Research article

Influence of side-chain structure of polycarboxylate dispersant on the performance of coal water slurry

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A B S T R A C T

Two kinds of polycarboxylate dispersants with different side-chain structures were synthesized with acrylic acid and sodium styrene sulfonate as the main chain, and native starch and methoxyl polyethylene glycol (MPEG1000) as the side chain. Their structures were characterized by FT-IR and 1H NMR. The dispersants were used for Shenhuo coal-water slurry. The optimum amount of dispersant, apparent viscosity, maximum slurry concentration and stability of the slurry were investigated. It was found that economically accessible polycarboxylate dispersant using starch as the side-chain (PC-St) endowed coal water slurry (CWS) with better dispersibility and stabilizing ability than that of polycarboxylate dispersant using methoxyl polyethylene glycol as the side-chain (PC1000). When the dosage of PC-St was 0.4 wt%, the maximum concentration of CWS could reach to 66.5%. The dispersing and viscosity-reducing mechanisms of the two dispersants were systematically elucidated through the investigation on the Zeta potential, adsorption, contact angle and X-ray photoelectron spectroscopy (XPS) analysis of coal particles. In comparison with PC1000, the PC-St dispersant had higher saturated adsorption amount on the surface of the coal and was able to provide greater electrostatic repulsion and better wetting effect for coal particles. Moreover, the thickness of the PC-St adsorption layer was 7.57 nm, which provided good steric hindrance to effectively reduce the aggregation among coal particles. It could be concluded that, compared with PC1000 PC-St had better viscosity-reducing ability and dispersibility, as well as stabilizing ability for CWS.

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1. Introduction

Recently, continuously increasing demands for energy have led researchers to find ways for new energy sources. Thus, they have directed their attention towards various methods of burning coal water slurries (CWS) for energy generation. It is a type of novel fuel, which consists of 60–75% coal, 25–40% water and about 1% chemical dispersants. It is desirable that the coal water slurry has high coal solids content and a low viscosity. Thus, Chemical additives (dispersants) are indispensable to control the viscosity in preparing desired CWS [1,2]. The traditional dispersants mainly include napthalene series, lignin series, humic acid series and their blending products [3–5]. However, traditional dispersants are not effective dispersants for CWS, because of the relatively complex chemical composition and the wide range of molecular weight distribution. The polycarboxylate dispersants have more advantages such as environment friendliness, high efficiency, flexible structure, wide applicable scope, etc. They have gradually replaced the traditional dispersants and obtained extensive application in CWS. The study showed that polycarboxylate dispersants with polyether side chains could effectively endow the surface of coal particles with a larger steric space hindrance to reduce the aggregation among coal particles and achieve efficient dispersion effect [6]. To be mentioned, the main raw materials are derived from expensive petroleum products, which significantly limit their applications.

In our previous study, the polycarboxylate dispersant with methoxyl polyethylene glycol (MPEG1000) as the side chain was applied in the preparation of CWS. We found that the side chain of the polycarboxylate dispersant had a decisive influence on the dispersion stability of CWS [7,8]. At the same time, the starch is a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds and its hydrophilic performance can be greatly enhanced after oxidation. Therefore, larger space steric effects among coal particles can be produced when it is used as a side chain [7]. Research on coal-water slurry dispersants based on biomass attracted more and more attentions due to their low costs, efficient sources, biodegradable features, etc. but the current studies were mainly confined to the primary modification of the natural products. Debadutta Das et al. [9,10] applied starch xanthide, starch phosphate and starch xanthate as dispersants in CWS, which displayed favorable stabilizing ability but relatively large usage was needed to reach a stable system. In this study, we have attempted to research on the synthesis of polycarboxylate dispersant with starch as the side chain.
Two kinds of polycarboxylate dispersants with natural starch and MPEG1000 as the side chain were synthesized and the corresponding dispersant was designated as PC-St and PC1000 respectively. The two dispersants were applied in Shenhua coal-water slurry, and the apparent viscosity, dispersibility and stability of the slurry were systematically compared. In addition, the dispersing mechanism was elucidated through the investigation on the wettability, adsorption, electrical charge, and adsorption capacity, and adsorption film thickness on the coal particles.

