

## Flocculation behavior of cationic pea starch prepared by the graft copolymerization of acrylamide for wastewater treatment

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**ABSTRACT:** To improve the flocculation efficiency of coal mine wastewater treatment, we synthesized a cationic flocculant by grafting acrylamide (AM) onto pea starch, and we performed the characterization with elemental analysis, Fourier transform infrared spectrometry, scanning electron microscopy, thermogravimetric analysis, and NMR. The effects of the synthesis conditions were also investigated, and the optimal synthesis parameters of the cationic flocculant were obtained. The mass ratio between pea starch and AM was 0.5 with a reaction temperature of 65 °C. The dosages of ceric ammonium nitrate and 3-chloro-2-hydroxypropyl-trimethylammonium chloride were 0.02 and 0.11 mol/L, respectively. Application experiments for wastewater treatment were carried out consequently, and the optimal dosage of cationic pea starch was 40 mg/L within the pH range 6–8. Compared with other traditional flocculation products, the cationic pea starch showed the best flocculation behavior for coal mine wastewater. Therefore, the cationic pea-starch-grafted AM may be applicable as a novel flocculant in wastewater treatment and has already demonstrated outstanding features. It is bound to replace other traditional flocculants in the future. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43922.

**KEYWORDS:** biodegradable; copolymers; degradation; functionalization of polymers; synthesis and processing

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### INTRODUCTION

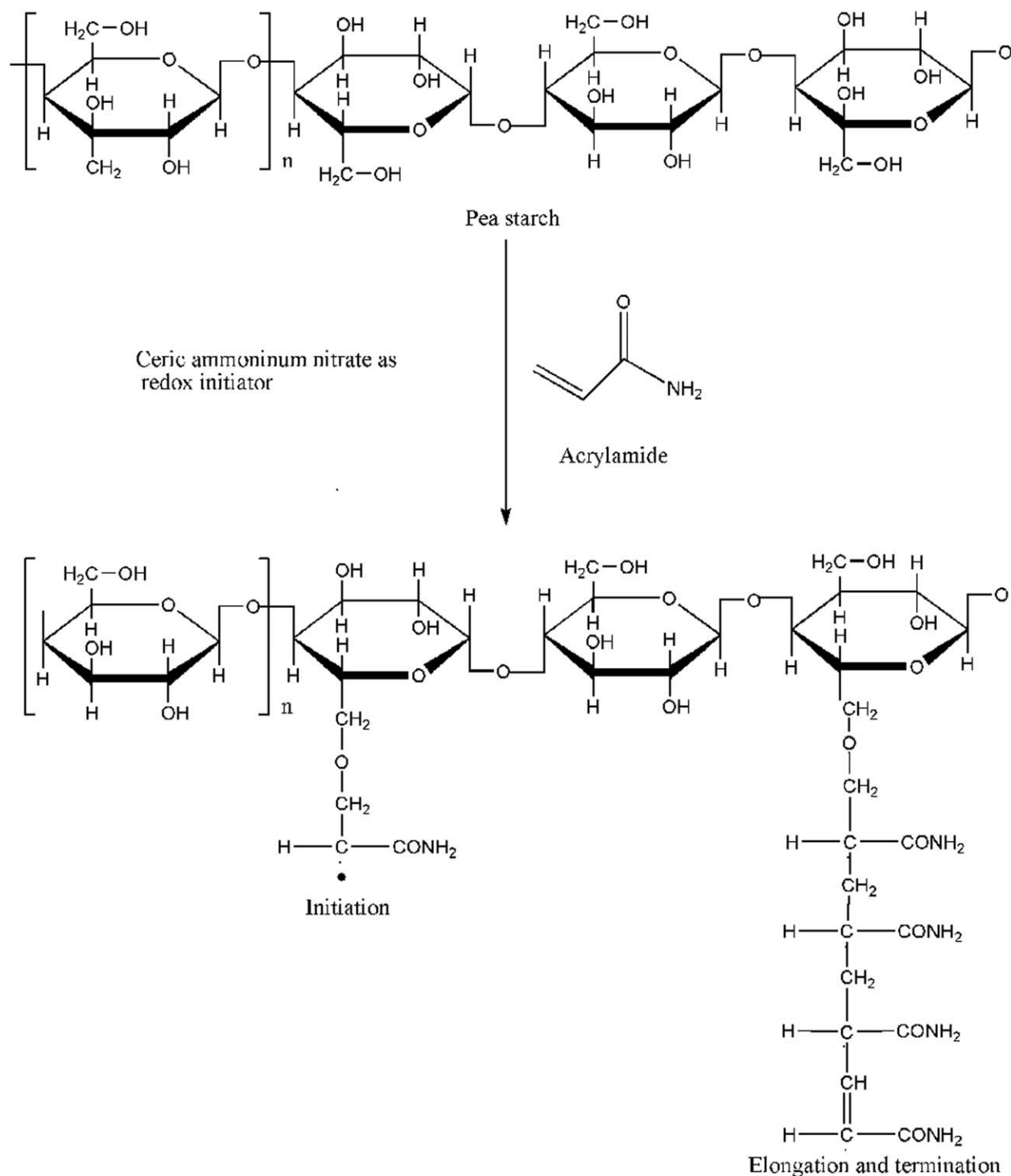
With the development of the coal chemical industry, massive quantities of freshwater turn into sewage water, and this can cause serious environmental problems.<sup>1–5</sup> According to government reports,<sup>6</sup> the total emissions of industrial wastewater in China amounted to 69.5 billion tons in 2013. Nowadays, people pay more attention to sewage disposal because of global environmental awareness and the severe implementation of sustainable development strategies. Flocculation is an efficient and economic technology for water purification, and the process of chemical flocculation is widely used to treat sewage water.<sup>7–11</sup> Flocculating agents basically include inorganic flocculants and organic flocculants.<sup>12–14</sup> Conventional inorganic flocculants, such as ferric salt, aluminum salt, and poly aluminum chloride (PAC), are slightly toxic and chronically remain inaccessible to degradation or decomposition.<sup>15</sup> Moreover, these flocculants can produce a large amount of sludge and residue during the treatment process; this tends to decrease the flocculation efficiency and also causes secondary pollution.<sup>16,17</sup> The other kind of flocculant is organic flocculants, for instance, polyacrylamide (PAM), and include natural or synthetic organic polymer flocculants. Because of the slow settling velocity and unstable floc of natural polymers, synthetic polymers contain more active

functional groups and stronger adsorption abilities, and their flocculation features for wastewater treatment have already been demonstrated.<sup>18–20</sup> However, the efficiency and application effects of most synthetic flocculants have proven to be disappointing. Nowadays, many new synthetic flocculants have been copolymerized by different starches, including potato, rice, maize, tapioca, and pea starches; these flocculants have distinctive features, including a high efficiency, biodegradability, biocompatibility, and low cost. Peas are planted extensively and have a significant amylose content, which tends to enhance the crosslinking effect on colloidal particles in wastewater.<sup>21</sup> Thus, the use of starch-grafted polyacrylamide (St-g-PAM) for wastewater treatment, especially with pea starch, was investigated in this study.

