Chemistry

PREPARATION OF SUPERABSORBENT POLYMERS BY THE INVERSE SUSPENSION METHOD

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Abstract. The superabsorbent polymers based on acrylic acid have been prepared in the presence of ammonium persulfate (APS) as initiator and N,N-methylene- bis- acrylamide (MBA) as crosslinking agent. The suspension polymerisation occurred in aqueous drops dispersed in toluene and stabilised by sorbitan monooleate. Some effects on the swelling degree and size particles such as concentrations of MBA and initiator, neutralization degree (D_n) were studied. Swelling degree 405g/g, reach maximum at 85°C and 0.09% crosslinking agent, 1.0% initiator, 75% degree of neutralization, 350 rpm agitation speed was observed.

1. INTRODUCTION

Superabsorbents are light crosslinked networks of hydrophilic polymers with a high capacity for water retention and have a variety of valuable applications [1]. Superabsorbents can absorb a large amount of water in a short time. They are used widely in sanitary goods, artificial snow, water- bloking cable... especially in agriculture and horticulture [2,3]. In this article, superabsorbent polymers based on acrylic acid were prepared by the inverse suspension polymerisation in the presence of $(NH_4)_2S_2O_8$ as initiator.

2. EXPERIMENTAL

2.1. Materials

The monomer and toluene were supplied from Merck. Acrylic acid was dried and distilled twice in the vacuum. N,N'- methylene- bis- acrylamide was also recrystallised from methanol. Sodium hydroxide (analytical grade) was supplied from BDH chemicals. Sorbitan mono- oleate was supplied by Aldrich. Ammonium persulfate (APS) was recrystallised twice by distilled water.

2.2. Preparation of superabsorbents [4]

The mixture of acrylic acid and sodium acrylate was prepared by partially neutralising acrylic acid with a predetermined amount of aqueous sodium hydroxide solution, after that the crosslinking agent, MBA was added. The total monomer concentration in the aqueous phase was kept constant, 40.0% w/w.

Polymerisation was carried out in a five- necked flask which was fitted with a stirrer, an efficient reflux condenser, nitrogen purging, a drip funnel and a thermocouple. Toluene, together with surfactant which was used at a concentration 0.35% w/w to the continuous phase, was poured into the reactor and heated to 85°C. Initiator was added to the aqueous monomer solution just before starting the reaction and the combined solutions were added dropwise to the content of the flask at feed of 10g/min prevented the formation of coagulum as the reaction product. Once all the monomer was added, stirring was continued for

another 120 minutes to ensure completion of polymerisation. The product was washed with ethanol and then dried in vacumn at 95^oC to constant weight.

2.3. Swelling measurement

- The samples (~ 0.1g) of the superabsorbent were immersed in water at room temperature until equilibrium was reached. The absorbability was determined by weighing the swollen gel after it had been allowed to drain on a sieve for 10 min. The swelling degree Q(g H_2O/g sample) is calculated using the following equation [2]:

$$Q = \frac{m - m_0}{m_0}$$

m_0: weight of dried polymer (g)
m: weight of swelling gel (g)

- The particle sizes were measured by the scanning electron microscopy. Scanning electron microscopy was performed on a JEOL Model JMS 5300.

3. RESULTS AND DISCUSSION

3.1. Effect of agitation speed

The effects of agitation speed on the swelling degree and particle sizes are illustrated in the Table 1.

Table 1. *Effect of agitation speeds on the swelling degrees and particle sizes*

Agitation speed (rpm)	Swelling degree (g/g)	Average particle sizes (μm)
200	352	600
250	371	578
300	389	525
350	405	510
400	395	475

Conditions of reaction: [MBA]=0.09%, [APS]=1.0%, D_n=75%

It is seen on Table 1 that the agitation speed has a significant effect on the average particle sizes and the swelling degree. The average particle sizes were decreased by the increase of agitation speed and the particle size was rather uniform at higher agitation speed. However, the swelling degree reaches maximum at 350 rpm agitation speed. It is explained that reducing the particle size leads to the increase of the swelling degree because when the particles laid side by side, some spaces could be left between the swollen particles. This space can be called interstitial volume which serves to accommodate additional water by a typical capillary action. If the particle size is too small, the swelling degree was decreased by changing the crosslinking density.

3.2. Effect of crosslinking agent

Effects of MBA concentration on the swelling degree and particle sizes are presented in Table 2.

As shown in Table 2, the swelling degree increases as MBA concentration varies from 0.05% to 0.09% and decreases considerably when MBA concentration is higher than 0.09%.

Table 2. *Effect of MBA concentration on the swelling degree and particle sizes*

MBA concentration (%)	Swelling degree (g/g)	Average particle sizes (μm)
0.05	325	497
0.07	375	502
0.09	405	510
0.11	355	512
0.14	305	518

Conditions of reaction: [APS]=1.0%, D_n=75%, agitation speed = 350rpm

This is due to a decrease in the space between the polymer chains as the crosslinking agent increases. Increasing MBA concentration did not affect significantly the mean particle sizes.