2. Materials and methods

2.1. Materials

Acrylic acid (AA), sodium styrene sulfonate (SSS), MPEG1000 were purified after being washed by 5 wt% sodium hydroxide. Analytical reagents potassium persulfate, sodium bisulfate, sodium hydroxide and hydrochloric acid (36%) were bought from Jinan Fengle Chemicals Company. Hydroquinone, isopropyl alcohol, and ethanol were provided by Xi’an Weber Liyang chemicals group. Industrial-grade amylase maize starch was produced by Shandong Huanong Special Corn Starch Co. Ltd. Shenhua coal used in this study was from Shaanxi province of China (as expressed in Table 1). The coal has a low degree of metamorphism with low content of sulfur and ash. Besides, the coal has a relatively high oxygen/carbon ratio and internal moisture content.

2.2. Preparation

2.2.1. Synthesis of coal-water slurry

The Shenhua coal was pulverized by a dry ball mill at 600 r/min before utilization. The concentration of coal-water slurry can be improved by pulverizing the coal into appropriate particle size distributions to make the coal powders pack closely. According to the multi-peak grade blending technology of Texaco, the particle size was adjusted to 20–40 mesh, 40–120 mesh, 120–200 mesh, 200–300 mesh and 300 mesh, respectively. Correspondingly, the mass fractions were 8%, 42%, 7%, 8% and 35%. The coal power was mixed and stirred with 0.2–1.0 wt% of dispersant (based on the weight of dry coal powders) and deionized water at 600 rpm for 10 min to ensure the homogenization of CWS [11–13].

2.2.2. Synthesis of polycarboxylate dispersants

Synthesis of PC-St: 5 g corn starch, 0.05 g potassium persulfate and 20 ml deionized water were placed in a three-necked flask equipped with a reflux condenser, feeding inlet and thermometer. The mixtures were stirred and heated to 90 °C for 30 mins to make the starch oxidize completely. After that, the mixtures were cooled to 80 °C, and the pH value was adjusted to 8. Then SSS and a small amount of sodium bisulfate were added. After being fully dissolved, potassium persulfate solution and AA were added drop-wise into the reactor. The mixture was allowed to react for 4 h at 80 °C. Afterwards, the reaction system was cooled to room temperature, the pH value was adjusted to 7–8 with 20% NaOH aqueous solution. Finally, a brown and clear PC-St emulsion was obtained.

Synthesis of PC1000: PC1000 was prepared with a certain proportion of AA, SSS and self-made acrylate monomers polyethylene glycol monomethyl ether (MPEGAA1000) according to the reference [15]. The as-prepared product displayed as an orange-yellow clear liquid. The molecular structure of two different polycarboxylate dispersants with different side chains was showed in Fig. 1.

2.3. Measurements

2.3.1. FT-IR studies and 1H NMR

FT-IR spectra of the dispersants prepared were recorded on German Brucker EQUI NX55 FTIR spectrophotometer based on the KBr disc technique in the range of 4000–400 cm$^{-1}$ [16].

$^1$H NMR spectrum of the dispersants was determined with German Brucker 400 MHz DRX-400 nuclear magnetic resonance instrument. The solvent was D$_2$O.

2.3.2. Performance testing of dispersants

The apparent viscosity of the CWS was tested by NXS-4C viscosity meter with shear rate 100 s$^{-1}$ at 25 °C. The water separating ratio (%) was also determined to evaluate the stability [17]. Zeta potential was tested by ZEN3690 Zetasizer(Malvern Instruments Corp.). A 0.2 g coal sample was added into a 150-ml conical flask and mixed with 50 ml distilled water. The coal-water slurry was shaken 2 h at constant temperature, and then the pH value was adjusted to 7. The supernatant was taken for the Zeta potential measurement, and an average of triplicates was determined.

2.3.3. Determination of rheological properties

Rheological properties of the CWS were determined by the R/S-SST Plus rheometer of Brookfield, with V40-20 rotor at 25 °C.

2.3.4. Determination of adsorption capacity

Apparent adsorption capacity of coal particles was measured by the residual mass concentration method, according to the reference [6].

2.3.5. Determination of contact angle of coal particles

Contact angle of coal particles was determined at 25 °C by DCAT21 interface tensiometer (German Oriental Delphi Company). The dynamic contact angle was measured with capillary rise method according to the reference [7].