### EXPERIMENTAL

#### Materials and Equipment

The following reagents were used in this experiment: pea starch (Chengdu Yangtian Food Co., Ltd.), acrylamide (AM; Xi'an Chemical Reagent Factory), ceric ammonium nitrate (CAN; Sinopharm Chemical Reagent Co., Ltd.), 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC; Tokyo chemical industry Co., Ltd.), NaOH and ethanol (Tianjin



**Figure 1.** Mechanism and method for the St-g-PAM copolymerization.

Chemical Reagent Co., Ltd.), and acetone and glacial acetic acid (Sinopharm Chemical Reagent).

The equipment used for the sample analysis was as follows: NMR instruments (liquid-phase AV 400 MHz and solid-phase

AV 600 MHz, Germany Bruker Optics, Inc.), a scanning electron microscope (EVO MA10, Germany Zeiss, Inc.), an elemental analyzer (Vario Macro Cube, Germany Element, Inc.), a Fourier transform infrared (FTIR) spectrometer (Vertex 7.0,

**Table I.** EA Results

Item	C (%)	H (%)	N (%)
AM	50.720	7.150	19.580
Pea starch	39.190	5.473	0.033
New flocculant	41.530	6.825	10.870

Germany Bruker Optics), a thermogravimetric analyzer (SDT-Q600, TA Instruments), and a visible-infrared spectrometer (VIS-7220, Beijing Rayleigh Analytical Instrument Co., Ltd.). Other apparatuses for the preparation of flocculant included an electronic balance (JM-B2003, China Yuyao Jiming Check Equipment, Inc.), an IR fast dryer (GZX-GF101, Shanghai Yaojin Medical Apparatus Co.), and an electric mixer (JJ-1, Changzhou Guohua Electrical Appliance Co., Ltd.).

#### Sample Preparation of the Starch-Made Flocculant

Starch (5 g) and anhydrous ethyl alcohol (100 mL) were added to a 500-mL, three-necked flask equipped with a polytetrafluoroethylene blender, reflux condenser, and CO<sub>2</sub> conduit. The starch and anhydrous ethyl alcohol were stirred under a CO<sub>2</sub> atmosphere in a water bath at 65 °C for 1 h. Then, the obtained gelatinized starch was mixed with AM and CAN and kept stirring to form a reaction mixture for a desired time under CO<sub>2</sub> protection; the reaction mechanism and synthetic route are presented in Figure 1. Thereafter, CHPTAC was used as a cationic etherification agent in the reaction mixtures, and the starch-made flocculant products were eventually achieved after the mixtures were dried and pulverized.

The purification of starch-made flocculant was carried out by the following procedures. First, the product was washed with 200 mL of acetone and was then smashed into powder after drying to produce the crude product of the flocculant. Next, the crude product was refluxed in a Soxhlet extractor for 12 h with a mixed solvent of glacial acetic acid and ethylene glycol (2:3 v/v); this was called the Varma method, and it could remove the unreacted AM or PAM from the crude product.<sup>22</sup> Eventually, the purified product of the copolymer flocculant was dried and pulverized again into powder, which would be used as the flocculant samples for further experimental investigation.

#### Evaluation of the Grafting Efficiency (GE)

GE was calculated with the following equation:

$$GE = \frac{M_g}{M_t} \times 100\% \quad (1)$$

where  $M_g$  is the quantity of purified St-g-PAM (g) and  $M_t$  is the total quantity of the mixture after the reaction (g).

#### Characterization

The elemental analysis (EA) of the starch, AM, and new flocculant (pea-starch-grafted AM) sample was conducted with a Vario Macro Cube analyzer, and the elemental contents of carbon, hydrogen, and nitrogen were calculated. FTIR spectroscopy was used to characterize the chemical structures of the pea starch, AM, and new flocculant samples by the KBr disc method. Scanning electron microscopy (SEM) was conducted to investigate the surface morphology of the mentioned samples.

Thermogravimetric analysis (TGA) was applied to measure the thermal stability of the samples at a heating rate of 10 °C/min under a nitrogen atmosphere. The <sup>1</sup>H-NMR spectrum of the new flocculant was recorded with deuterium oxide (D<sub>2</sub>O) as the solvent. The cross-polarization/magic angle spinning (CP/MAS) <sup>13</sup>C-NMR images were detected with 4-mm MAS probe at a spinning rate of 14 kHz and a resonance frequency of 150.9 MHz. A contact time of 2 ms, a recycle delay of 5 s, and 4000 accumulations were also used for the <sup>1</sup>H-<sup>13</sup>C CP/MAS measurements, and the chemical shifts of <sup>13</sup>C were externally referenced to tetramethylsilane.

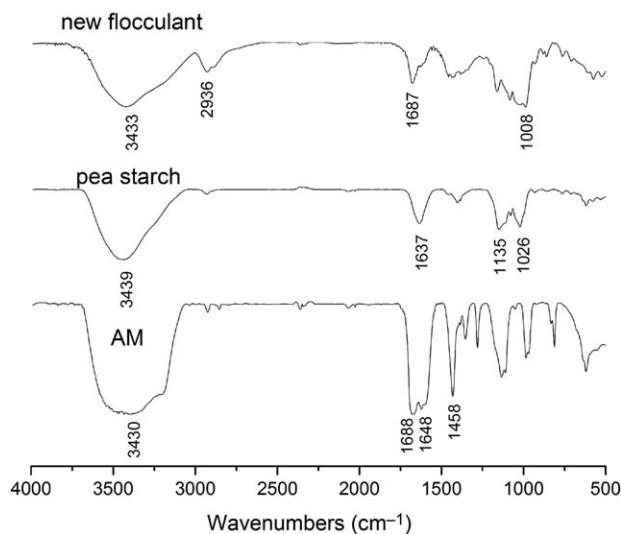
#### Flocculability Testing

A certain amount of flocculant was introduced into a 50-mL beaker filled with coal mine wastewater and stirred for 1 min, and then, the upper clear liquid was separated after 15 min of sedimentation; the transmittance of this liquid was measured with a spectrophotometer at a wavelength of 610 nm. The coal mine wastewater samples were provided by Shanxi Ximing Coal Group Co., Ltd., and had specific parameters as follows: pH = 7.5, turbid degree = 4750 NTU, chemical oxygen demand (COD) = 85 mg/L, suspended substance (SS) = 1050 mg/L, iron ion content = 8.98 mg/L, and manganese ion content = 7.75 mg/L.

