

SYNTHESIS AND PROPERTIES OF ACRYLIC-BASED SUPERABSORBENTS WITH ENHANCED CROSSLINKING ON PARTICLE SURFACE

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Abstract A series of acrylic-based superabsorbent resins were synthesized by inverse suspension polymerization, using potassium persulfate as the initiator, *N*, *N'*-methylene bisacrylamide (BIS) and divinylbenzene (DVB) as the multiple crosslinking agents. The morphology of the resulting superabsorbent resins revealed by SEM demonstrated that a hard shell layer was indeed formed due to surface crosslinking. The swelling and deswelling properties, and the mechanical strength of superabsorbents were investigated. The results indicated that the adding time of DVB and the amount of DVB participated in the crosslinking show a significant influence on the properties of superabsorbents. When DVB was added in polymerization later, the amount of DVB participated in reaction decreases and the surface crosslinked shell becomes thinner. It is suitable for DVB to be introduced in the later stage of the polymerization process, because the absorption rate of resin is efficiently improved in conjunction with higher water absorption. Furthermore, it was found that the mechanical strength of swollen superabsorbent with surface crosslinking was indeed enhanced in comparison with that of the conventional one.

Keywords: Superabsorbent; Inverse suspension polymerization; Water absorption; Surface crosslinking; Mechanical strength.

INTRODUCTION

Superabsorbent polymers (SAPs) can absorb water more than a hundred fold of its own weight and retain the water even under pressure. SAPs were extensively investigated by many researchers after the first preparation through grafting copolymerization of acrylonitrile onto starch and other polysaccharides^[1–3]. The hydrophilicity of SAPs is derived from the hydrophilic groups, such as carboxylic acids, alcohols, amides, and sulfuric acids. Owing to their excellent water absorption capacity, SAPs have great advantages over traditional water-absorbing materials (such as cotton, sponge, fiber, pulp, *etc.*), and have been widely used in sanitary goods, agriculture and horticulture, artificial snow, architectural material and so on^[4].

Among the recently developed SAPs, acrylic acid (AA)-based SAPs have been extensively studied because AA is cheap and readily polymerized to form a high molecular weight polymer. Although AA-based SAPs have high absorption ability, their absorption rates and the strength of swollen SAPs become lower after a short initial absorption stage due to the “softening effect”. Many efforts have been made to improve the absorption rate and the strength of swollen SAP^[5–10]. Chen *et al.*^[5] introduced interconnected pores to the SAPs in order to increase the absorption rate, and these SAPs were synthesized by crosslinking polymerization in the presence of gas bubbles produced by the chemical reaction between acids and NaHCO₃. Kabiri *et al.*^[6] have prepared porous SAPs through a rapid convenient solution polymerization of partially neutralized AA using acetone and sodium bicarbonate as porosity generators, resulting in a faster absorbing rate. Suda *et al.*^[7] also synthesized porous acrylamide-acrylic acid copolymer SAP through foam polymerization. Ma *et al.*^[8] enhanced the water-absorbing properties of acrylic acid-acrylamide (AA-AM) copolymer SAP by treating it in supercritical CO₂. Although the above methods can improve the absorption capacity and absorption rate of SAPs, the strength of the swollen SAPs was inevitably decreased due to the formation of porous structure. Russian researchers^[9] invented a way of

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reinforcing mechanical properties of swollen SAPs without loss of the swelling ability by filling them with stiff-chain linear polyelectrolyte. Ren *et al.*^[10] improved the wet strength of poly(diallyldimethyl-ammonium chloride) SAPs by preparing the interpenetrating polymer network (IPN) with a natural macromolecule, kappa-carrageenan. However, the absorption rates of above enhanced SAPs have not been reported.

In our previous work^[11], AA-AM copolymer SAPs were synthesized using inverse suspension polymerization to improve its salt resistance. Aiming at improving the property of SAP, oil-soluble and water-soluble crosslinking agents will be added during AA-AM copolymerization to form enhanced surface crosslinking in this work. The morphology, swelling kinetics and mechanical strength of the resulting SAPs will be investigated.

EXPERIMENTAL

Materials

Commercial grade AA was vacuum distilled before use. AM was recrystallized in acetone. Potassium persulfate (KPS) was recrystallized in water. *N,N'*-methylene bisacrylamide (BIS) was purchased from Fluka (Switzerland). Divinylbenzene (DVB), Span-60, cyclohexane, sodium hydroxide and methanol were all analytical grade and used without further purification. Water used in all studies was distilled and deionized to pH $\approx$ 7.0.

