



Synthesis Study of Nucleus-cell Style High-property

Water-absorbent Polymer

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Abstract

In this paper, MBA was used as crosslinker, SiO₂ and carboxymethyl cellulose as the nucleus-maker, nucleus-cell style SAP was synthesized by AA-AM-AMPS three-member copolymerization. The multiple of water-absorbent by SAP could reach 1150 times by the optimization of the technological conditions. Nucleus-cell style SAP has a good command of fluidity and wet-resistance, it can keep its fluidity 15 hrs after exposure under the air with the humidity of 84%. The best proportion of AA, AM, AMPS is 13:3:4, and the best content of SiO₂ is 0.8%.

Keywords: Water-absorbent polymer, Nucleus-cell style, Step-crosslinking

Water-absorbent polymer, a kind of function material, can absorb water weigh as hundreds times even thousands times as themselves. SAP has been applied in industry, agriculture, medical and treatment, gardening, etc. SAP developed very fast in nearly years. Different kinds of SAP have been prepared, such as synthesized polymers, amyllum species, cellulose species, etc. SAPs from modified amyllum or cellulose can be biodegraded but are easy to corrupt and conglomerate. Their heat resistance, water-keeping performance and gel intensity are poor. Also preparation process is complicated. Two kinds of technology were used to make SAP by acryl acid. One was solution polymerization (disc polymerization) process; the other was reversal-phase suspension polymerization process. At present, SAP made by solution polymerization was of poor moisture proof and was prone to absorb moisture at ambient temperature and at usual relative humidity in practically application. This make it inconvenient to apply, store, transport, packing, produce and machining. Even make it incapable to use. A kind of core-shell high-quality SAP had been synthesized by reverse-phase suspending polymerization in this work. Monomers ratio and other process conditions were studied. FTIR and High power microscope were used to observe core-shell forming and association.

1. Experimental

1.1 Materials

Acryl acid(AA), Acrylamide(AM), 2-acrylamide-2-methyl-propane sulfoacid sodium (AMPS), N,N-methylene-bis-acrylamide(MBA), ammonium persulfate(APS), hydrosulfite of sodium, sodium hydroxide, cyclohexane, surfactant(SP-85, OP-7), carboxymethyl cellulose. All were chemically pure. Silicon dioxide(superfine powder-700 mesh size) was supplied by Chengdu chemical plant.

1.2 Procedure

First, AA was neutralized by NaOH solution and neutralization degree reached 80-85%; second, some AM, AMPS, cross-linker MBA as well as initiator solution were added in and were stirred to get A solution(water phase). Composite surfactant (SP-85:OP-7=1:1) were added in cyclohexane phase and were stirred to disperse enough, so B solution was gotten. B solution was placed into a four-neck flask and was stirred, and then 95% A was added in slowly. They reacted one hour at certain temperature. Then residual A solution as well as cross-linker, cellulose, SiO₂ was added in the flask too. The reaction went on for another three hours. After filtration and separation quickly, product was washed by methanol and was dried to get granular polymer.

1.3 structure and properties test

(1) Test of water- absorbent speed (whirlpool method): pour water in beakers; put beakers on magnetic stirring apparatus; turn on it and muddler make water whirlpool. Pour 0.5g SAP into water and record time by stopwatch until whirlpool disappears. Find out the relationship between water-absorbent and the time.

(2)multiple test of absorbing and solution (net method): put 1g SAP in beakers. Put 0.9% NaCl solution, 0.9% CaCl₂

solution, distilled water, tap water, and soil lixivium etc into beaker respectively. When SAP absorbs liquid balance, excrement liquid is filtered by 100-mesh net. Weight and work out the absorbing & solution multiple.

$$Q=(W1-W2)/M \quad (1)$$

In formula: Q- absorbing & solution multiple; W1-SAP weigh after absorbing(g); W2- net weigh(g); M-SAP weigh(g).

(3) fluidity test(angle of repose): samples in filler flow to horizontal desktop spontaneously. Test samples' angle of repose. Fluidity is poor if the angle is greater than 45° , and fluidity is good if it is smaller than 45° .

(4) test of humidity resistance: judge samples' humidity resistance by test their hygroscopic capacity at different time and moisture condition.

(5) observe samples' morphologies by high-quality microscope.

(6) FTIR : FTIR was got by NiColet-170SX instrument after samples were dealt with KBr by pressed disc method.