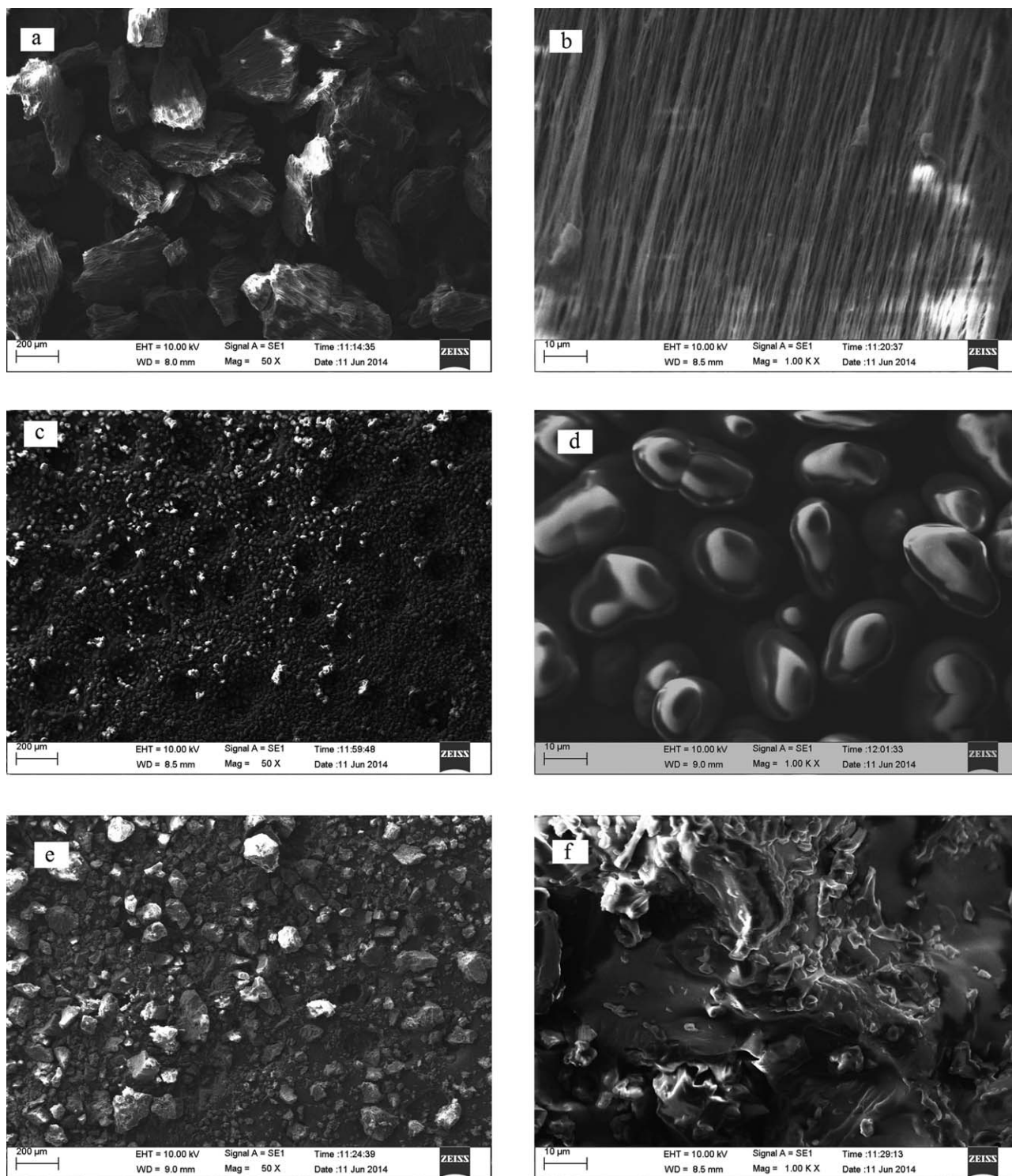
## RESULTS AND DISCUSSION

### EA

The EA results of the pea starch, AM, and new flocculant (copolymer of pea starch grafted to AM) are given in Table I. It is apparent from the table that the C, H, and N contents of the new flocculant were between those of AM and pea starch. A significant increase in the percentage of nitrogen in the new flocculant confirmed the successful grafting of AM onto the backbone of the pea starch,<sup>23</sup> and this was strong proof that the copolymerization occurred. We concluded from Table I that AM actually grafted onto the pea starch during the copolymerization and produced the new flocculant with specific features and performances.



**Figure 2.** FTIR spectra of the AM, pea starch, and new flocculant.



**Figure 3.** SEM photographs of (a) AM (50 $\times$ ), (b) AM (1000 $\times$ ), (c) styrene (50 $\times$ ), (d) styrene (1000 $\times$ ), (e) St-g-PAM (50 $\times$ ), and (f) St-g-PAM (1000 $\times$ ).

### FTIR Spectrometry Analysis

The FTIR spectra were detected to obtain the characteristic functional groups of the pea starch, AM, and new flocculant, as shown in Figure 2. We observed from the figure that the pea starch revealed a broad peak at  $3439\text{ cm}^{-1}$ , which was due to the stretching vibrations of O—H.<sup>18</sup> The peaks at 1637 and

$1026\text{--}1135\text{ cm}^{-1}$  corresponded to the characteristic absorptions of C—O and C—O—C, respectively.<sup>20,24</sup> In the AM spectrum, the strong absorption peak at  $3430\text{ cm}^{-1}$  was attributed to the N—H stretching vibrations of the primary amide. The bands at 1688, 1648, and  $1458\text{ cm}^{-1}$  represented the stretching vibrations of C=O, C=C, and —CH<sub>2</sub>, respectively.<sup>25</sup>

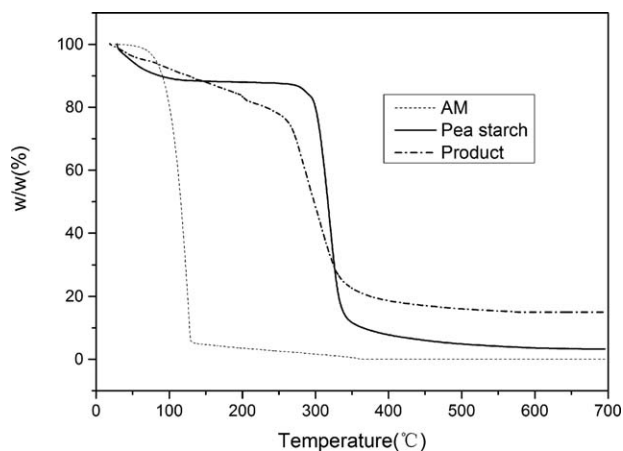


Figure 4. TGA curves of the AM, pea starch, and St-g-PAM.

Apparently, the spectrum of the new flocculant showed a few notable differences compared with the pea starch and AM. The O—H stretching band of the pea starch backbone and the N—H stretching band of the PAM chains overlapped each other, and this led to a combined peak of O—H and N—H groups for the new flocculant at  $3433\text{ cm}^{-1}$ . The peak at  $2936\text{ cm}^{-1}$  was mainly due to the characteristic absorption of  $-\text{CH}_2-$ , and the peak at  $1008\text{ cm}^{-1}$  was attributed to C—H in-plane bending of the glucose groups. Furthermore, an extra band at  $1687\text{ cm}^{-1}$  of the new flocculant was assigned to the C=O stretching vibrations, and the missing peak at  $1648\text{ cm}^{-1}$  denied the existence of C=C in the new flocculant.<sup>12,26</sup> Therefore, the successful grafting of amide chains onto the polysaccharide backbone proved to be an efficient approach to the synthesis of pea-starch-grafted AM as a new flocculant for wastewater treatment.

#### SEM Analysis

The SEM micrographs of the AM, pea starch, and new flocculant are shown in Figure 3. It was obvious from the figure that the morphological characteristics changed significantly; this was mainly due to the grafting of the AM and pea starch, and the new flocculant had a totally different morphology than the AM or pea starch. As shown in Figure 3, the original crystal form [Figure 3(c,d)] of pea starch also developed into an amorphous state [Figure 3(e,f)] after grafting. This indicated that the copolymerization actually took place between the pea starch and AM, and the new copolymer of St-g-PAM was synthesized as a result.