Table 1

<table>
<thead>
<tr>
<th>Items</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt</td>
<td>11.97</td>
</tr>
<tr>
<td>Mad</td>
<td>3.67</td>
</tr>
<tr>
<td>Ad</td>
<td>10.08</td>
</tr>
<tr>
<td>Vd</td>
<td>33.96</td>
</tr>
<tr>
<td>Cd</td>
<td>55.9</td>
</tr>
<tr>
<td>Hd</td>
<td>4.55</td>
</tr>
<tr>
<td>Od</td>
<td>12.17</td>
</tr>
<tr>
<td>Nd</td>
<td>0.97</td>
</tr>
<tr>
<td>St.d</td>
<td>0.24</td>
</tr>
</tbody>
</table>
3.1. Structure of side-chain polycarboxylate dispersants

3. Results and discussion

3.1. Structure of side-chain polycarboxylate dispersants

As shown in Fig. 2, the adsorption peaks at 3000–3700 cm\(^{-1}\) and 1719 cm\(^{-1}\) were due to \(-\text{COOH}\) groups. The peaks at 1560 cm\(^{-1}\) and 1450 cm\(^{-1}\) could be ascribed to the vibration of the benzene ring. The peaks at 1160 cm\(^{-1}\), 1033 cm\(^{-1}\) and 616 cm\(^{-1}\) were assigned to the vibration of sulfonic acid groups. A typical adsorption peak at 1114 cm\(^{-1}\) was corresponding to the ether bond. The peak at 1014 cm\(^{-1}\) was resulted from the stretching vibration of C–O in the starch chain. It was also worthy to note that the characteristic peak of vinyl groups at 1650–1600 cm\(^{-1}\) disappeared, indicating the radical copolymerization was completely finished.

The infrared spectra of PC1000 in Fig. 2 showed the characteristic absorption peaks of carboxyl groups appeared at 3430 cm\(^{-1}\), 1724 cm\(^{-1}\) and 1287 cm\(^{-1}\). The peaks at 1575 cm\(^{-1}\) and 1450 cm\(^{-1}\) were corresponding to the vibration of the benzene ring. The bending vibration peak of C–H in the secondly substituted para-position of benzene was at 830 cm\(^{-1}\). Two peaks at 1190 cm\(^{-1}\) and 1043 cm\(^{-1}\) were the evidence of stretching vibration of the sulfonic acid group. The typical peak at 1114 cm\(^{-1}\) could be ascribed to absorption of the ether bond in polyethylene glycol. There was no characteristic absorption peak of the C=C double bond at 1631 cm\(^{-1}\), suggesting that the C=C double bond has mainly participated in the free radical copolymerization reaction. The peaks of PC-St and PC1000 in FT-IR were listed in Table 2.

As demonstrated in Fig. 3 by the \(^1\)H NMR, the chemical shift \(\delta = 4.7\) was the chemical shift of D\(_2\)O solvent. For PC-St, \(\delta = 7.0–7.8\) was the chemical shift of H protons in the benzene ring, testifying SSS was grafted onto the starch chain. \(\delta = 5.0–5.5\) was the chemical shift of H protons in R–OH of the starch chain. \(\delta = 3.0–4.0\) was the chemical shift of H protons of alkyl groups attached to the ether bonds in the starch chain. \(\delta = 1.8–2.3\) was the chemical shift of H protons of C connected with carboxyl group in the starch chain. \(\delta = 1.2–1.7\) was the chemical shift of H protons of –CH\(_2\)-- in the main chain. The above FT-IR and the \(^1\)H NMR results demonstrated that starch was successfully grafted onto the main chain composed of SSS and AA.

For PC1000, \(\delta = 7.0–7.7\) was the chemical shift of H protons in benzene ring. \(\delta = 2.2–2.5\) was the chemical shift of H protons of –CH\(_2\)-- connected with benzene ring in the main chain of copolymer, showing that the benzene ring existed in the molecular structure of the copolymer. \(\delta = 4.0–4.2\) was the chemical shift of H protons of –CH\(_2\)-- connected with the ester group in the side-chain. \(\delta = 3.3–3.7\) was the chemical shift of H protons of –CH\(_2\)-- connected with ether bond in the side-chain. \(\delta = 3.25\) was the chemical shift of H protons of –CH\(_3\) at the end of the side-chain of acrylate monomers polyethylene glycol monomethyl ether (MPEGAA), \(\delta = 1.9–2.3\) was the chemical shift of H protons of –CH\(_2\)-- and –CH\(_2\)-- connected with –C=O in the main chain of the copolymer. \(\delta = 1.10–1.75\) was the chemical shift of H