Polymerization

SAPs were prepared through an inverse suspension polymerization process using a 500 mL five-necked and jacketed glass reactor fitted with a mechanical stirrer, a nitrogen inlet, a condenser, a dropping funnel and a thermometer. A predetermined amount of NaOH solution was carefully introduced into AA to obtain a partial neutralized acrylate solution (under ice water cooling). Then, accurately weighed AM, BIS and KPS were added and dissolved to form the dispersed phase solution. Span-60 was added into cyclohexane to form the continuous phase. The dispersed phase and continuous phase were mixed in the reactor with vigorous mechanical agitation at a speed of about 450 r/min. The reaction mixture was heated and polymerization was carried out under N₂ atmosphere. The auto-acceleration of polymerization would occur intensely and the particle size could not be controlled if the reaction temperature started at 65°C. Therefore, the polymerization reaction was run from 55°C to 65°C slowly to prevent the aggregation of particles. The predetermined amount of oil-soluble crosslinking agent, DVB, was added into the reaction mixture at regular intervals (shown in Table1). The polymerization was continued for about 3.5 h and then dehydrated by azeotropism. The reaction was discontinued and the suspension was poured into methanol to precipitate the resin. The resulting resin was filtered and washed with methanol several times, and dried under vacuum for 24 h before being weighed. The polymerization conditions were as follows: the concentration of monomers was 37.5 wt%, the neutralization degree 75%, the content of initiator 0.275 wt% based on monomers and the oil/water phase ratio 3:1 (V/V).

Characterization

The concentration of DVB in cyclohexane after polymerization was measured by using a Cary 100 Bio UV-Visible Spectrophotometer (Varian, U.S.A). Before UV measurement, the resulting polymer dispersion was centrifuged at 10000 r/min, and filtered to remove the solid content. The residual solution was diluted to a low concentration by cyclohexane and introduced into a quartz cell for UV measurement.

The morphology of dried SAP resins was observed by using a scanning electron microscope (SEM, Philips XL30). SAP particles were sectioned to expose their interior structure and golden-coated under vacuum. SEM microphotographs were taken at an acceleration voltage of 10 kV.

The swelling kinetics of the SAPs was measured gravimetrically in water at room temperature. The samples were sieved through 20–40 mesh screen. After filtering with a 100-mesh nylon pocket, the weight changes of samples were recorded at the courses of swelling at regular intervals. Water uptake (*WU*) is calculated as follows:

$$WU = (W_t - W_d)/W_d \quad (1)$$

where, W_t is the weight of the sample at regular intervals and W_d is the weight of dried sample.

The weight loss of SAPs, which has already absorbed 20-fold of water to their own weight, was determined by using a thermogravimetric analyzer (TGA, TGA-Pyris 1, Perkin Elmer). TGA results were recorded from 25 to 250°C with a heating rate of 10 K/min under N₂ atmosphere.

The strength of swollen SAPs was determined by using an apparatus, composed of stainless steel cylinder, Perspex (clear PMMA) piston, sample pond (details are shown in Fig.1), and a universal material testing machine (Zwick, RoellZ202, Germany). Approximately 10 g swollen sample was put into the apparatus for each measurement.

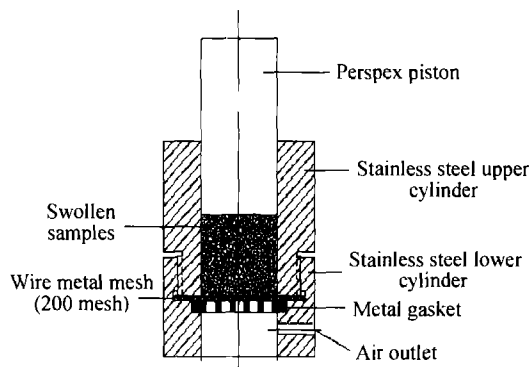


Fig. 1 Apparatus used to measure the mechanical strength of SAPs

RESULTS AND DISCUSSION

Participation of DVB Crosslinking Agent in Crosslinking of SAP

Only water-soluble crosslinking agents were used in the conventional AA-based SAPs preparation. The aim of adding DVB in this work is to enhance the surface crosslinking and form SAP particles with hard shell layer.