#### TGA

The TGA curves of the AM, pea starch, and St-g-PAM under a nitrogen atmosphere are shown in Figure 4. As shown in the figure, the weight loss of AM was measured within 80–125°C; this was due to the evaporation of small molecules. In case of the original pea starch, three weight loss stages were observed: the first stage of weight loss from indoor temperature to 120°C was supposed to be derived from water loss, whereas the weight loss stage within 260–350°C was due to the splitting of surface hydroxyl groups. The last weight loss stage at 350–580°C was attributed to the rupture of the main chains of starch and key bonds;<sup>18</sup> this could have been due to the depolymerization of the macromolecules that took place to form anhydro-D-

glucopyranose, 2-furaldehyde, and a range of lower molecular weight volatile and gaseous fragmentation products.<sup>19</sup> In the case of the new flocculant, three distinct stages were also observed with the increase in the degradation temperature at 50–278, 279–360, and 361–550°C. The weight loss in the first region (50–278°C) was mainly due to the elimination of water by the degradation of the polysaccharide backbone; the second degradation (279–360°C) was attributed to the decarbonylation (elimination of CO) of pea starch. In the final stage, the degradation weight loss process was largely due to the release of  $\text{NH}_3$  from the PAM chains.<sup>27</sup> Therefore, We concluded from the TGA results that the grafting of PAM chains onto the starch backbone may have enhanced the thermal stability of pea starch. The modified pea starch could produce higher amount of residues (15%) compared with that of the original pea starch (3%) after decomposition at 700°C; this was due to the introduction of PAM in the new flocculant.

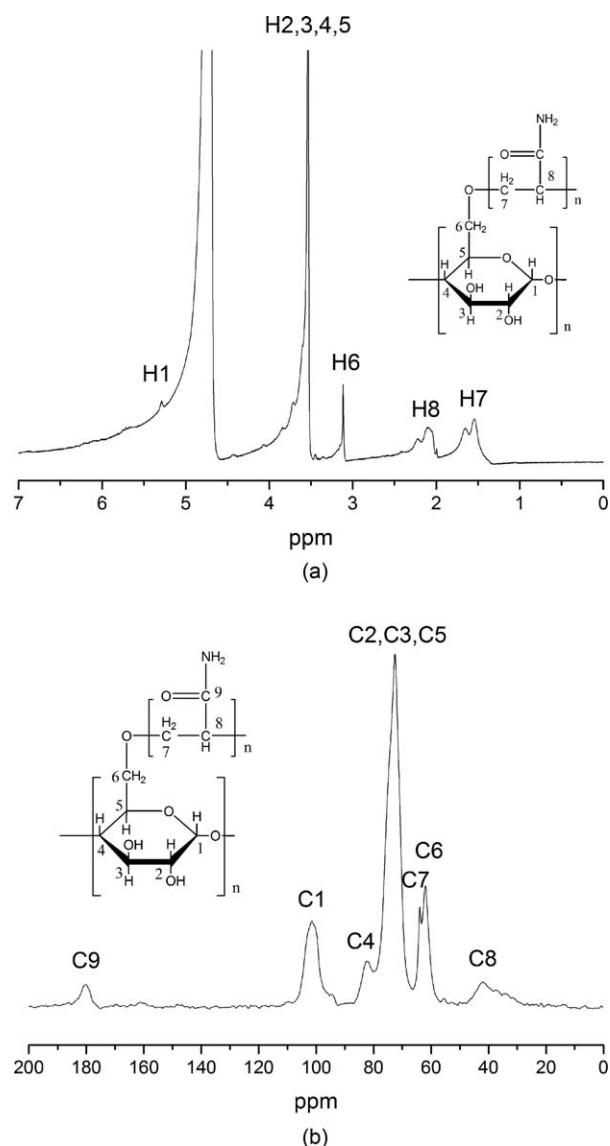
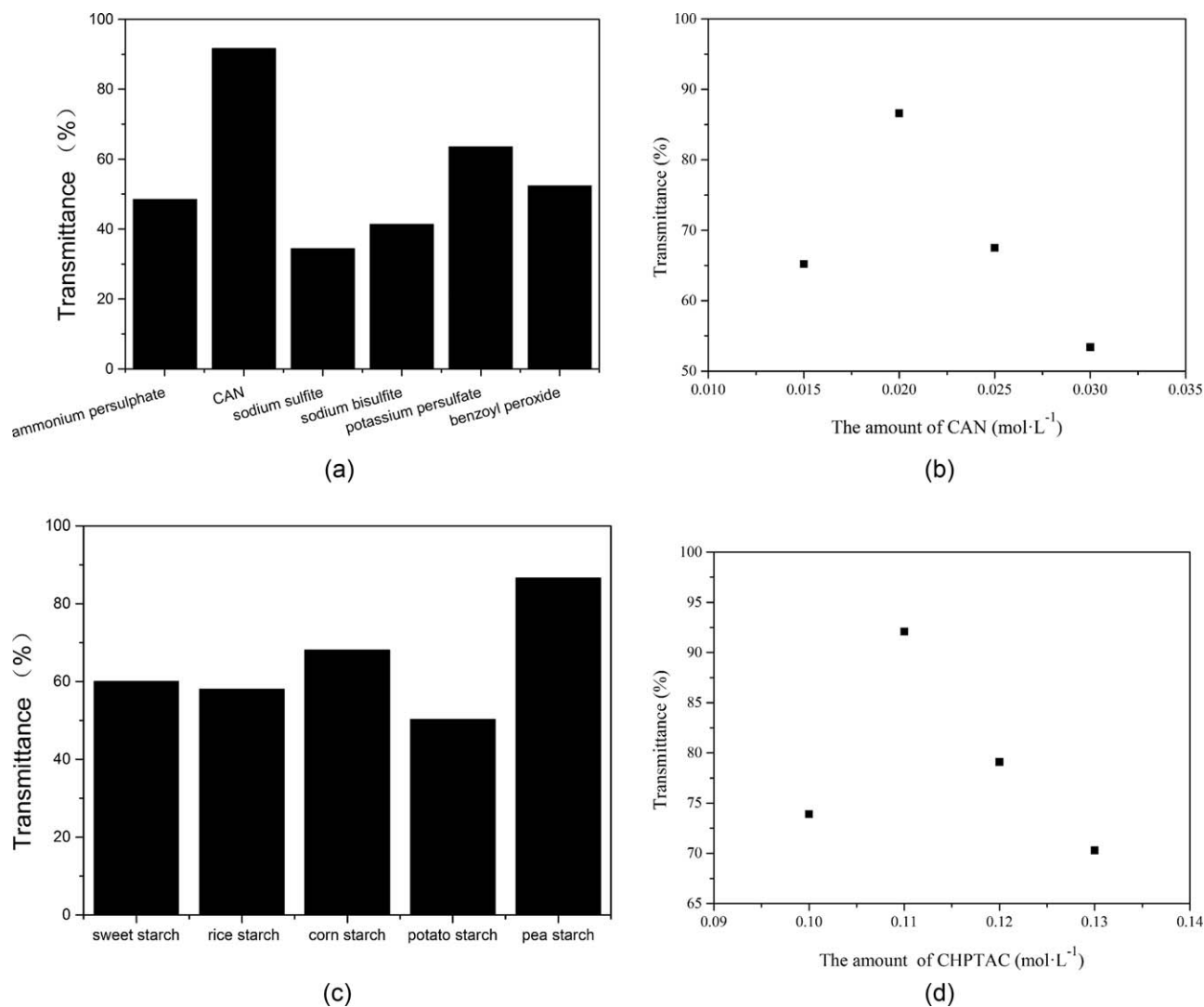


Figure 5. (a)  $^1\text{H}$ -NMR spectrum of St-g-PAM in  $\text{D}_2\text{O}$  at 25°C and (b) CP/MAS  $^{13}\text{C}$ -NMR spectrum of St-g-PAM at a spinning rate of 14 kHz.