2. results and discussion

2.1 monomers affection on SAP'S properties

Figure 1 presented that water-absorbent multiple decreased and salt water-absorbent multiple increased, while degree of cross linking, degree of neutralization and reaction temperature kept invariable with AM monomer's increasing. AM contained amido which belonged to non-ion hydrophilic group and was of strong property of salt-resistance. With amido increasing, -N-H-O-hydrogen bonds tended to form between polymer chains within network structure. Cohesive energy increased. Intensity increases and water-absorbent multiple decreased. With AMPS monomer's ratio increasing, salt-absorbent ratio and water-absorbent ratio increased accordingly. -SO₃H was strong hydrophilic ionic group. With its ratio increasing, ionicity of SAP network increased too. The osmotic pressures both in network and out network increased, and then water-absorbent increased accordingly. Ion in solvent had important influence on water-absorbent performance of SAP. The influence of Ca²⁺ was stronger than Na⁺ at the same concentration. Ca²⁺ entered into SAP net and was easy to form complex compound with carboxylic radical, which reduced repulsion between anions, so increased elastic behaviour of gelatum made water-absorbent multiple of SAP decrease. In thermodynamics opinion, Flory quantitatively stated how water-absorbent performance of SAP related to ion concentration in solvent, charge density of polymer, degree of cross linking and the appetency of groups in net to water. With degree of cross linking increasing, water-absorbent multiple decreased; with ion concentration in solvent increasing, water-absorbent multiple decreased too. In order to improve water-absorbent multiple and water-absorbent speed, strong hydrophilic groups including hydrophilic non-ionic groups could be introduced in polymer. Experimental results accorded with that theory basically. Of its performances, water-absorbing multiple, water-absorbing speed, gel intensity and salt resistance were mostly pursued by people and also were considered in actual application. According to molecule designing opinion, copolymerization of two members or three members even several members was valid way to improve SAP performances. When any two components of AA, AM and AMPS copolymerized, the most water-absorbing multiple was 916 times. While three components copolymerized, it increased to 1150 times.

Figure1 showed that water-absorbing speed rate curve of core-shell SAP was "S" shape. Shell made speed rate slower at the beginning. When shell split, water entered in quickly. Proper thickness of shell didn't influence water-absorbing multiple and speed rate. The shell could protect SAP against moisture. During the process of water-absorbing, SAP surface carried through hydration ionization firstly. More was hydration ionization degree, more would water-solubility increase. sol came into being and ion film did simultaneously, which held back water's penetration and influenced water-absorbing speed rate, so ionic group content couldn't be more, otherwise water-absorbing multiple would decrease. Amido was of stronger hydrophilicity and formed hydrogen bond with water molecule, which increased the hydrophilicity and improved water-absorbing speed rate greatly. Core-shell SAP could achieve water-absorbing saturation in 10 minutes.

Figure 2 showed that moisture absorption speed of core-shell SAP was slower at the incipient stage in humidity atmosphere, which was mostly due to consumed time for polymer hydration and molecule chain stretching. As long as polymer chains stretched out, water-absorbing speed would accelerate. In the case of the protection of shell, water-absorbing speed stayed slow because of poor affinity between water molecules and SAP. That was why core-shell resin owned better humidity resistance than general polymer. At 84% relative humidity, core-shell SAP could keep better fluidity after 15 hours at ambient temperature. Angles of repose were test to compare fluidity. That of Core-shell SAP was 36° and that of non-core-shell production was 44° .

2.2 temperature's influence on synthesis

It could be seen form figure 3 that polymerization reaction kept stable and water-absorbing multiple was small at low temperature. When temperature rose to 70°C , water-absorbing multiple of SAP achieved the highest peak. After that, water-absorbing multiple went down with temperature's continuous rising. Synthesising SAP belonged to free radical polymerization and exothermic reaction, while initiator's decomposing belonged to endothermic reaction. At low

temperature initiator decomposed slowly. Their concentration and initiating efficiency were low, too. Cessation reaction and growth reaction was a pair of competitive reaction. The former activation energy (about 8.5-17kg/mol) was lower than the latter's (about 17-34 kg/mol). Low temperature would make monomers' residual large and polymer molecular weigh small, which would have influence on water-absorbing multiple of SAP. Although suspending liquid could eliminate heat, AA polymerization was exothermic reaction, when temperature rose, initiator composed fast and initiating efficiency improved to make core temperature high. This made AA self-polymerize and cross-link, so that polymer clew couldn't stretch and water-absorbing multiple decreased. Figure 2 displayed that monomers' residual decreased with temperature rising at various temperature, which accorded with the above conclusion.

2.3 degree of neutralization's influence

Figure 4 indicated that water-absorbing multiple of SAP became larger with degree of neutralization increasing when other condition stayed unchanged. When degree of neutralization achieved 85% liquid-absorbing multiple reached the peak. Since the acidity of -SO₃H group was stronger than that of -COOH, when AMPS was added in the neutralized AA solution, AMPS would react with sodium acrylate and -COOH would be released, so in fact neutralization in general polymer was smaller than the data calculated on AA, which could be seemed as the concentration of AA increased. Reaction activity of AA was stronger than that of acrylate, AM and AMPS, so AA likely self-cross link, which made swelling capacity of polymer net decrease and water-absorbing multiple as well as water-solubility become small. When neutralization exceeded 85%, would -COONa group increase. This reduced self-cross linking, but water-solubility increased, so water-absorbing multiple and speed would reduce too.