The adding time of DVB has great influence on the participation degree of DVB in crosslinking reaction, and the properties of the resulting SAPs. Here, four sorts of polymerizations with different adding times of DVB and two routine polymerizations without addition of DVB were investigated. UV spectral measurements were carried out on the residual polymerization solutions. A typical UV spectrum of residual solution of polymerization with the addition of DVB, is shown in Fig. 2. It can be seen that the spectrum presents the “five finger absorption peaks”, which is the characteristic of benzene group, with the vibration wavelength at 261, 255, 249, 244 and 239 nm, respectively. It is worth to note that the peak at 255 nm is the most intense one, the peak intensity of which was used to measure the content of DVB in the solution.

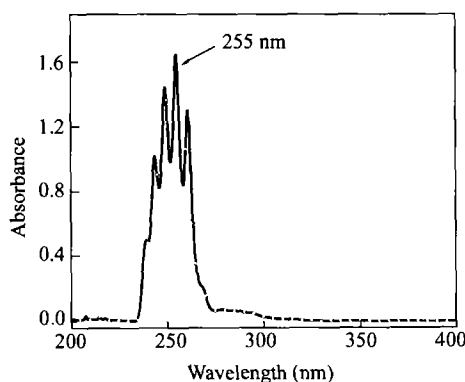


Fig. 2 UV spectrum of solution containing DVB

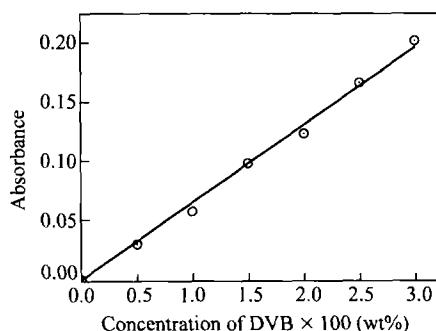


Fig. 3 Relationship between absorbance and concentration of DVB

The concentration of DVB in residual solution of polymerization can be calculated from the linear working curve (cf. Fig. 3), which was obtained by plotting the UV absorbance at 255 nm against different concentrations of DVB solutions in cyclohexane.

From Table 1, it is confirmed that the oil-soluble crosslinking agent, DVB, had participated in the crosslinking copolymerization with the consumed fraction ranging from 32.95% to 81.52%. It is also found that the fraction of DVB participated in polymerization decreases as expected as DVB added in the later stage of polymerization. According to the mechanism of radical polymerization^[12], the conversion from monomer to polymer increases with increasing reaction time, which results in the viscosity increasing with the reaction time. When DVB was added in the earlier stage, it was easier for DVB molecules to diffuse into the reacting droplet and participate in the crosslinking reaction due to the lower viscosity.

Table 1. UV absorption analysis and DVB distribution after polymerization

Sample No.	Initial concentrations of the added crosslinkers		Adding time of DVB after the start of polymn. (h)	Absorbance	Residual DVB		DVB participated in polymerization	
	BIS (wt%)	DVB (wt%)			Concentration (wt%)	Fraction (%)	Concentration (wt%)	Fraction (%)
S1	0.05	0	—	0	0	0	0	0
S2	0.02	0	—	0	0	0	0	0
S3	0.02	0.03	0	0.036	0.0055	18.48	0.0245	81.52
S4	0.02	0.03	1.5	0.082	0.0125	41.71	0.0175	58.29
S5	0.02	0.03	3	0.131	0.0201	67.05	0.0099	32.95
S6	0.05	0.03	—	—	—	—	—	—

Morphology of SAP Particles

The morphologies of SAP particles crosslinked by BIS and DVB crosslinkers, and that of SAP particles crosslinked only by BIS crosslinker, are illustrated in Fig. 4.