**Figure 6.** Relationship between the synthesis factor and flocculation performance of the new flocculant: (a) different initiators, (b) different amounts of CAN, (c) different kinds of starch, and (d) different amounts of CHPTAC.

### NMR Analysis

The new flocculant was investigated by <sup>1</sup>H-NMR spectroscopy, and the results are shown in Figure 5(a). NMR showed that the resonance at  $\delta = 5.3$  ppm could be attributed to the H1 proton and the resonance at 3.2 ppm could be attributed to the H6 proton. The resonances within 3.6–3.8 ppm could be attributed to the H2, H3, H4, and H5 protons on the pea starch backbone. The absence of ethylenic proton peaks (6.2 and 5.7 ppm for the protons on  $\text{CH}_2=\text{CH}-$ ) showed that the  $\text{C}=\text{C}$  of AM was open and the copolymerization was smooth. Furthermore, the resonances at 2.1 and 1.5 ppm were attributed to the protons of the  $-\text{CH}$  (H8) and  $-\text{CH}_2$  (H7) groups of amide in the PAM molecule, respectively.<sup>28</sup>

CP/MAS <sup>13</sup>C-NMR was used to evaluate the short-range ordered structures of the new flocculant, and the results are shown in Figure 5(b). Chemical shifts appeared at  $\delta$  values of 75.8 ppm (C2, C3, C5), 102.5 ppm (C1), 62.1 ppm (C6), and 81.1 ppm (C4), respectively. The absorption peak at 182 ppm represented the amide carbonyl carbon (C1); the signals

appearing at 42.5 and 64.5 ppm were associated with C8 and C7 ( $-\text{CH}_2-\text{CH}_2-$ ), respectively, which were formed during the polymerization. AM had two peaks at 130 and 133 ppm for  $\text{sp}^2$ -hybridized carbon atoms ( $\text{CH}_2=\text{CH}-$ ),<sup>29,30</sup> which disappeared in the new flocculant. So the absence of peaks at  $\delta$  values of 130 and 133 ppm and the presence of peaks at  $\delta$  values of 42.5 and 64.5 ppm provided effective evidence that the PAM chains were grafted onto the backbone of pea starch.

### Effect of the Initiator

In recent years, many initiators for triggering graft copolymerization have been studied; these include CAN, potassium persulfate, sodium sulfite, sodium bisulfite, benzoyl peroxide, and ammonium persulfate, and they usually produce free-radical sites on the polymer.<sup>31,32</sup> The effects of different initiators were investigated and discussed under the same conditions. The mass ratio between pea starch and AM was 0.5, and the synthesis temperature of the new flocculant was 65 °C. The mentioned initiators were used to synthesize different types of cationic pea starch flocculant, and then, flocculation experiments for coal

**Table II.** Amylose Contents and Coagulation Performances of Different Starches

Category	Amylose content (%)	Flocculation performance
Pea starch	41	Strong
Corn starch	27	Weak
Sweet potato starch	25	Weak
Rice starch	23	Weak
Potato starch	20	Weak

mine wastewater treatment were conducted to study their application effects. In comparison with other initiators, including potassium persulfate, sodium sulfite, and ammonium persulfate, the new flocculant triggered by CAN demonstrated the best flocculation effect in the wastewater treatment, as shown in Figure 6(a). The outstanding initiation effect of CAN was mainly because its ceric (IV) ions created more active sites on pea starch through the direct participation of the electron-transfer process. The active sites created by CAN were presumed and proven to be responsible for promoting the extent of the graft copolymerization onto pea starch.<sup>33</sup>

The dosage effect of the CAN initiator on coal mine wastewater treatment is shown in Figure 6(b). As shown in the figure, the wastewater transmittance increased with increasing CAN dosage, and the transmittance reached its maximum value of 86.6% with an optimal CAN dosage of 0.02 mol/L. We found that the homopolymer formation was considerably less at a low initiator concentration, whereas there was significant homopolymer formation beyond a certain value. The further increase in the initiator concentration resulted in a decrease in the transmittance of treated coal mine wastewater. This was probably due to the formation of ceric salt, which took part in the termination of the growing grafted chain in the copolymerization. At a higher ceric ion concentration, an increase was expected in the reaction steps involving ceric ions; this led to a rise in the number of starch radicals terminated before monomer addition.<sup>34</sup> Another factor contributing to the decrease in the grafting levels at a higher initiator concentration was the increase in the homopolymer formation, which competed with the grafting reaction for available monomer.<sup>35</sup> So, the optimal dosage of CAN was 0.02 mol/L.

#### Influence of the Reactants

**Removal Efficiency of Different Starches.** AM and five different kinds of starch were used to produce the new flocculants by a graft copolymerization reaction under the same conditions. The pea starch graft copolymer flocculation showed the best performance, as shown in Figure 6(c).

Amylose and amylopectin were the two basic ingredients of the  $\alpha$ -glucan polymers for starch. The dendritic structures inside the amylopectin tended to create an obvious steric hindrance effect, which could bring about negative effects for wastewater treatment. In this case, the amylose structure could deal with sewage water efficiently. As shown in Table II,<sup>36</sup> pea starch had

the highest amylose content among the five kinds of starch, so the graft copolymer of pea starch proved to be the best flocculant among all of the starches. Therefore, the following study focused on pea starch.

The data in Table II and Figure 6(c) show that pea starch had an outstanding flocculation performance; we observed that when there was more amylose in the starch, the coagulation performance for coal mine wastewater treatment was better.

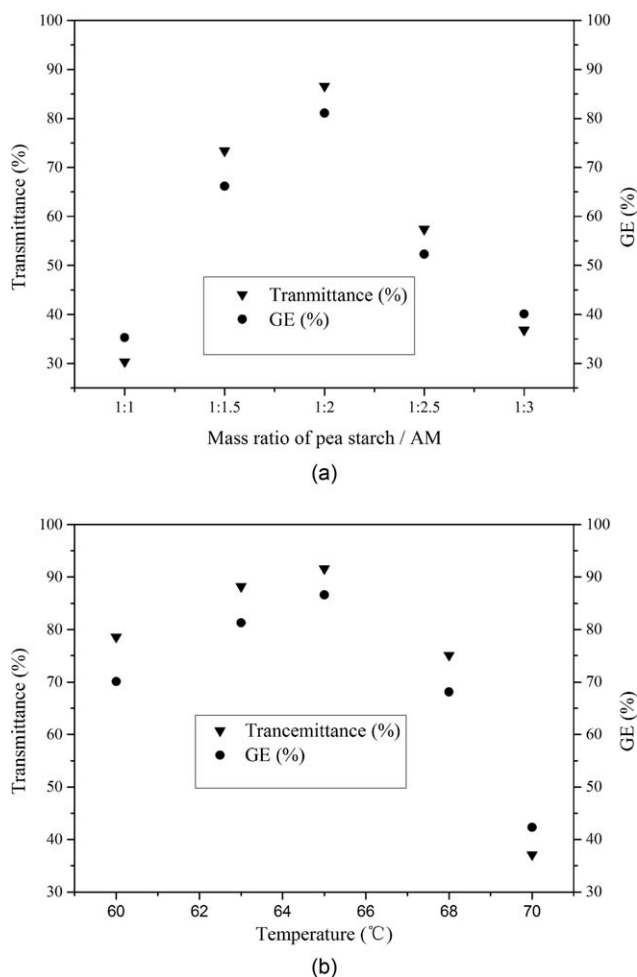
#### Influence of the Cationic Etherifying Agent on the Graft Copolymer.