**Table 2**
The peaks of PC-St and PC-1000 in FT-IR.

<table>
<thead>
<tr>
<th>Dispersants</th>
<th>Peaks</th>
<th>Bonds or groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-St</td>
<td>3000–3700 cm(^{-1}) and 1719 cm(^{-1})</td>
<td>–COOH</td>
</tr>
<tr>
<td></td>
<td>1560 cm(^{-1}) and 1450 cm(^{-1})</td>
<td>Benzene ring</td>
</tr>
<tr>
<td></td>
<td>1160 cm(^{-1}), 1033 cm(^{-1}) and 616 cm(^{-1})</td>
<td>Sulfonic acid group</td>
</tr>
<tr>
<td></td>
<td>1114 cm(^{-1})</td>
<td>Ether bond</td>
</tr>
<tr>
<td></td>
<td>1014 cm(^{-1})</td>
<td>C–O (in starch)</td>
</tr>
<tr>
<td>PC-1000</td>
<td>3430 cm(^{-1}), 1724 cm(^{-1}) and 1287 cm(^{-1})</td>
<td>Carboxyl group</td>
</tr>
<tr>
<td></td>
<td>1575 cm(^{-1}) and 1450 cm(^{-1})</td>
<td>Benzene ring</td>
</tr>
<tr>
<td></td>
<td>830 cm(^{-1})</td>
<td>C–H</td>
</tr>
<tr>
<td></td>
<td>1190 cm(^{-1}) and 1043 cm(^{-1})</td>
<td>Sulfonic acid group</td>
</tr>
<tr>
<td></td>
<td>1114 cm(^{-1})</td>
<td>Ether bond</td>
</tr>
<tr>
<td></td>
<td>1631 cm(^{-1})</td>
<td>C=C</td>
</tr>
</tbody>
</table>

**Table 3**
Chemical shifts of different H protons by the \(^1\)H NMR.

<table>
<thead>
<tr>
<th>Dispersants</th>
<th>Chemical shift/(\delta)</th>
<th>H protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-St</td>
<td>7.0–7.8</td>
<td>Benzene ring</td>
</tr>
<tr>
<td></td>
<td>5.0–5.5</td>
<td>R–OH of starch chain</td>
</tr>
<tr>
<td></td>
<td>3.0–4.0</td>
<td>Alkyl groups attached to the ether bonds in starch chain</td>
</tr>
<tr>
<td></td>
<td>1.8–2.3</td>
<td>H protons of C connected with carboxyl group in starch chain</td>
</tr>
<tr>
<td></td>
<td>1.2–1.7</td>
<td>–CH(_2)-- in the main chain</td>
</tr>
<tr>
<td>PC-1000</td>
<td>7.0–7.7</td>
<td>Benzene ring</td>
</tr>
<tr>
<td></td>
<td>2.2–2.5</td>
<td>–CH(_2)-- connected with benzene ring</td>
</tr>
<tr>
<td></td>
<td>4.0–4.2</td>
<td>–CH(_2)-- connected with ester group in side-chain</td>
</tr>
<tr>
<td></td>
<td>3.3–3.7</td>
<td>–CH(_2)-- connected with ether bond in side-chain</td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td>–CH(_3) at the end of side-chain of acrylate monomers polyethylene glycol monomethyl ether (MPEGAA)</td>
</tr>
<tr>
<td></td>
<td>1.9–2.3</td>
<td>–CH(_2)-- and –CH(_2)-- connected with –C=O in main chain of copolymer</td>
</tr>
<tr>
<td></td>
<td>1.10–1.75</td>
<td>–CH(_2)-- in main chain of copolymer</td>
</tr>
</tbody>
</table>
protons of $-\text{CH}_2-\$ in the main chain of the copolymer. A summary of chemical shifts of different H protons was presented in Table 3. $^1$H NMR spectrum, together with FT-IR results, proved that PC1000 was the copolymer of sodium styrene sulfonate and acrylic acid-grafted by polyethylene glycol mono methyl ether.