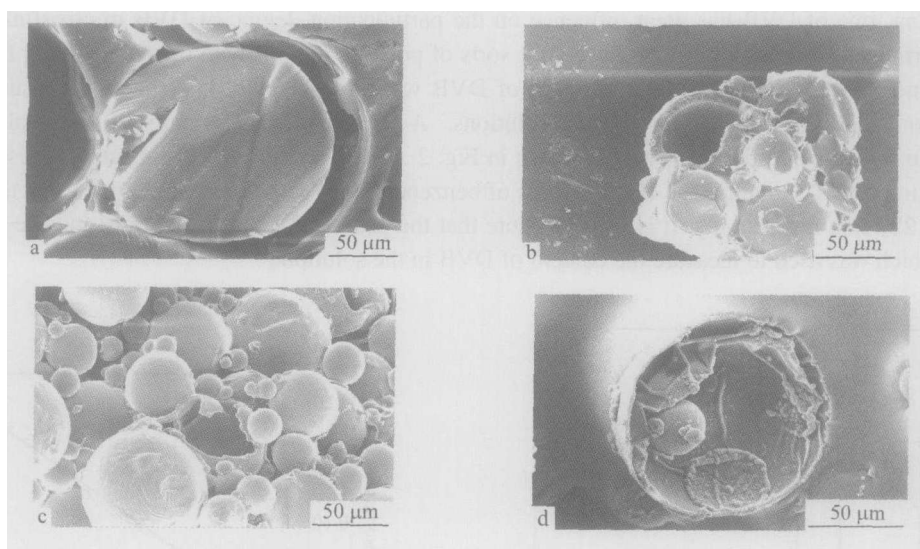


Fig. 4 SEM microphotographs of different dry SAPs
a) S1; b) S3; c) S4; d) S5

It is shown in SEM microphotographs that the SAP particles (S1) synthesized by a routine way have a homogeneous inside structure (Fig. 4a), whereas the SAP particles (S3–S5) crosslinked by both BIS and DVB have distinct shell structure and rather hollow inside (Figs. 4b–d), which manifests that the surface crosslinking has been formed. Furthermore, when the adding time of DVB was put forward, the thickness of the shell increased, which was due to the participation of a higher amount of DVB in the surface crosslinking reaction

(cf. Table 1). During the azeotropic dehydrating process, water contained in SAP particles would diffuse out from inside to outside, and the particles would shrink. For SAP particles with no enhanced surface crosslinking (S1), this shrinkage became more pronounced and the resulting particles still exhibit homogeneous structure. However, the shrinkage of SAP particles with enhanced surface crosslinking (S3–S5) would be hindered by their surface layers with enhanced crosslinking. As a result, the inside of particle was relatively empty, and the surface area became a shell.

Swelling and Deswelling Properties of SAPs

The swelling kinetics of SAPs prepared by different methods in deionized water is shown in Fig. 5. It can be seen that the absorption rates of SAPs increase with the increase in the amount of BIS added, but the water absorptions inevitably decrease (eg. S1 and S6). It can also be seen that the initial absorption rate of sample S5 is greater than that of samples S1 and S2 without the loss of water absorption. So, it is demonstrated that the surface crosslinking is an efficient way to increase the absorption rate without the loss of absorption ability. When DVB was introduced in the early stages (S3 and S4), the swelling curves of the SAPs are characterized by a slow initial stage. This phenomenon has also been observed for water absorption into hydrophobic, ionizable copolymer gels^[13]. In addition, the water absorption increased as the adding time of DVB was put forward.

According to the Tanaka-Fillmore theory^[14],

$$D = K/F_r \quad (2)$$

where D is the diffusion coefficient of the gel network, which can represent the absorption speed. K is the longitudinal bulk modulus of the network, and F_r is the coefficient of friction between the network and the gel fluid. It is well known that an increase in the amount of BIS would favor the formation of a denser polymer network and reduce the chain length between crosslinks, which may result in the increase of both K and F_r . However, when oil-soluble crosslinking agent, DVB, was introduced to form surface crosslinking of SAP particles, the modulus (K) of the network would increase and the friction coefficient (F_r) hardly increases. As a result, the absorption rate is increased.

More DVB would take part in the crosslinking reaction and a thicker surface crosslinking layer is formed, when DVB is added in the earlier stage of polymerization. Thus, the hydrophobic property of resin becomes stronger and the absorption rate decreases at the initial water absorption stage. On the other hand, the thicker surface crosslinking layer would increase the prevention to the inside sol fraction from escaping outside. As a result, the obtained SAP still had higher water absorption as shown in Fig. 5.

The deswelling properties of various SAPs were evaluated by TGA, the results of which are presented in Fig. 6.