To study the influence of the cationic etherifying agent on the graft copolymer, we carried out a few experiments and found out CHPTAC had a superior effect on the pea starch grafted AM. Different etherifying agents of CHPTAC and glycidyl trimethyl ammonium chloride (GTA) for St-g-PAM synthesis were investigated and compared. The experimental results indicated that the new flocculant produced by CHPTAC had an excellent flocculation ability (92% transmittance), which was apparently higher than that of GTA etherification (85%), and the transmittance of the new flocculant undoubtedly surpassed that without an etherifying agent (75%). This was mainly because the hydroxyl inside pea starch could combine with amine compounds by etherification and bring positive charges sourced from nitrogen atoms of amine compounds to the functional groups of St-g-PAM. The modified pea starch was more likely to eliminate the electric charges of suspended particles in coal mine wastewater and was prone to accelerating the destabilization and sedimentation of these fine particles.

On this basis, we studied the optimal dosage of CHPTAC used for new flocculant synthesis, and the result is shown in Figure 6(d). As shown in Figure 6(d), the peak transmittance appeared when the concentration of the etherifying agent CHPTAC was 0.11 mol/L. Then, the light transmittance decreased with increasing amount of CHPTAC. This was because only hydroxyl groups on the starch could be etherified, and the steric effect increased with increasing etherifying agent dosage under a constant amount of hydroxyl groups. This eventually led to a decrease in the light transmittance. So, the optimal dosage of CHPTAC was 0.11 mol/L.

#### Influence of the Synthesis Factors of the New Flocculant

**Effect of GE.** To study the GE influence of the new flocculant on wastewater treatment, we used a calculation method [eq. (1)] to evaluate the GE of new flocculants, which were prepared with different starches and different mass ratios between pea starch and AM. The experimental results show that the pea starch grafted AM achieved its maximal GE of 80.6% under the same synthesis conditions, and the GEs of the other starches followed the order: Corn starch (73.1%) > Sweet starch (64.3%) > Rice starch (61.8%) > Potato starch (53.7%). These starches tended to behave in accordance with their amylose contents (Table II) and flocculation effects [Figure 6(c)]. Moreover, GE of the new flocculants prepared by pea starch varied greatly depending on the pea starch/AM mass ratio and reaction temperature, so these factors are the focus of the following discussion.



**Figure 7.** (a) Effect of the pea starch/AM mass ratio on GE and flocculation and (b) effect of the reaction temperature on GE and flocculation.

**Mass Ratio of Pea Starch to AM.** Because the pea starch showed the best removal efficiency of coal mine wastewater, it was crucial to determine the grafted mass ratio of pea starch to AM during the graft copolymerization. A mass ratio experiment was carried out, and the results are shown in Figure 7(a).

As shown in Figure 7(a), with increasing polymerization ratio (pea starch/AM, wt %), the transmittance increased and reached its peak at 1:2. Then, there was a decreasing reduction between the mass ratio and transmittance. The same trend of GE could be deduced from the influence of the mass ratio (pea starch/AM), which presented its peak value of 81.1% at a mass ratio of 1:2. We also observed in the figure that the flocculant with a high GE had a better coagulation effect. This was largely because the new flocculant with a higher GE contained more PAM chains and tended to accumulate a favorable net structure; this was helpful for capturing fine suspended particles in coal mine wastewater.<sup>36</sup> The experimental results indicated that the copolymerization was enhanced before the polymerization ratio was 1:2; then, copolymerization decreased, and the homopolymerization of AM began to rise after a ratio of 1:2. When the mass ratio reached 1:3, the copolymerization between pea starch and AM was greatly weakened, and the homopolymerization of

AM dominated the reaction. As a result, the optimal mass ratio of pea starch to AM was 1:2.

**Effect of the Reaction Temperature.** Figure 7(b) shows the coagulation activity and GE values of the new flocculants prepared at different synthesis temperatures. It is apparent in the figure that the flocculation ability and GE of the new flocculant both increased before 65 °C, whereas the flocculation effect and GE decreased significantly when the reaction temperature was higher than 65 °C. The transmittance of coal mine wastewater and GE even decreased to 37.1 and 42.3%, respectively, when the reaction temperature reached 70 °C. So, the optimal reaction temperature of St-g-PAM synthesis was 65 °C with a maximal transmittance and GE of 91.6 and 86.6%, respectively. The reason could be explained as follows: the reaction efficiency, cross-linking degree, and molecular weight of the new flocculants increased along with increasing reaction temperature; this enhanced the adsorption ability and coagulation effect of the new flocculant. However, the macromolecular configuration and molecular chain length were matters of great concern in bridging flocculation with polymer flocculants. Because of the damage of the molecular structures and chains in the high-temperature region, the bridge formation could be broken or destroyed when the reaction temperature climbed over 65 °C, and the flocculating activity dropped dramatically as a result.<sup>37</sup> Furthermore, when the flocculant formed fibrous textures and loose structures, the long-chain polymer molecules tended to adsorb on the surface of the suspended particles. This reduced the distance between suspended particles in the aqueous phase; the fine particles were prone to gathering, and thus, the flocs could be separated by gravity and settled rapidly.<sup>19</sup>

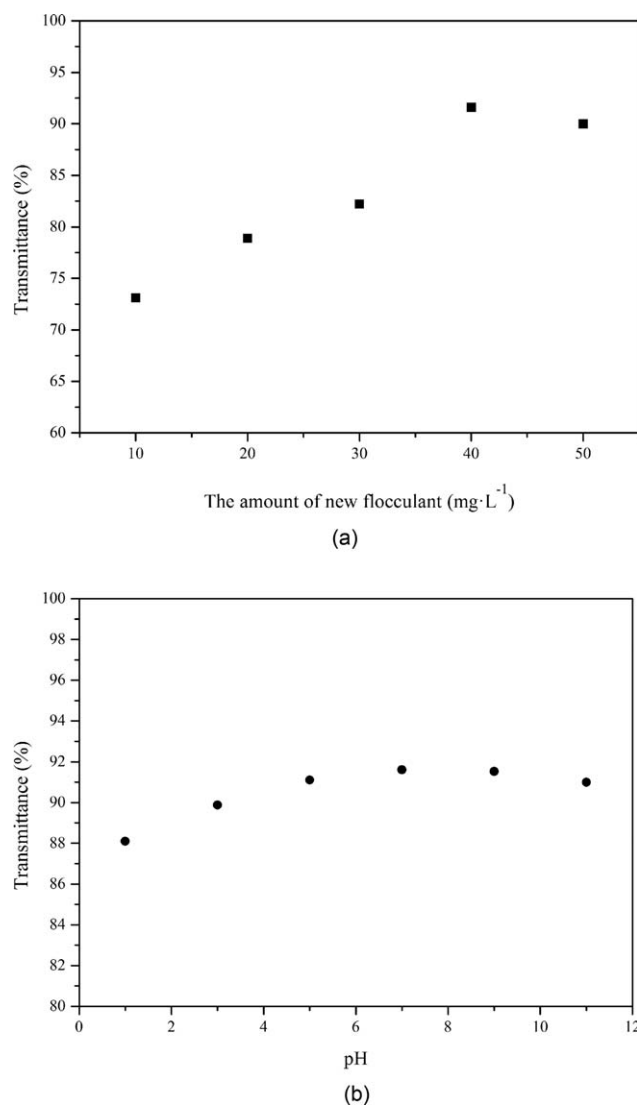
#### Application Conditions of the New Flocculant