3.2. Influence of dosage of dispersants on apparent viscosity of CWS

The apparent viscosity of 65 wt% CWS versus dispersant concentration was tested at a shear rate of 100 s$^{-1}$, as shown in Fig. 4. From Fig. 4, with the increasing amount of dispersant, the apparent viscosity of CWS decreased sharply and increased subsequently. In general, the quantity of dispersant adsorbed on the surface of coal particles increased gradually with the increase of the dispersant dosage [20]. The surface of the coal may interact with the dispersant through hydrogen bonding, electrostatic and hydrophobic interactions. The reduction in viscosity could be due to the space steric hindrance resulting from long side chain and electrostatic repulsion of anions. The viscosity reached the minimum when the dosage of dispersant arrived at 0.45 wt% (PC-St and PC1000). However, the viscosity increased when the dispersant dosage was greater than 0.45 wt%. This phenomenon can be ascribed to the denser distribution of a long side chain on the surface of coal particles when further increased the dispersant concentration. Thus chain entanglements tended to take place and the viscosity was thereby increased.

It could also be seen from Fig. 4 that the viscosity reducing effect of PC-St was better than that of PC1000. The apparent viscosity of CWS reduced to a minimum of 667.2 mPa·s by adding 0.45 wt% dispersant PC-St. It was demonstrated that the viscosity reduction ability of the dispersant was related to the structure of the side chain. On the one hand, the starch was composed of hundreds of glucose units. As a dispersant with a long side chain, it could provide steric protection of the coal particles from agglomeration and reduce the apparent viscosity. On the other hand, the hydrophilicity of starch was greatly enhanced because hydroxyl groups were oxidized to carboxyl groups after oxidation, which was beneficial to improve the hydrophilicity and thereby increase the dispersibility of coal particles in water. Therefore, natural starch grafted polycarboxylate dispersant PC-St had a better dispersing and viscosity-reducing effect on Shenhua coal-water slurry. The apparent viscosity of CWS reached 684.2 mPa·s with 0.4 wt% dispersant PC-St. The influence on the apparent viscosity between the dosage of 0.45 wt% and 0.4 wt% did not make great difference. So we applied 0.4 wt% in the follow-up study taking the cost of the dispersant into account.

3.3. Influence of slurry concentration on the apparent viscosity of CWS

The variation of apparent viscosity with CWS concentration was measured and the dosage of dispersant was kept at 0.4 wt%. The maximum slurry concentration was the concentration at which the apparent viscosity of the CWS reached 1000 mPa·s. As depicted in Fig. 5, the
apparent viscosity increased with the increase of slurry concentration. The free volume among coal particles was larger and agglomeration was rare at relatively low slurry concentration, resulting in lower apparent viscosity. With the increase of slurry concentration, the free volume became smaller and contact probability among coal particles increased. Thus the agglomeration and friction coefficient among coal particles were greatly increased, leading to higher apparent viscosity and worse mobility [21,22]. When the dosage of dispersant PC-St was 0.4 wt%, the highest concentration of CWS could reach 66.5%, which was higher than that of CWS prepared with PC1000 dispersant.

3.4. Zeta potential of CWS

According to theories of stability of charged colloidal particles, proposed by Derjguin, Landau, Verwey and Overbeek (DLVO theories), the prerequisite to keep particles disperse was the electrostatic repulsion must be stronger than the Van der Waals force between particles [23]. Larger absolute value of Zeta potential and stronger electrostatic repulsion made coal particles disperse more easily. Thus, the Zeta potential of coal particle surface was an important indicator to evaluate the dispersibility and stabilizing ability of coal particles in water.

The influence of the two dispersants on Zeta potential was studied. The results were shown in Fig.6. The Zeta potential of coal particles was $-11.9$ mV when no dispersant was added. Although the positive and negative charge regions simultaneously existed on the surface of coal particles [24], the coal particles displayed negative characteristic. The two dispersants were both anionic surfactants. Negative charge on the surface of coal particles increased with the adsorption of anions of the dispersants. The absolute value of Zeta potential on the coal particle surface increased at first and finally kept invariable when the adsorption reached saturation. The molecular structure of dispersants had a great influence on the Zeta potential of coal particles. For PC-St, more carboxyl groups appeared in the structure as a result of oxidation of starch, which could form better electrostatic adsorption with cationic surface of coal particles than that of PC1000. The Zeta potential of CWS with the addition of PC-St dispersant changed from $-11.9$ mV to $-47.8$ mV, which was more favorable to the dispersion and stability of CWS.