2.4 Influence of addition of SiO₂ on the effect on SAP core-forming

Table 3 presented that humidity-resistance time of SAP increased with addition of SiO₂ but the correlation was not direct proportion. When SiO₂ quantity was little, particle surface of SAP couldn't be covered fully. When SiO₂ quantity reached 0.8%, the complete film formed and humidity-resistance performance was promoted greatly. The addition quantity of SiO₂ was not very large, so its influence on water-absorbing multiple and speed rate was little.

2.5 FTIR analyses

Figure 5 showed that Si-O stretching vibration was at 1108 cm⁻¹ and flexural vibration was at 474cm⁻¹. Vibration peaks of -OH and Al-O occurred at 3412cm⁻¹ and 619cm⁻¹ respectively since the purity of SiO₂.

Figure 6 showed that 1570cm⁻¹ peak came from C=O stretching vibration of amide group and carboxyl. Dissymmetric stretching vibration of S=O occurred at 1330cm⁻¹ and its stretching vibration was at 1058cm⁻¹. 3412cm⁻¹ peak of -OH mean that -SO₃H existed. 1174cm⁻¹ and 513cm⁻¹ peaks represented stretching vibration and flexural vibration of Si-O respectively, which indicated that SiO₂ was grafted at SAP surface and formed shell.

2.6 SAP morphology observation by microscope

Figure 7 showed that SAP made from reversal-phase suspending process were uniform spheres. Figure 8 presented the morphology after water-absorbing. Shell was obvious and it broke up after water-absorbing. Figure 9 showed the SAP morphology from solution polymerization processing. The powder products derived from massive products when they were cracked. Most particles were irregular.

Conclusion

- When MBA was used as cross-linker and SiO₂ was used as the nucleus-maker, SAP was synthesized by AA-AM-AMPS three-member copolymerization in reversal-phase suspending processing. The SAP possessed better water-absorbing capability. The water-absorbing multiple of SAP under the processing of optimizing the technological conditions could reach 1150 times. SAP possessed good fluidity and humidity-resistance. It could keep some fluidity after exposure to the air with 84% humidity for 15 hours.
- No agglomeration and no adhesion occurred in the preparation processing. Hard operating process was overcome. The particles of SAP were uniform.
- Under the preparation processing, temperature should be controlled from low to high. This could control the polymerization reaction effectively.

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Table 1. Influence of Monomer composition to absorbent resin (SAP) performance

Content of Monomer components W(AA+AM+AMPS)%	Distilled water absorption rate g/g	Salt water (0.9%) absorption rate g/g	CaCl ₂ (0.9%) absorption rate g/g	Tap water absorption rate g/g	Leaching of soil absorption rate g/g
100+0+0	683	58	42	487	284
90+3+5	846	103	57	531	323
85+6+10	917	112	66	663	416
80+10+10	913	136	83	727	518
75+10+15	1020	148	96	786	542
70+15+15	1080	156	102	834	584
65+15+20	1150	230	113	897	672
60+15+25	830	211	106	710	524
50+25+25	610	88	62	580	390
90+0+10	720	89	58	716	462
80+0+20	857	109	88	792	503
70+0+30	916	112	99	842	594
90+10+0	586	67	46	513	281
80+20+0	537	74	64	488	228
70+30+0	469	83	71	420	206

Table 2. Monomer AA remains measures in SAP at different temperatures

Temperature (°C)	40	50	60	70	80	85
Monomer Residual (ppm)	630	447	325	240	188	160

Table 3. Influence of SiO₂ joins quantity to SAP coring effect and performance

No	Amount of Joinning SiO ₂ (%)	Fangshi Continue time (h)	Absorbent water rate (g/g)	Absorbent Water speed (g/s)	note
1	0.2%	0.8	1143	6	
2	0.4%	3	1157	8.5	
3	0.6%	7	1146	9	
4	0.8%	20	1150	9	
5	1.0%	22	1138	10	