**Dosage of the Flocculant.** The new flocculant made from pea starch and AM was prepared under the optimal copolymerization ratio (1:2) and reaction temperature (65 °C). The effects of the new flocculant dosage were investigated, and the results are shown in Figure 8(a). The experimental data depicted that the optimal dosage of the new flocculant was 40 mg/L, and the transmittance of treated sewage water could reach 91.6%. With increasing flocculant dosage, the bridging and charge neutrality of the new flocculant were enhanced, and the new flocculant became more prone to collecting fine suspended particles and accelerating the sedimentation velocity of flocs inside the coal mine wastewater. Nevertheless, when the dosage of the new flocculant was over 40 mg/L, the electric charges of wastewater were overneutralized and induced the like charges to repel each other; this could result in a steric hindrance increase in the suspended particles and a slight decline in the transmittance. Therefore, the most appropriate dosage of new flocculant for the wastewater treatment was 40 mg/L.

**Effects of the pH on Sewage Water Treatment.** Under the optimal addition dosage of 40 mg/L, the sewage water at different pH values was investigated, and the effects of the pH are shown in Figure 8(b).

As shown in Figure 8(b), the new flocculant displayed a distinctive performance on sewage water treatment in a wide pH range (from 5 to 10). Only when the pH value of the wastewater was





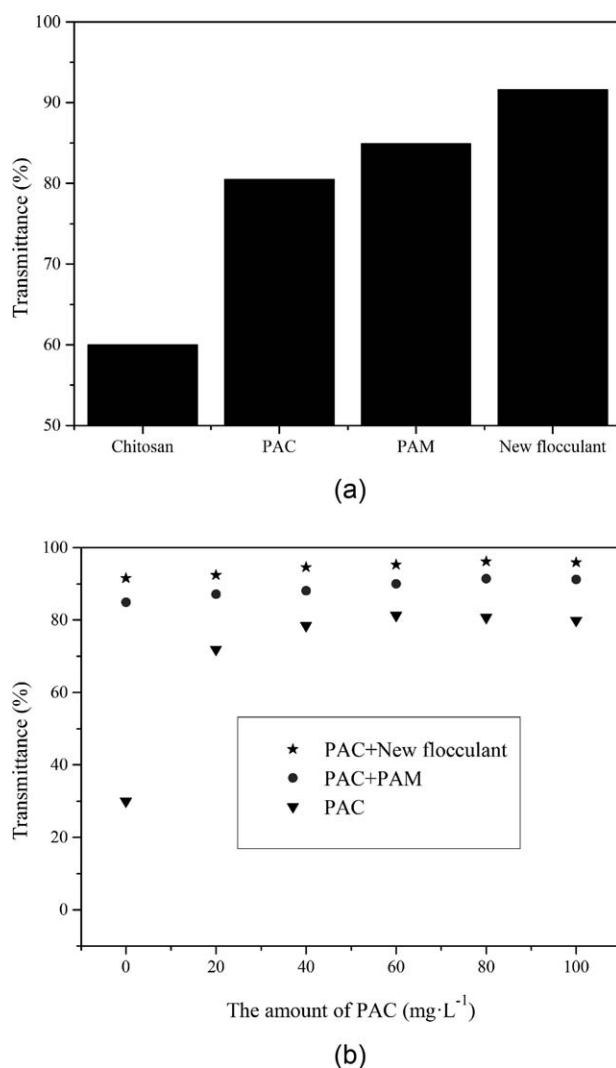
**Figure 8.** Effect of the operation conditions on sewage water treatment: (a) flocculant dosage and (b) pH.

less than 5 or more than 10 did the sewage treatment effect of the new flocculant tend to decline slightly. Because most coal mine wastewater has a pH value of 6–8, the new flocculant will accordingly enjoy promising market prospects in the future.

**Performance Comparisons of Typical Flocculants.** To test the performance of the new flocculant on sewage water treatment, the traditional flocculants chitosan, PAC, and PAM were used in comparison experiments. As shown in Figure 9(a), the new flocculant demonstrated an obvious superiority for coal mine wastewater treatment, and the transmittance of its treated sewage water exhibited the highest value. This was because grafted pea starch could form a network between large numbers of colloidal particles, and this led to the best flocculation effect.

Being a typical inorganic flocculant, PAC is widely used in coal mine wastewater treatment in industrial and commercial areas. Different flocculants combined with PAC were prepared, and the amount of PAM and new flocculant used in the experiment was its optimal dosage, respectively. The composite flocculants

PAC and PAM (30 mg/L) plus PAC and the new flocculant (40 mg/L) plus PAC were introduced into sewage water, and the transmittances of the sewage water were measured and compared, as shown in Figure 9(b). When PAC was added to the coal mine wastewater samples, the transmittance of the sewage water increased gradually until its dosage was over 40 mg/L, and after that, the treatment efficiency remained at about 80%. That was because the PAC inorganic molecule structures, unlike the organic new flocculant, which had a long branched chain, could not ideally capture tiny particles in the sewage water. As shown in Figure 9(b), we also found that when PAC was added to the new flocculant at the optimal dosage, the transmittance of coal mine wastewater almost remained stable with increasing PAC amount. Compared with the results shown in Figure 8(a), the new flocculants with or without PAC did not show much performance differences for wastewater treatment. This illustrated that the new flocculant could also be used for sewage water treatment separately; this means that it could simplify the wastewater disposal process. The new flocculant with the



**Figure 9.** Performance comparisons of typical flocculants: (a) performance of the chitosan, PAC, PAM, and new flocculant and (b) performance of the PAC dosage of the composite flocculant.

**Table III.** Wastewater Treatment Results under Optimal Operation Conditions

Item	Concentration (mg/L)				Transmittance (%)
	Iron	Manganese	COD	SS	
Wastewater sample	8.98	7.75	85	1050	30.1
PAM + PAC	0.80	0.15	25	13	91.4
New flocculant + PAC	0.71	0.13	21	10	96.2

additive of PAC revealed the best flocculation effects, and a 96% transmittance was achieved. It remarkably exceeded the traditional mixture of PAM and PAC. This was due to the fact that pea starch had hydrophilic and semirigid macromolecular frames, and PAM had slender and flexible molecular chains. Hence, pea starch and PAM could be successfully combined into a new flocculant, which had more molecular spaces to form compact reticular structures. It could thus easily capture fine particles and promote the coagulation effect in coal mine sewage water. Under the previous optimal operation conditions, comparison experiments were carried out to determine the actual effects in the wastewater samples. Different flocculants were used, and the treatment results of coal mine wastewater (pH = 7) are shown in Table III.

