

Study on the Preparation of Corn Starch Salt-resistant Water Retention Agent and Properties of Retention Agent Combined with Coal Gangue Pottery

Shengjie Fu, Xiaoyu Fang and Yonggang Li¹

¹ College of Chemical Engineering, Qinghai University, Xining 810016, PR China
E-mail: li.yonggang@126.com

Abstract. Environmental protection agent is widely used in agriculture because of its ability to absorb water, water retention and salt resistance. In this study, Qinghai corn starch was used as raw material. A high absorbent resin was prepared using acrylic acid and acrylamide as monomer, N, N-methylene diacrylamide as cross-linking agent and ammonium persulfate as initiator for graft copolymerization. The Optimized experimental conditions as follows: monomer (acrylamide + acrylic) : Qinghai corn starch = 12 (mass ratio), acrylamide content was 12% (wt %). The concentration of the initiator was $a/2$. The absorption rate of the product reached 1548g/g, and the salt absorption rate was 96g/g (0.9 wt% KCl solution). Then on this basis, the water absorption rate of retention agent combined with coal gangue pottery is 1549g/g, and the salt absorption rate is 97g/g. The results showed that the water retention agent not only has good water retention and salt resistance, but also its water retention and salt resistance are not affected by the combination with Coal gangue pottery.

1. Introduction

Corn starch (CS) is considered to be a kind of environmental friendly material because of its low cost, safety and health and good biodegradation performance, often as a graft polymer material to research and product super absorbent polymers [1]. In spite of retention agent of CS showed good water imbibition and begin to be reserached and used widely, its salt resistance didn't get enough attention[2]. The retention agent would be further limited to the use of salinity soil remediation, such as saline-alkali land in Qinghai salt lake area[3]. At the same time, the governance of desertification needs that water retaining agent has a good performance of water keeping and salt resistance, in order to achieve the effect of water imbibition and fertilizer imbibition[4].

Ceramsite has larger specific surface area, relatively stable chemical properties and good adsorption, which ensure the soil is loose and breathable[5]. So ceramsite is widely used in soil improvement [6]. Our lab had done a lot of research on ceramsite preparation of coal gangue of Qinghai Reshui coal industrial park. The coal gangue ceramsite can be used in soil repairing and water retaining and fertilizer keeping[7].

Considering the characteristics of water retention agent and adsorbent pottery. This Study used CS as main material, acrylic acid (AA) and acrylamide (AM) as graft monomer, ammonium persulfate as initiator on graft copolymerization, prepared injectivity resin and test its water retention and salt resistance. In the end, combine the water protection agent with the coal gangue ceramic granule and test combination's water retention and salt resistance.

2. Experimental Part



Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.

2.1. Experimental Materials

Qinghai CS(industrial grade); acrylic acid(AR); acrylamide (AR), ammonium persulphate(AR);N,N-methylene diacrylamide(AR); NaOH(AR).

2.2. Preparation of Retention Agent

2.2.1. Starch gelatinization. Five grams of CS was dissolved in 50 mL distilled water in a 100mL beaker with magnetic stirring at 65°C. Cooled to 20°C after 2 h.

2.2.2. Configuration of monomer solution. Added 43mL of acrylic acid into the 4 mouth flask, 1mol/L NaOH solution was added for partial neutralization. Then, ammonium persulfate was added as initiator. The mixture was stirred for 5mins under nitrogen and then added acrylamide.

2.2.3. Graft copolymerization. Added 0.01 g N,N'-methlenebisacrylamide in the 4 mouth flask under nitrogen. Then, gelatinized starch was added after 5 mins. Until it became a paste of polymerization at 70°C. After standing for 2h, the product was washed with ethanol and deionized water.

2.3. Retention Agent Combined with Coal Gangue Pottery

The coal gangue is prepared in the laboratory (coal gangue is from Qinghai hot water coal industry park). The diameter of the coal gangue is 5-7mm, the accumulation density is 423 kg/m³ and the volume density is 889 kg/m³. Coat the coal gangue ceramic granule with the water protection agent. After drying, the thickness is 3mm, and the ceramic particles are not exposed directly.