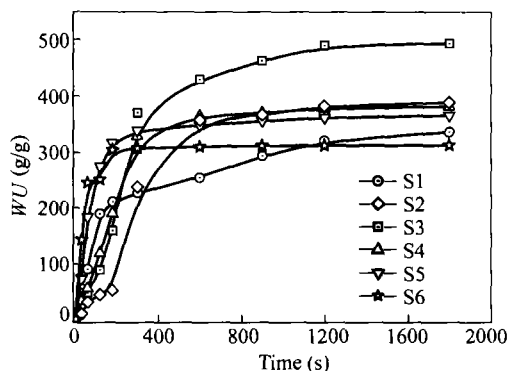


Fig. 5 Variations of water absorption with time for different SAPs

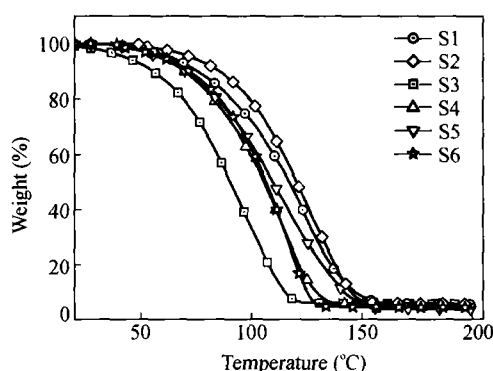


Fig. 6 TGA curves of different SAPs

It can be seen that swollen SAPs lose their weight at the beginning of heating procedure and the deswelling course of SAPs accelerates with the increase in temperature. A small amount of absorbed water still remains as

the temperature is higher than 150°C. Comparing the TGA curves of different SAPs, it can be seen that SAPs prepared by surface crosslinking (S3–S6) dehydrate faster than the conventional SAPs crosslinked only by BIS (S1 and S2). Furthermore, the dehydrating rate of SAPs increases as DVB is added earlier in polymerization. The conventional SAPs have a uniform crosslinking structure in the whole particle, while SAPs with enhanced surface crosslinking have a relative hard shell on each particle. During the dehydration process, the channels for the diffusion of water to the surface of conventional SAPs (S1 and S2) would collapse and water cannot easily pass through the surface, whereas SAPs with surface crosslinking have a relative hard shell to avoid the “collapse impeding effect”. When DVB was introduced at the earlier stage of polymerization, most of them would participate in the crosslinking reaction, which would lead to form a thicker and harder shell layer. As a result, water molecules could escape from the inside to the outside with lesser difficulty.

Mechanical Strength of Swollen SAPs

A typical stress-strain curve of a swollen SAP is shown in Fig. 7. The stress applied to the swollen SAP increases with the increase in strain. It is worth noting that at point “a” in Fig. 7, the stress increases abruptly as the strain increases, which is caused by the initial cracking of swollen SAP particles. Therefore, the stress at point “a” is defined as the ultimate compression pressure (UCP) of the swollen SAP, which can be used to characterize the mechanical strength of swollen SAPs^[15].

The UCP of different swollen SAPs is compared in Fig. 8. It can be seen that the mechanical strength of swollen SAPs can be enhanced as expected by increasing the amount of BIS or surface crosslinking with DVB. It can be also concluded that surface crosslinked SAPs with the earlier addition of DVB have a higher UCP. The reason is that the earlier introduction of DVB would lead to the formation of a thicker and harder surface crosslinked shell.

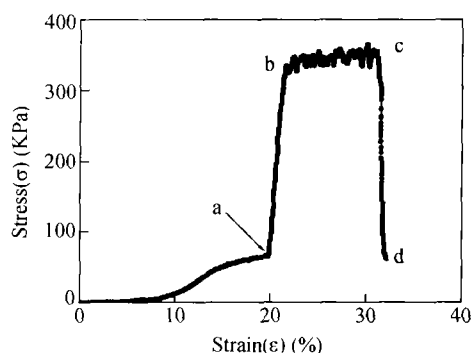


Fig. 7 Typical stress-strain curve of a swollen SAP

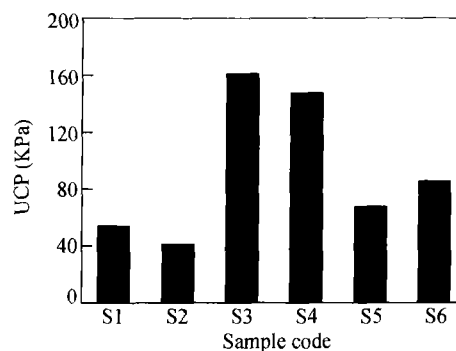


Fig. 8 Comparison of mechanical strength of different swollen SAPs

CONCLUSIONS

AA-based SAPs with enhanced surface crosslinking were prepared through inverse suspension polymerization by using multiple crosslinking agents. The participation of oil soluble crosslinking agent, DVB, in copolymerization was confirmed. SEM microphotographs showed that the resulting SAPs with enhanced surface crosslinking had a relative hard shell. From the swelling kinetics curves, it is concluded that the absorption rate could be improved by enhanced surface crosslinking with higher absorption, and the adding time of DVB has serious influence on the swelling characteristic. TGA results showed that SAPs with enhanced surface crosslinking had a higher dehydration rate. The mechanical strength of swollen SAPs would be increased when the enhanced surface crosslinking was introduced into SAPs particles by using of hydrophobic crosslinking agent, DVB.

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