Table III shows that the complex of the new flocculant and PAC had as its overwhelming feature a particle-removal effect, as shown by the iron, manganese, COD, and SS concentrations.

## CONCLUSIONS

A new flocculant produced by pea-starch-grafted AM was synthesized by copolymerization. The graft copolymer used in sewage water was characterized through various physicochemical techniques, including EA, FTIR spectroscopy, SEM, TGA, and NMR. The characterization results of the new flocculant indicated that AM was used as a basic monomer to successfully copolymerize the macromolecular frames of pea starch. The flocculation efficiency and operation conditions of the graft copolymer were investigated through experiments in coal mine sewage water. The optimal synthesis parameters for the new flocculant were as follows: CAN dosage = 0.02 mol/L, CHPTAC dosage = 0.11 mol/L, reaction temperature = 65 °C, and mass ratio between pea starch and AM = 0.5. The transmittance reached 91.6% when the optimal dosage of new flocculant was 40 mg/L; this showed an obvious treatment effect of sewage water compared to PAM. Moreover, the compound of the new flocculant and PAC demonstrated an outstanding effect compared to the traditional mixture of PAM and PAC. The new flocculant had a few features, including environmentally friendliness, easy degradation, wide availability, and low cost. Therefore, it will undoubtedly have wide applications in the future.

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## REFERENCES

- Bian, Z.; Inyang, H. I.; Daniels, J. L.; Otto, F.; Struthers, S. *Min. Sci. Technol.* **2010**, *20*, 215.
- Guo, Z. C.; Fu, Z. X. *Energy* **2010**, *35*, 4356.
- Kim, Y. M.; Park, D.; Lee, D. S.; Park, J. M. *J. Hazard. Mater.* **2008**, *152*, 915.
- Huo, H.; Lei, Y.; Zhang, Q.; Zhao, L.; He, K. *Energy Policy* **2012**, *51*, 397.
- Dong, G. X. *China Stat.* **2013**, *61*, 22.
- National Bureau of Statistics of the People's Republic of China. *China Statistical Yearbook*; China Statistical Publishing House: Beijing, **2014**.
- Bolto, B.; Gregory, J. *Water Res.* **2007**, *41*, 2301.
- Harif, T.; Khai, M.; Adin, A. *Water Res.* **2012**, *46*, 3177.
- Jarvis, P.; Sharp, E.; Pidou, M.; Molinder, R.; Parsons, S. A.; Jefferson, B. *Water Res.* **2012**, *46*, 4179.
- Yang, Z.; Yuan, B.; Huang, X.; Zhou, J. Y.; Cai, J.; Yang, H.; Li, A. M.; Cheng, R. S. *Water Res.* **2012**, *46*, 107.
- Zhang, Z. Q.; Xia, S. Q.; Zhang, J. A. *Water Res.* **2010**, *44*, 3087.
- Bharti, S.; Mishra, S.; Sen, G. *Carbohydr. Polym.* **2013**, *93*, 528.
- Mishra, S.; Sen, G.; Rani, G. U.; Sinha, S. *Int. J. Biol. Macromol.* **2011**, *49*, 591.
- Rani, P.; Sen, G.; Mishra, S.; Jha, U. *Carbohydr. Polym.* **2012**, *89*, 275.
- Gao, B. Y.; Wang, Y.; Yue, Q. Y. *Acta Hydrochim. Hydrobiol.* **2013**, *33*, 365.
- Xing, W.; Ngo, H. H.; Guo, W. S.; Wu, Z. Q.; Nguyen, T. T.; Cullum, P.; Listowski, A.; Yang, N. *Sep. Purif. Technol.* **2010**, *72*, 140.
- Moreno-Chulim, M. V.; Barahona-Perez, F.; Canche-Escamilla, G. *J. Appl. Polym. Sci.* **2003**, *89*, 2764.
- Lin, Q. T.; Peng, H. L.; Zhong, S. X.; Xiang, J. X. *J. Hazard. Mater.* **2015**, *285*, 199.
- Cao, J. P.; Zhang, S.; Han, B. L.; Feng, Q. L.; Guo, L. F. *J. Appl. Polym. Sci.* **2012**, *123*, 1261.
- Yang, Z.; Wu, H.; Yuan, B.; Huang, M.; Yang, H.; Li, A. M.; Bai, J. F.; Cheng, R. S. *Chem. Eng. J.* **2014**, *244*, 209.
- Lin, L. S.; Guo, D. W.; Zhao, L. X.; Zhang, X. D.; Wang, J.; Zhang, F. M.; Wei, C. X. *Food Hydrocolloids* **2016**, *52*, 19.
- Song, W. Q.; Guo, Z. C.; Zhang, L. Q.; Zheng, H. J.; Zhao, Z. W. *Radiat. Phys. Chem.* **2013**, *91*, 114.

23. Kaitya, S.; Isaaca, J.; Kumara, P. M.; Boseb, A.; Wong, T. W.; Ghosha, A. *Carbohydr. Polym.* **2013**, *98*, 1083.
24. Yang, L. P.; Zhou, Y. B.; Wu, Y. M.; Meng, X.; Jiang, Y. M.; Zhang, H. W.; Wang, H. S. *Carbohydr. Polym.* **2016**, *137*, 305.
25. Vijan, V.; Kaity, S.; Biswas, S.; Isaac, J.; Ghosh, A. *Carbohydr. Polym.* **2012**, *90*, 496.
26. Sen, G.; Singh, R. P.; Pal, S. *J. Appl. Polym. Sci.* **2010**, *115*, 63.
27. Sasmala, D.; Singhb, R. P.; Tripathy, T. *Colloids Surf. A* **2015**, *482*, 575.
28. Lim, Y. M.; Yao, S. G.; Gras, S. L.; McSweeney, C.; Lockett, T.; Augustin, M. A.; Gooley, P. R. *Food Hydrocolloids* **2014**, *40*, 16.
29. Li, J.; Sun, C. R.; Zhang, X. Q. *Polym. Compos.* **2012**, *33*, 1737.
30. Song, Y. B.; Zhou, J. P.; Zhang, L.; Wu, X. J. *Carbohydr. Polym.* **2008**, *73*, 18.
31. Kim, B. S.; Mun, S. P. *Polym. Adv. Technol.* **2009**, *20*, 899.
32. Gupta, K. C.; Khandekar, K. *J. Appl. Polym. Sci.* **2002**, *86*, 2631.
33. Joshi, J. M.; Sinha, V. K. *Polymer* **2006**, *47*, 2198.
34. Razi, A. F. L.; Qudsieh, I. Y. M.; Yunus, W. M. Z. W.; Ahmad, M. B.; Rahman, M. Z. A. *J. Appl. Polym. Sci.* **2001**, *82*, 1375.
35. Gupta, K. C.; Khandekar, K. *J. Appl. Polym. Sci.* **2006**, *101*, 2546.
36. Ma, Y. F. M.S. Thesis, Northwest University, Xi'an, China, **2012**.
37. Kavaliauskaite, R.; Klimaviciute, R.; Zemaitaitis, A. *Carbohydr. Polym.* **2008**, *73*, 665.