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Preparation of Anionic Polyacrylamide-Grafted Starch Flocculant and Its Application

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Key words: anionic polyacrylamide, flocculant, coal slurry wastewater, starch, graft.

Abstract. An anionic polyacrylamide-grafted starch (St-g-APAM) flocculant for the coal slurry waste water, was prepared by using corn starch and acrylamide (AM) as monomers, acrylic acid (AA) as anionic monomer through solution polymerization. The effects of initiator concentration, reaction temperature, and monomer concentration on percentage of grafting and the grafting efficiency were investigated. The results show that the optimal conditions of the polymerization are as follows: the monomer to substrate ratio of 2.0, AM:AA ratio of 2:1, potassium persulfate of 0.7 x 10^{-3} mol/L, reaction time of 4h, the reaction temperature of 50°C. The additional dosage of St-g-APAM is varying between 10 and 20 mg/L to obtain good flocculation capability.

Introduction

Flocculation is a means of removing organic and inorganic contaminants from wastewater and involves the aggregation of dispersed particles into larger flocs that can be separated from the water [1]. Now, a wide range of flocculants are extensively used in various industries [2]. According to the composition they can be divided into two categories, organic and inorganic flocculants. Both organic and inorganic flocculants are used in various kinds of flocculation phenomena [3-5]. Inorganic flocculants are inexpensive, but less effective. The organic flocculants are essentially polymeric in nature. Synthetic polymers are very efficient flocculants. However, they cause environmental problems that they are not readily biodegradable and some of their degraded monomers such as acrylamides (AMs) are neurotoxic and even show strong human carcinogenic potential [6]. To solve these problems, substitutes of natural polymers, such as starch, chitosan, cellulose, and so on have been investigated as an attractive alternative because natural polymers and their derivatives are biodegradable as well as their degradation intermediates are harmless to human beings and environment.

Starch is one of the most abundant natural polymers in the world, and as an important derivative of starch flocculant, anionic polyacrylamide-grafted starch (St-g-APAM) were prepared conventionally by two-step method, firstly grafting AM to starch, and then adding formaldehyde and dimethylamine through Mannich reaction, which is complicated and not environmental friendly [7-9].

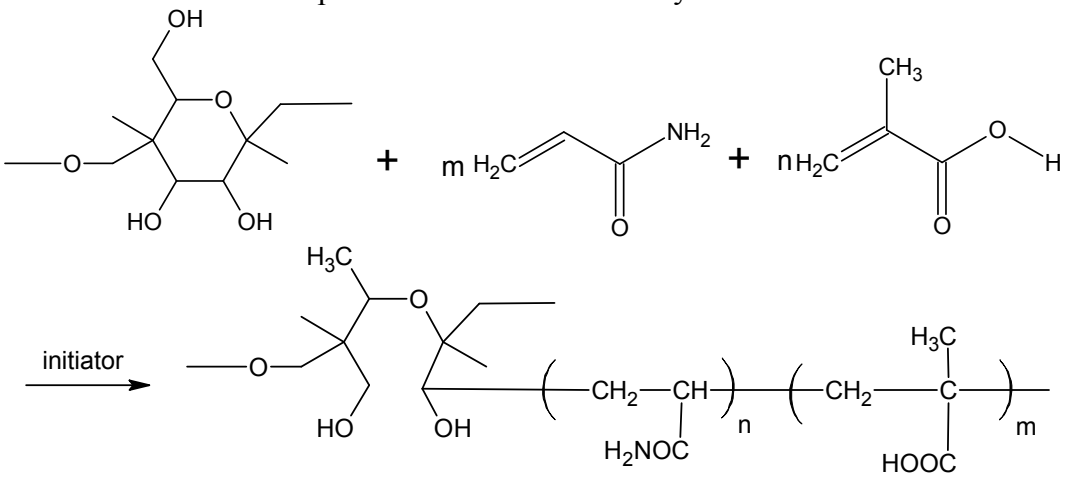
In this article, the starch was introduced into the flocculant because of its biodegradable property and relatively low price. St-g-APAM was prepared by one-step reaction with AA as anionic monomer, which can avoid the toxicity of the formaldehyde. The application in the treatment of coal slurry wastewater was discussed.

Experimental Chemicals

Acrylamide (AM), acrylic acid (AA), potassium persulfate, hydrochloric acid, sodium hydroxide, acetone, acetic acid glycol, and sodium hydroxide were supplied by Beijing Chemical Plant (China). Corn starch was obtained from Simeite Food, China.