3.3. Effect of initiator

Effects of the initiator concentration (APS) on the swelling degree and particle sizes are illustrated in Table 3.

Table 3. *Effect of APS concentration on swelling degree and particle sizes*

Initiator concentration (%)	Swelling degree (g/g)	Mean particle sizes (μm)
0.4	305	625
0.6	342	580
0.8	386	545
1.0	405	510
1.2	375	485
1.4	315	440

Conditions of reaction: [MBA]=0.09%, D_n=75%, agitation speed = 350rpm

The swelling degree increases as the APS concentration increases from 0.4% to 1.0% and decreases with a further increase in the concentration of APS. This is due to an increase in the number of radicals produced as the concentration of APS increases. This increases the rate of polymerisation thereby lowering the crosslinking density, which is resposible for decrease in swelling degree.

3.4. Effect of degree of neutralization

Effects of the degree of neutralization (D_n) on the swelling degree are presented in Table 4.

The swelling degree increases with the increase of D_n to 75% and decreases when D_n is higher than 75%. This is due to the electrostatic repulsion setted up by the negatively charged carboxyl groups attached on the polymer chains tends to expand the network. However, with the further increase of D_n, sodium ions reduce tremendously the electrostatic repulsion by screening the negative charges of carboxyl groups . The same result was reported by other authors [1].

Table 4. *Effect of degree of neutralization on swelling degree*

Degree of neutralization (%)	Swelling degree (g/g)
65	335
70	374
75	405
80	382
85	329

Conditions of reaction:[MBA]=0.09%, [APS]=1.0%, agitation speed=350rpm

The time required to reach the maximum swelling degree of the superabsorbent was studied and the results are presented in figures 1 and 2, respectively. The results indicate that the superabsorbent absorbs maximum water within 30 min. All the gels have good absorbency.
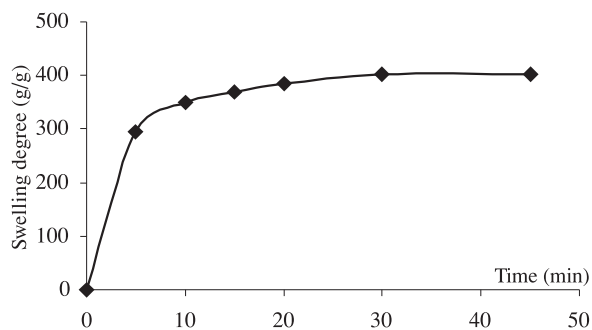
Fig. 1. Swelling degree vs time of superabsorbent in distilled water
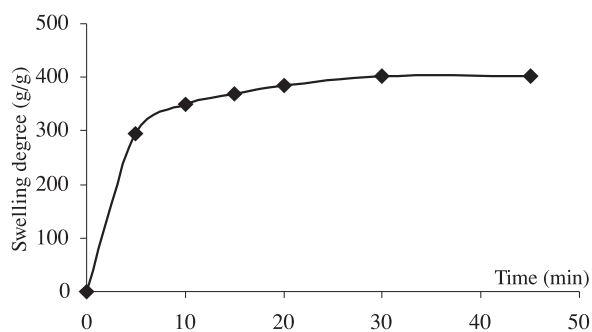
Fig. 2. Swelling degree vs time of superabsorbent in 0.9% NaCl solution

CONCLUSIONS

The superabsorbents based on acrylic acid were prepared by the inverse suspension polymerisation. The effects of some factors such as MBA concentration, initiator concentration and degree of neutralization were studied. The rate of water absorption was

also measured in distilled water and 0.9% NaCl solution. The superabsorbent has high water absorbency (Q_{max}= 405g H_2O/g) and fast swelling capacity. Application of this superabsorbent in agriculture and horticulture will be carried out in the coming time.

REFERENCES

1. Chen J., Zhao Y., An efficient preparation method for superabsorbent polymers, *J. Appl. Polym. Sci.*, **74** (1999) 119-124.
2. Buchholz F. L. and Peppas N. A., 1994, *Superabsorbent Polymer*, Eds. ACS Symp. Ser. 573, American Chemical Society, Washington, DC.
3. Henderson J. C. and Hensley D. L., Efficacy of a hydrophilic gel as a transplant aid, *HortScience*, **21** (4) (1986) 991-992.
4. Raju K. M. and Raju P., Synthesis and swelling properties of superabsorbent copolymers, *Advances in Polymer Technology*, **20** (2) (2001) 146-154.
5. Omidian H., Hashemi S. A., Sammes P.G., Meldrum I., Modified acrylic-based superabsorbent polymers (dependence on particle size and salinity), *Polymer*, **40** (1999) 1753-1761