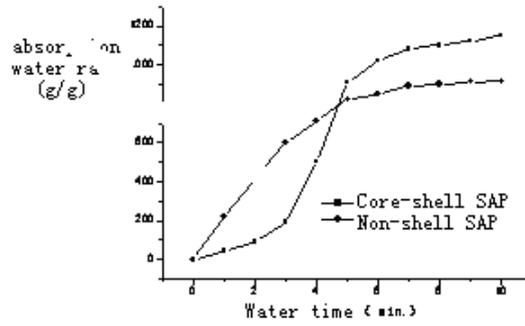
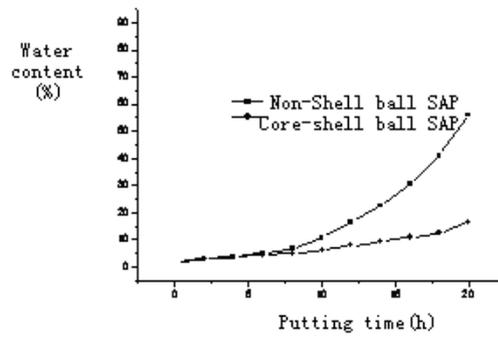


Fig1 Absorbing water speed of SAP



Note: The relative humidity of 84%
Fig2 Moisture absorption performance of SAP

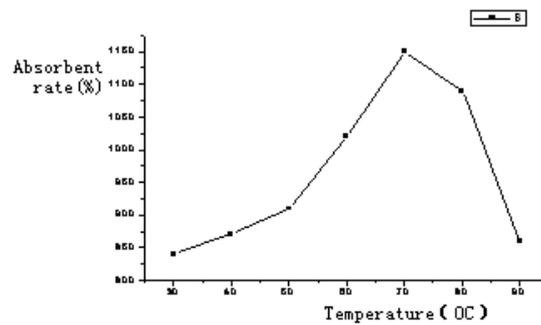


Fig 3 Influence of temperature to SAP absorbing water percentage

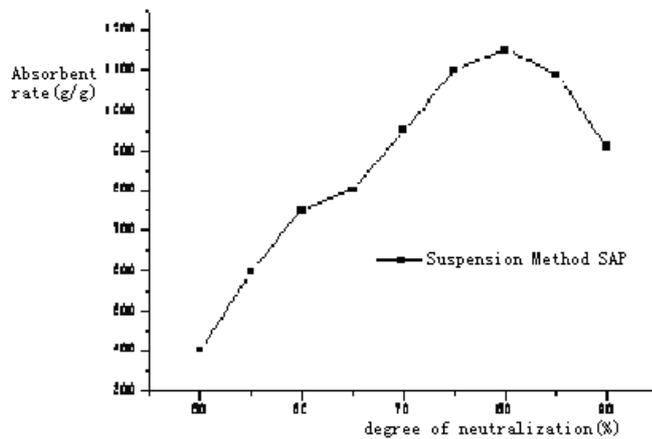


Fig 4 influence of neutral to SAP absorbing water percentage

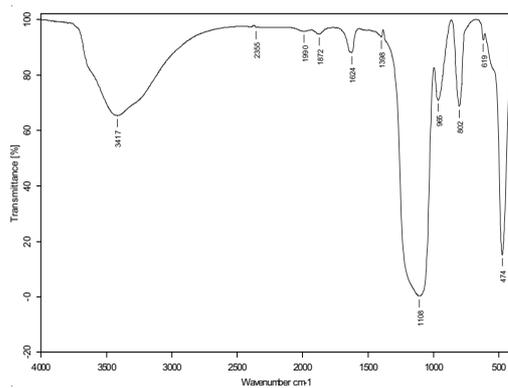


Figure 5. Infrared light spectrogram of SiO2

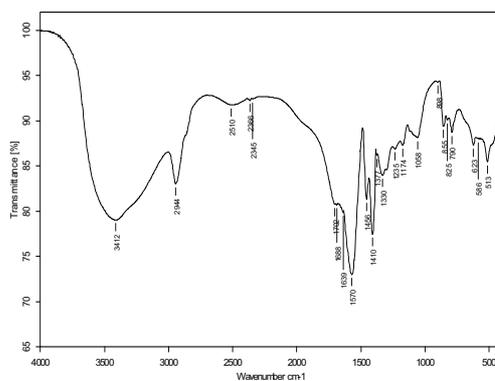


Figure 6. Infrared light spectrogram of SiO2 superficial stem grafting SAP

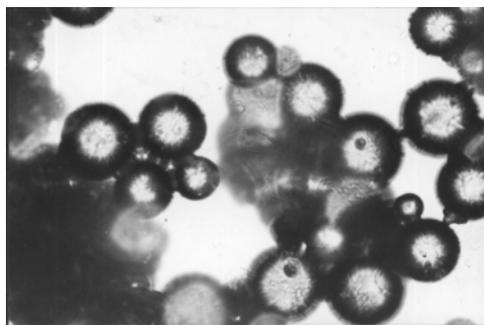


Figure 7. High power microscope chart of SAP by opposition suspension method preparation



Figure 8. Chart after nuclear shell SAP absorbing water



Figure 9. SAP microscope chart by solution polymerization preparation