Preparation of St-g-APAM Flocculant

The reaction was carried out in a 250-mL four-necked round-bottom flask equipped with a stirrer, a thermometer, a condenser, and nitrogen gas inlet. The flask was heated in a thermostatic water bath. Corn starch and 50-mL deionized water was poured into the flask and preheated for 50 min at 85°C. After the starch was gelatinized (starch slurry turned to a transparent solution), the flask contents were cooled to 40°C. Then, AM, acrylic acid, and a red-ox initiator (ammonium persulfate-urea) were added, and the mixture was allowed to react for 2-6 h at 55°C under N_2 protection. The product was washed with 200 mL acetone after dried and crushed. The crude product was obtained. Then, the crude product was washed three times with the solution of glacial acetic acid and ethylene glycol with a ratio of 40:60. The refined final product was obtained. The synthetic reaction is shown in Scheme 1.



Scheme 1 The synthetic reaction of St-g-APAM.

FT-IR Analysis

The chemical structure of the St-g-APAM flocculant was characterized by KBr disc method with a NEXUS-470 FTIR (Nicolet) spectrophotometer.

Flocculation Testing

Coal slurry of 30 g and water of 0.5 L were added to a 0.5-L beaker. First, the solution was stirred for 15 min by a mechanical stirrer at a fast speed of 300 rpm/min, then the speed was adjusted to 120 rpm/min. The flocculants were added and stirred for 1 min, which would mix the flocculants and generate a small flocculation. Finally, it was stirred for 5 min at a low speed of 40 rpm/min, to promote the growth of flocculation; the upper clear liquid was taken out after standing for 15 min, then its percentage transmittance (T%) was measured at 550 nm by using a spectrophotometer (model number 722, Shanghai Precise Instrument Plant, China).

Results and Discussion

IR Spectra of APAM. The FTIR spectra of St-g-APAM is shown in Fig. 1. The broad band at 770 cm-1 is due to the stretching mode of the glucose ring. The intense and broad peak at 1024-1052 cm-1 is assigned to glucose ring of C-O stretching. Two peaks at 1400 and 2920 cm-1 are corresponding to the characteristic absorption of C-C and -CH2-, respectively. The peak at 3300 cm-1 is due to -OH stretching vibration. The peak of 1720 cm-1 is attributed to carboxyl, which is connected to the -COOH, which is a strong evidence of incorporation of an anionic moiety onto the backbone of the starch.

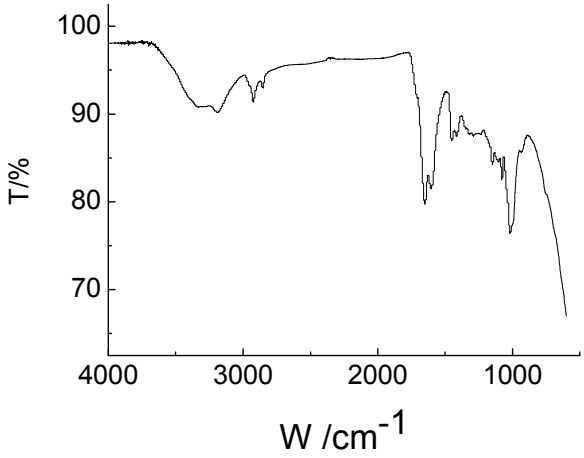


Fig. 1 FT-IR spectrum of the St-g-APAM

Effect of Different Doctors on Grafting Parameters

Monomer. The effect of the monomer to substrate ratio on grafting parameters is shown in Fig. 2. It shows that PG and GE increase with the monomer to substrate ratio when it is less than 2.0. However, they all show decreasing trends when the monomer to substrate ratio is more than 2.0. The average number of free radicals increases with the monomer concentration which can increase them. However, when the total monomer mass increases to a certain value, the polymerization rate is accelerated and the residue monomer increases, which can result the decrease of PG and GE. The highest value of PG and GE appear at the monomer to substrate ratio 2.0.

Monomer Ratio. PG and GE increase with the amount of AM is shown in Fig. 3. The reactivity of AM is much higher than AA, therefore, the higher is the content of AM, the higher PG and GE are. But the anionic degree will decrease with the amount of AM. PG and GE reach their highest values at the AM: AA ratio of 2:1.