2.4. Performance Test of Water Protection Agent

2.4.1. Determination of Water Absorption Rate. Weigh 0.3g water retention agent accurately. Add it to 1kg deionized water in the mixing conditions. Stand for three hours and take out the product after absorbing water. Drain its surface with water absorbent paper and its mass is m_1 . Thus, the water absorption rate of the sample is S_1 (g/g). The calculation formula of water absorption rate [8] is following:

$$S_1 = (m_1 - 0.3) / 0.3 \quad (1)$$

2.4.2. Determination of Salinity Resistance. The salt resistance of water retention agent is the water absorbent capacity in a certain concentration of salt solution. The determination of the salinity is usually using 0.9%(wt) NaCl solution [9]. Considering that the fertilizers used in agriculture mainly include nitrogen fertilizer and potash fertilizer. In this paper, the determination of salt resistance mainly used 0.9% urea solution(Nitrogen-containing non-electrolytes) and 0.9% KCl solution(contains potassium and a valence ion can be electrolyzed).

When measuring the salt resistance, weigh 0.5g water retention agent accurately at first. Then add it to the 500g target concentration of salt solution with mixing. Static 3h to absorb water, then remove the product after expanding. At last, absorb water from its surface with water absorbent paper and its mass is m_2 . The salt absorption rate of the sample is S_2 (g/g). The formula for calculating the salinity resistance of water retention agent [10] is following:

$$S_2 = (m_2 - 0.5) / 0.5 \quad (2)$$

3. Results Discussion

The experimental conditions we chose: The content of AM is 10 wt% of the total (wt), monomer content (AM + AA) :CS= 10, acrylic neutralization is 70 wt%, and initiator concentration is 0.1 wt%(relative to monomer). The single factor variables are discussed .

3.1. Influence of the Content of AM on the Product's Absorbability

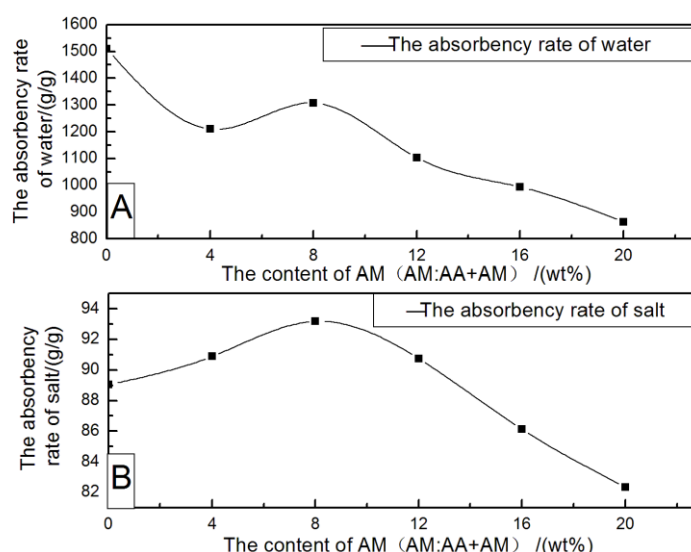


Figure 1. Influence of acrylamide content on the amount of liquid absorbed.

According to Figure 1, when AM accounted for 0% to 8%, product's salt absorption rate increases with the increase of the mass ratio. Bibulous rate drops in AM content from 0% to 4%, increases at 4 to 8% range. When the content of AM exceeds 8%, the absorption rate of the product decreases with the increase of mass ratio.

When AM is 4%, the water absorption rate decreases. Because the addition of AM reduces the hydrogen bonds formed with water and carboxyl. When the content of AM increases to 8%, the water absorption rate and salt absorption rate become higher. It is due to the synergistic effect of a certain number of different hydrophilic groups on the large molecular chain. Since $-\text{CONH}_2$ is a non-ionic group, the degree of dissociation in water is small and the influence of ions is small. Therefore, the introduction of nonionic monomers enhances resin's anti-electrolyte ability and the salt absorption rate of the product. But there is a moderate amount of it[11]. When dosage more than 8%, due to the hydrophilicity of $-\text{CONH}_2$ is not as good as $-\text{COOH}$, excessive dosage leads to water absorbent and electrolyte resistance decreases. Thus it can be seen that a mixture of different hydrophilic groups in the appropriate copolymerization is one of the effective ways to improve the ability of water-absorbing resin to resist salt. [12]

3.2. Influence of the Initiator Concentration on the Absorption Rate of the Product

As shown in Figure 2, with the increase of the trigger dose. The product absorption rate rises at first and there is the peak around $a(a=1/1200)$. Then the absorbent rate shows a decreasing trend when the initiator concentration was greater than a .

