
1:3	Rate of the reaction decreased	The product is in the form of granule

Starch:AAM:AA = 0.075:0.25:0.17 (mol); the degree of neutralization, 0.75; [crosslinking agent], 0.08% (w/w).

TABLE IV  
Absorbency of Starch-graft-Poly (potassium acrylate-co-acrylamide)

Sample	Particle size (mm)	Monomer conversion (%)	Absorbency (g/g)	
			Deionizing water	0.5% Mineral water
G <sub>4</sub>	1.40 ~ 1.65	97	420	150
G <sub>6</sub>	1.35 ~ 1.80	95	423	148
G <sub>7</sub>	1.50 ~ 1.70	98	415	147
G <sub>8</sub>	1.40 ~ 1.60	98	425	152
G <sub>10</sub>	1.45 ~ 1.80	97	418	150
PNaAA	0.15 ~ 0.45	98	650	87

PNaAA: poly(sodium acrylate).

Starch:AAM:AA = 0.075:0.25:0.17 (mol); water:oil = 1:1.5 (v/v); the degree of neutralization, 0.75. [crosslinker] = 0.08% (w/w).

satisfies the need of irrigation using slightly salty water.

The S-g-P(KAA-co-AAM) graft copolymeric gel belongs to an anionic-type absorbent. Its swelling behavior can be affected by the salt solution. Addition of some salts to the polymer solution leads to network contraction. Because the repulsive carboxylate group on the polymeric chain was shielded by the bound cation, the osmotic pressure difference between the gel network and the external solution decreased. Therefore, the polyelectrolyte component in the gel cannot imbibe as much salt water as pure water. However, the water absorbency of the superabsorbent in an unpure water medium is not too low because the nonionic component that exists in the gel has a little influence of ionic concentration.

In addition, experiments also show that the swelling capacity of the copolymeric gel is very dependent on

the pH. The water absorbency was low in a strongly acidic region, because the carboxylate side chains of the potassium acrylate in the gel became the carboxylic group, thus decreasing the charge density of anions on the network. However, the water absorbency increased with increase of the pH value when its value was lower than pH 8.0. The reason is that the anions of base-hydrolyzed acrylamide and the carboxylate group inside the network will increase with an increase of the pH. The water absorbency decreased with a further increase of pH value over 8.0. This result is primarily due to the decrease of the osmotic pressure difference between the gel and external solution. However, the absorbency of the gel had only a little change when pH went from 5.0 to 10.0 (see Fig. 5). This behavior was explained by the buffer action of the sodium carboxylate group with acid and base.<sup>10</sup> This property is very significant for application.

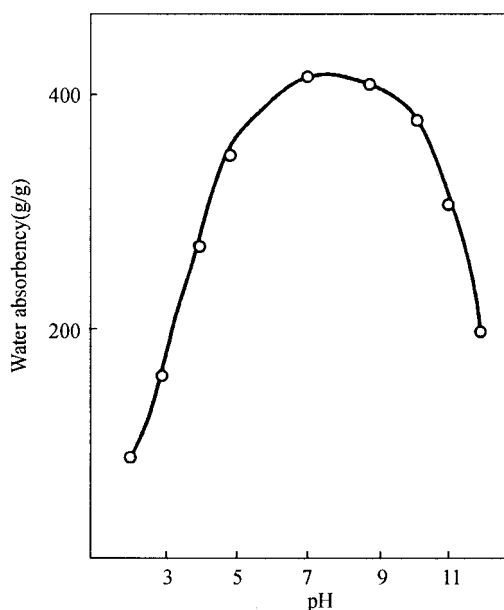


Figure 5 Effect of pH value on water absorbency.

### The water retention capacity

The key properties of a superabsorbent polymer are its swelling capacity under defined loadings. Water re-