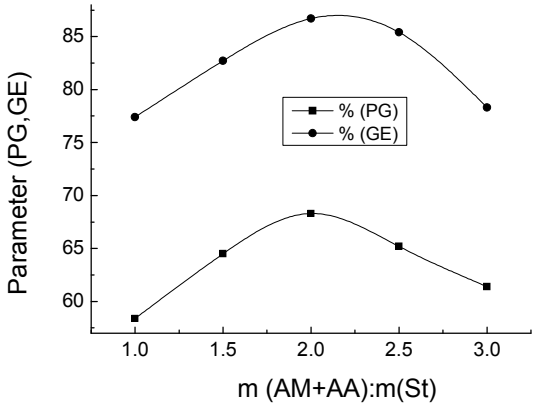


Fig. 2 Effect of the monomer to substrate ratio on grafting parameters.

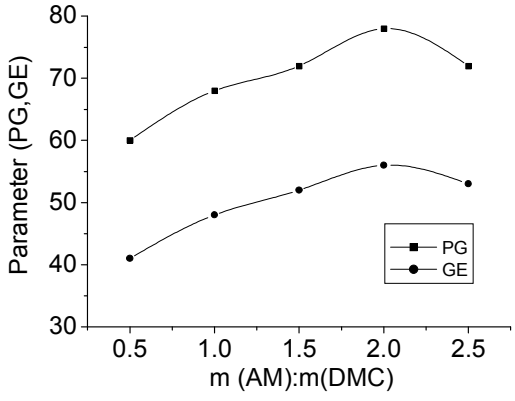


Fig. 3 Effect of monomer ratio on grafting parameters.

Initiator Concentration. The effect of potassium persulfate on grafting reaction is shown in Fig. 4. The reaction has not been observed when the potassium persulfate is 0.1 x 10-3 mol/L. It is suggested the radical initiator is locked inside a cage when it is very less, which may cause side reaction and consume the initiator. This phenomenon is called “cage effect”. When the initiator increases, the radical initiator is sufficient enough to come out from the cage to initiate the grafting process, and therefore, PG and GE increase with the initiator. When the potassium persulfate is 0.7 x 10-3 mol/L, the grafting reaction reaches its maximal point with PG and GE values of 75 and 88%, respectively.

Temperature. PG and GE firstly increase and then decrease with reaction temperature is shown in Fig. 5. It is suggested the thermal motion of the molecules increases with the increase of the temperature, and more free radicals will be formed, and hence, the chain growth will be accelerated, resulting a higher PG and GE. But when the temperature exceeds 50°C, molecular chains of St-g-APAM may be broken, the chain transfer and chain termination of the reaction and polymerization rate also increase, which causes a obvious drop of GE at 55°C. So 50°C has been regarded as the optimal reaction temperature and has been used in following discussion.

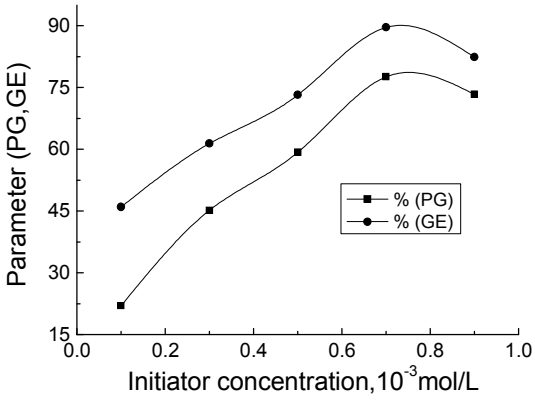


Fig. 4 Effect of potassium persulfate on grafting parameters.

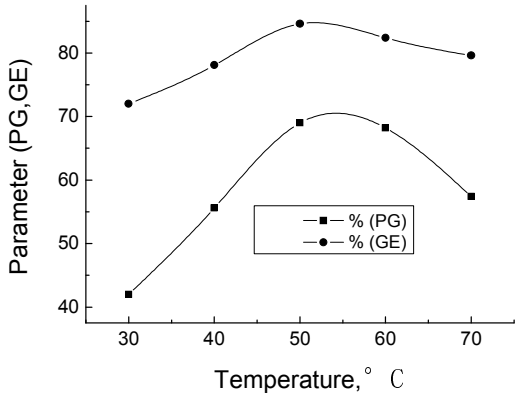


Fig. 5 Effect of reaction temperature on grafting parameters.