When the dosage of initiator is low, the number of grafted active centers generated on the starch skeleton is correspondingly less, the polymerization rate is slow and the crosslinking degree is not enough, the absorbability performance is not good. However, when the dosage is large enough, it can improve the polymerization speed. But at the same time, it also increases the chance of the chain termination, and the monomer has more chance to increase which means the absorption performance is reduced. The test results show that the absorbent rate reaches its peak when the initiator concentration is a . [13]

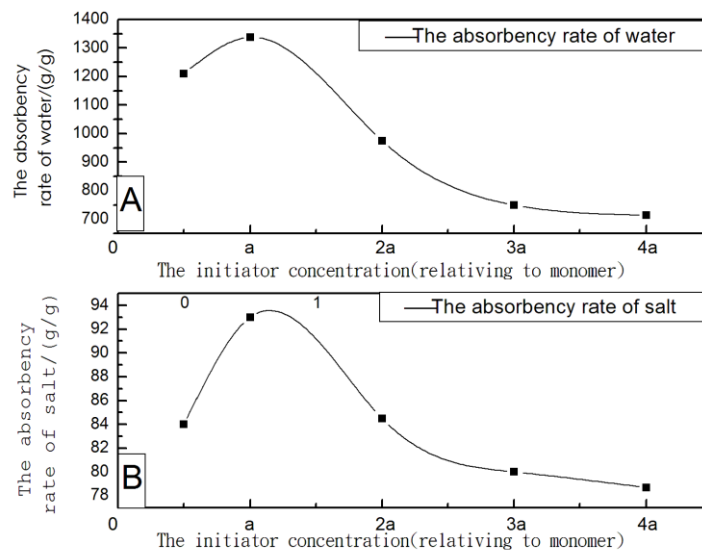


Figure 2. Relationship between the concentration of initiator and the amount of product absorbent ($a = 1/1200$).

3.3. Influence of the Neutralization of Acrylic Acid on Product Performance

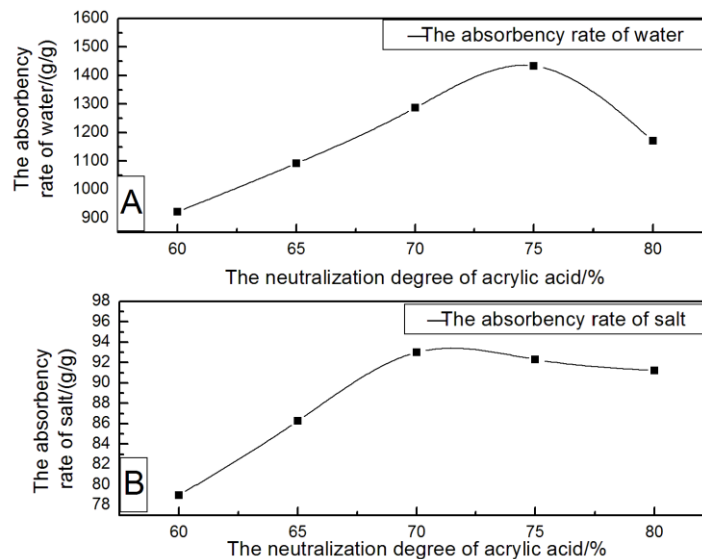


Figure 3. The effect of acrylic neutralization on product performance.

As shown in Figure 3, when the AA neutralization (Dn) is 75%, the absorption rate shows the upward trend. And at Dn=75%, the absorption rate reaches its peak. When the Dn is low, the -COO content is low, but the -COOH content is high. At the same time, the reaction is intense, and it is easy to form the highly crosslinked polymers. The concentration of ions in the structure of the polymer network is small, and the permeability of the polymer network is low, which leads to the low absorption rate. When the Dn is larger than 75%, the degree of cross-linking is decreased on the one hand and the

strong hydrophilic -COO is increased on the other hand with the increase of Dn. It makes the increase of the inner osmosis pressure in the crosslinking network, which leads to the increase of the absorption rate. However, when the Dn is too high, the reactants are less interrelated and the product crosslinking is weaker, high content of the coo-content can also increase the waterborne of the resins. So the absorption rate shows a downward trend. [14]