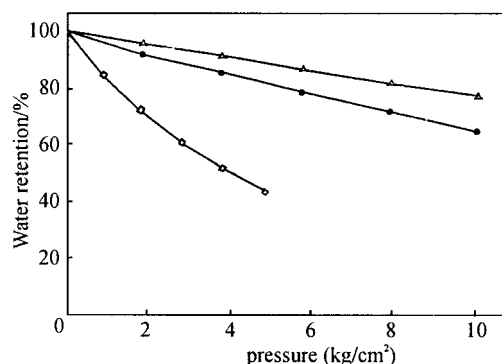


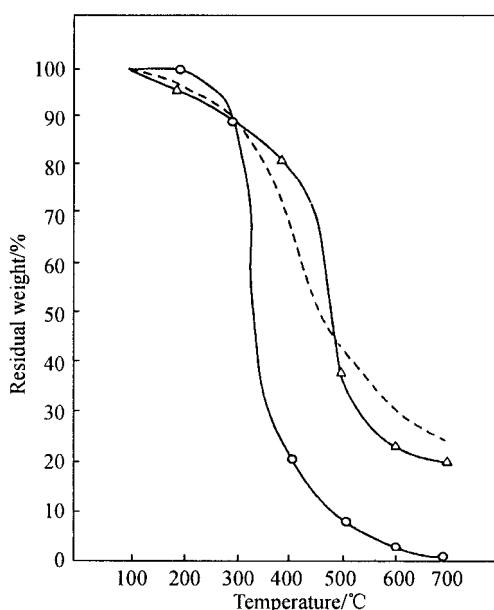
Figure 6 Percentage of water retention of the copolymer gel under load. (Δ—Δ) After surface crosslinking; (●—●) without surface crosslinking; (◇—◇) poly(sodium acrylate).

tention under externally applied pressures was measured with methods from ref. 11. The results in Figure 6 show that the water retention capacity reached 67% when pressure is 10 kg/cm<sup>2</sup> (0.98×10<sup>6</sup> Pa). After surface crosslinking with diglycidyl ethers,<sup>12</sup> water retention capacity reached 78% under same pressure. No water was released by centrifuging at 1500 g for 20 min. This shows that surface crosslinking of the resin particles significantly improved its swelling capacity under pressure. In addition, the rate of absorbing water had increased more than threefold after surface crosslinking. A similar test was run with poly(sodium acrylate), which was prepared by solution polymerization. Its percentage of water retention was lower. The water retention was less than 50% when pressure was 5 kg/cm<sup>2</sup>.

Increase of compressive strength of the resin is related to its chemical composition and its structure. Here, the contribution of acrylamide and crosslinker is solid. However, structure of the graft copolymer possibly modifies some of the properties of starch.

### Thermal properties of the gel

Thermal properties of the graft copolymer was investigated using a WCT-1 thermogravimetric analyzer (TGA)-co-differential thermal analyzer (DTA) in air atmospheres. A heating rate of 10°C min<sup>-1</sup> was employed. Relative thermal stability of the graft copolymer was evaluated by determining copolymer decomposition temperature (PDT) and integral procedural decomposition temperature (IPDT).<sup>13</sup>



**Figure 7** Thermal behavior of graft copolymer. (○—○) Starch; (△—△) P(KAA-co-AAM); (—) S-g-P(KAA-co-AAM).

**TABLE V**  
Results of Thermogravimetric Analysis of S-g-P (KAA-co-AAM) and Other Samples in Air Atmosphere

Sample	PDT (°C)	IPDT (°C)
Corn starch	277	348
P(KAA-co-AAM)	166	581
S-g-P(KAA-co-AAM)	172	624

The thermogravimetric traces obtained for starch, poly(potassium acrylate-co-acrylamide) [P(KAA-co-AAM)] samples, and S-g-P(KAA-co-AAM) samples in air atmosphere are shown in Figure 7. PDT and IPDT were determined (see Table V). In these samples about a 5–10% loss in weight was observed below 100°C. This was attributed to absorbed water and was not taken into consideration while plotting the weight loss vs temperature curves. Figure 7 shows that starch degradation is faster than others. About 80% weight loss takes place in the temperature range of 220–350°C for starch and it can degrade completely at 700°C. The PDT for starch and the P(KAA-co-AAM) sample was found to be 277 and 166°C, respectively. The PDT for the S-g-P(KAA-co-AAM) sample was in between that of starch and P(KAA-co-AAM). Their degradation occurs in three distinct stages. In P(KAA-co-AAM), maximum weight loss is observed around 500°C. However, in the S-g-P(KAA-co-AAM) sample, a residual weight of 40% was observed at 500°C. The S-g-P(KAA-co-AAM) and P(KAA-co-AAM) samples cannot degrade completely at 700°C because inorganic salt exists in these remnants. A interesting feature of the IPDT result is that the S-g-P(KAA-co-AAM) sample has higher IPDT than other samples. These studies have indicated that grafting of P(KAA-co-AAM) onto starch leads to an overall improvement in the thermal stability. It is possible that during degradation, IPDT values for the graft copolymer increased as a result of some reaction that occurred between starch and polymer chains.

### CONCLUSION

S-g-P(KAA-co-AAM) can be prepared in inverse suspension. When both granular starch and concentrated aquatic solution were used, a large particle size and a high strength resin was formed. Surface crosslinking of the SAP particles significantly improves swelling capacity under pressure because the particle structure does not change. Here special crosslinkers may be necessary in order to obtain high swelling capacities under pressure. The thermal analysis data show that the graft copolymer is different from P(KAA-co-AAM) and starch. It has higher integral procedural decomposition temperature. This shows a synergistic effect of the grafted copolymer. In addition, the gel contains

varied hydrophilic groups, and so stability in the salt solution is efficiently improved.

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