Time. The effect of reaction time on grafting was observed in Fig. 6. As it can be seen in Fig. 8, with the reaction time, the T% much increased before 4h, then increased slowly. It is suggested that the concentration of monomer became less and less after 4h with the polymerization. So the optimum reaction time is 4h.

Flocculation Characteristics of St-g-APAM. Flocculation performance of St-g-APAM is shown in Fig. 7. As it can be seen in Fig. 7, with the increase of St-g-APAM, the T% increased. When the dosage of St-g-APAM was 15 mg/L, T% reached the highest. However, T% would descend if St-g-APAM dosage continued to increase. Because of less flocculant dosage, its ability of electricity and adsorption bridging got to be enhanced. With the dosage increasing, the capacity of adsorption started to increase. Nevertheless, the adsorbed particles would be wrapped by the excessive polymer flocculant, so that they could not coagulate but dispersed when the dosage used was excessive. The results of experiments show that when the additional dosage of St-g-APAM is varying between 10 and 20 mg/L, floccules are coarse, and subsidence velocity is fast, and water quality is good.

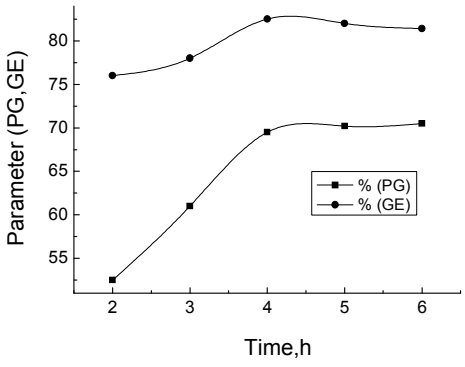


Fig. 6 Effect of reaction time on grafting parameters.

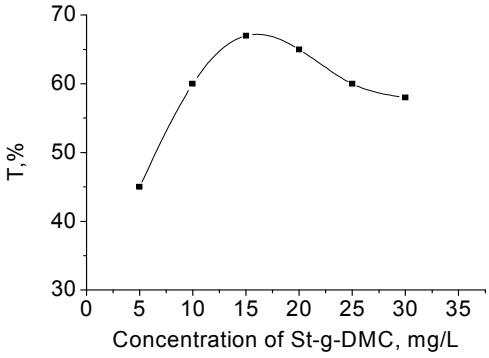


Fig. 7 Flocculation performance of St-g-APAM

Conclusions

St-g-APAM can be synthesized by AM, AA, and starch with only one-step reaction. The PG and GE of the St-g-APAM are affected by temperature, the ratio of monomer and starch, the ratio of AM and AA, the initiator concentration, reaction time of 4h, and the reaction temperature. The PG and GE of St-g-APAM can reach 56% and 78%, respectively, under optimal conditions. The optimal conditions of the polymerization are as follows: the monomer to substrate ratio of 2.0, AM:AA ratio of 2:1, potassium persulfate of 0.7 x 10-3 mol/L, reaction time of 4h, the reaction temperature of 50°C. The additional dosage of St-g-APAM is varying between 10 and 20 mg/L to obtain good flocculation capability.

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References

[1] Q. Chang, X. Hao, L. J Duan: Hazard Mater, Vol. 159 (2008), p.548.

[2] J.D. Swift, K. Simic, P.D. Fawell: Int JMin Process 2004, Vol. 73 (2004), p.103.

[3] S. Duzyol, A. Ozkan: Sep Purif Technol, Vol. 72(2010), p.7.

[4] V. K.Tyagi, Abid A.Khan, A. A. Kazmi, A. K. Chopra: Sep Sci Technol, Vol. 45(2010), p.626.

[5] M.Guida, M.Mattei, C. D.Rocca, G. Melluso, S. Meric: Desalination, Vol. 211(2007), p.113.

[6] I. L.Shih, Y. T.Van, L. C.Yeh, H. G.Lin, Y. N. Chang: Bioresour Technol, Vol. 78(2001), p.267.

[7] X. X.Guo, F. Z. Shu, Z. J.Ben, Z. Y. Jin: Starch/Starke, Vol. 58(2006), p.464.

[8] A. N. Jyothia, K. N.Rajasekharanb, S. N. J. Moorthya: Starch/Stake, Vol. 57(2005), p.556.

[9] R. Nystrom, K.Backfolk, J. B. Rosenholm: Physicochem Eng Aspects, Vol. 219(2003), p.55.