3.4. Influence of Monomer and Qinghai Corn Starch Ratio on Product Performance

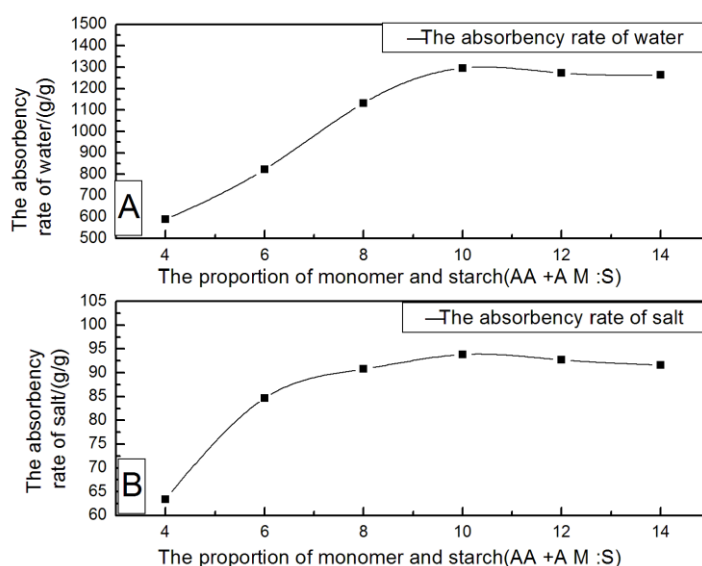


Figure 4. The effects of the monomer and starch ratio (AA + A M: S) on product performance.

Figure 4 is the relationship between AA + AM: S(w t) and product absorption rate. When AA + AM: S < 10, the absorption rate increases with AA + AM: S. When the mass ratio is 10, the absorbant rate reaches its peak. Starch is used as grafting skeleton in polymer, but it does not absorb water better. The starch content is too high which makes the grafting side chain is short, the network structure is small and the absorption rate is low. But as AA + AM: S ratio increases, starch content is not enough. When AA + AM: S > 10, the absorption rate of the product has decreased due to the increase probability of the monomer and the increase of the crosslinking degree of the graft side. [15]

3.5. Process Condition Optimization

In order to get the water retention agent with better salt resistance, we analyzed the single factor experimental results. Results show that when AM content at about 8%, initiator concentration between $a/2$ and $2a$, acrylic acid neutralization degree at around 75% and AA + AM: CS at around 10, the salt absorption rate water retention agent is highest. According to the above, the factors of orthogonal test are determined in Table 1.

Table 1. Factor levels

Factor	Content of AM (wt%)	Concentration of initiator (relative to monomer)	Neutralization of acrylic (%)	AA+AM :CS
Level 1	7	$a/2$	64	9
Level 2	9	a	70	11
Level 3	11	$2a/3$	76	13
Level 4	13	$2a$	82	15

The results of the orthogonal test are: when AM content is 12 %, initiator concentration is $a/2$, AA neutralization degree is 80 %, AA + AM: CS= 12, the product has better anti-salt performance. The absorption rate is 1548g/g, and the salt absorption rate is 96g/g. Dang Jing and her team[16] used corn starch as material, acrylic acid as monomer for grafting copolymerization to the water absorbent resin preparation. The water absorption rate is 730g/g, and they have no salt-resistant analysis. Comparing our preparation with theirs, the water absorption rate of the product was increased by 818g/g, and the salt resistance reached 96g/g.

3.6. Properties of Water Retention Agent and Its Using with Coal Gangue Pottery

By orthogonal experiment to obtain better formula to test the resistance to salt water retention agent. As shown in Table 2, the non-electrolyte urea has no influence on the salt resistance. But the electrolyte solution leads to a decrease in water absorbent capacity.

The data in the Table 1 prove that the water retention agent and the salinity resistance of the pellet are unchanged. Because of the simple adsorption of the clay, the amount of adsorption is very small and has no direct effect on the water retention agent. What's more, because the clay is porous inside, there is a certain adsorption to the plant's desired nutrients such as nitrogen and potassium fertilizer. Thus the water retention agent combined with coal gangue are in line with the agriculture's and forestry's actual needs.

Table 2. Water absorption rate and salt rate measurement data

Absorption medium	DI	Urea	KCl solution
Absorbent rate of water retention agent/(g/g)	1548	1481	96
Absorbent rate of water retention agent combined with Coal gangue pottery/(g/g)	1549	1484	97

4. Conclusion

This work used Qinghai corn starch as the raw material, grafted acrylic acid and acrylamide for the preparation of water retention agent with good salt resistance. The optimized process is: AM content is 12 %, initiator concentration is $a/2$, AA neutralization degree is 80 %, AA + AM: CS= 12, the product has better anti-salt performance. The absorption rate is 1548g/g, and the salt absorption rate is 96g/g. The water absorbent rate reaches 1549g/g and the salt absorption rate is 97g/g after the water protection agent and the coal gangue are used together. At this time, the water retention ability and the ability to resist salt are not affected. In summary, it is of practical value that the water retaining agent uses together with the ceramic grain.

5. Reference

- [1] Ying Ma, Jinlong Zhang. Current situation and development goals of corn processing industry [J]. *Heilongjiang grain and oil technology*, 2001,(02):10-13.
- [2] An overview of the prevention and improvement of saline alkali land in the northwest region [J]. *Xinjiang agricultural science*, 1962,(08):295-296.
- [3] Mingli Li, Yun Tong, Fang Li, Shunrong Yang. Development status and research progress of ceramic-clay concrete [J]. *Concrete world*, 2010,(09):16-18.
- [4] Ming Zhou, Wanfen Pu, Yan yang . Optimization of the synthesis conditions of high-absorbent resin for anti-salt starch grafts [J]. *Petrochemical*, 2003,(04):314-316.
- [5] Wang rui, Li qian, Qinyan Yue, Nana Peng, Baoyu Gao, Wang yan. Preparation of wheat straw/modified bentonite based high absorbent resin [J]. *Journal of shandong university*, 2014, 42(06):115-120.
- [6] party jing, wang rumin, wang xiaojian, cheng lei. Preparation and performance of corn starch grafting acrylic acid high absorbent resin [J]. *China adhesive*, 2009,18(04):45-48.
- [7] guo self-hua. Research on high absorbent resin [J]. *Science and technology information*, 2009,(01):2.
- [8] LI Zongjin, ZHU Ding. Property Improvement of Portland Cement by Incorporating with Metakaolin and Slag[J]. *Cement and Concrete Research*, 2003, 33:579-584

- [9] Z.Zhang, P.Chen, X.F. Du. et al. Effects of amylose content on prop-erty and microstructure of starch- graft- sodium acrylate copolymers[J].*Carbohydrate Polymers*,2014,102,453- 459.
- [10] L.Huang, C.M. Xiao, B.X. Chen. A novel starch- based adsorbent for removing toxic Hg (II) and Pb (II) ions from aqueous solution[J]. *Journal of Hazardous Materials*,2011,192,823- 826.
- [11] Asaka H,Yada A,Saeki S. Absorbents for salt — containing water: JP ,8016 016 [P] . 1980 — 02 — 04.
- [12] D D Vu, P Stroeven, V B Bui. Strength and Durability Aspects of Calcined Kaolin-blended Portland Cement Mortar and Concrete[J]. *Cement and Concrete Composites*, 2001,23:471-478
- [13] Prinya Chindaprasirt, Chai Jaturapitakkul, Theerawat Sinsiri. Effect of Fly Ash Fineness on Compressive Strength and Pore Size of Blended Cement Paste[J]. *Cement and Concrete Composites*, 2005,27: 425-428
- [14] KIATKAMJORNWONG S,CHOMSAKSAKUL W,SONSUK M. Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide[J]. *Radiation Physics and Chemistry*,2000,59 (4) :413-427.
- [15] BHUNIYA S P,RAHMAN M S,SATYANAND A J,et al. Novel route to synthesis of allyl starch and biodegradable hydrogel by copolymerizing allyl -modified starch with methacrylic acid and acrylamide[J]. *Journal of Polymer Science:Part A: Polymer Chemistry*,2003,41 (11) :1 650-1 658.
- [16] J.R. Witono, I.W. Noordergraaf, H.J. Heeres, et al. Water absorp-tion, retention and the swelling characteristics of cassava starch grafted with polyacrylic acid [J] . *Carbohydrate Polymers*,2014,102, 453- 459.

Acknowledgments

This work was supported by the “Chunhui Plan” of Ministry of Education PRC (z2016096) and the “Principal Cup” innovation entrepreneurship incubation project of Qinghai University (2017-xzb-05k)