3.5. Influence of adsorption capacity of dispersants on the surface of coal

When the dispersant was adsorbed on the coal surface, a layer of hydration film was formed to reduce Gibbs free energy of the coal water dispersion system and prevent the agglomeration of coal particles, resulting in a stable CWS system. The arrangements of dispersant on the surface of coal particles and adsorption film thickness were both related to adsorption capacity of dispersants on the coal surface [25]. The relationship between adsorption capacity and equilibrium mass concentration at 25 °C of PC-St and PC1000 dispersants on Shenhua coal surface were depicted in Fig. 7. It showed that the adsorption capacity increased with the increase of the equilibrium concentration of the dispersant and adsorption platform appeared with further increase of the equilibrium concentration of the dispersant. The adsorption isotherms of Fig. 7 were fitted with two common adsorption models Langmuir (1) and Freundlich (2). The fitting results were shown in Table 4. In the formulas, $\Gamma$ means adsorption quantity (mg/g); $\Gamma_\infty$ means saturated adsorption quantity (mg/g); $c$ means the equilibrium concentration of the dispersant (mg/L); $K$ represents Langmuir equilibrium constant; the constant of Freundlich adsorption capacity is expressed by $k$; Parameter of adsorption strength is $n$.

\[
\Gamma / \Gamma_\infty = \frac{Kc}{1 + Kc} \quad (1)
\]

\[
\Gamma = kc^{1/n} \quad (2)
\]

<table>
<thead>
<tr>
<th>Dispersants</th>
<th>Langmuir equation</th>
<th>$\Gamma_\infty$ (mg/g)</th>
<th>$K$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-St</td>
<td>$\Gamma = \frac{2.97}{1.72 \times 10^{-2}}$</td>
<td>2.97</td>
<td>1.72 × 10$^{-2}$</td>
<td>0.9316</td>
</tr>
<tr>
<td>PC1000</td>
<td>$\Gamma = \frac{1.81}{0.40 \times 10^{-2}}$</td>
<td>1.81</td>
<td>0.40 × 10$^{-2}$</td>
<td>0.9614</td>
</tr>
</tbody>
</table>

![Fig. 8. The surface contact angle on Shenhua coal.](image8.png)

![Fig. 9. XPS elemental scanning spectra of Shenhua coal.](image9.png)

![Fig. 10. Si2p scanning spectra of Shenhua coal.](image10.png)
As demonstrated in Fig. 10, the intensity of photoelectron Si2p on the integration of the peak area (as shown in Table 5). The adsorption layer thickness on the surface of coal. Thus it could be concluded that the adsorption of the two dispersants on the surface of coal particles was monolayer adsorption [26]. The saturated adsorption capacity of PC-St was 2.97 mg/g, apparently higher than that of PC1000 (1.81 mg/g). This might be due to a large number of carboxyl groups existing in PC-St after oxidation of starch. The carboxyl groups on the side chain can also be anchored on cationic regions of coal particles and provide good steric hindrance for the dispersion of CWS. In contrast, PC1000 was adsorbed on coal particles only through the main chain, so the adsorption quantity was relatively small.

3.6. Influence of dispersants on wettability of coal

The contact angle of the coal-water interface reflected the average wettability of coal particles. The hydrophilicity increased with decreasing contact angle. As shown in Fig. 8, the contact angle of Shenhua coal particles in water was 72.6°, and the contact angle decreased after they adsorbed dispersant. Coal particles that adsorbed PC-St showed the smallest contact angle, demonstrating that PC-St possessed the better wettability. The main reason was that the adsorption capacity of PC-St on the coal particles reached the maximum, and PC-St possessed sulfonic acid groups and a large number of carboxyl groups. These structure characteristics made it easier to hydrophilically modify the coal surface, which was favorable to the wettability of coal particles. This could solve the contradiction of the incompatibility between coal and water, increasing the stability of CWS.

3.7. Influence of dispersants on adsorption film thickness on the coal surface and the stability of CWS

Elemental scanning spectra of Shenhua coal before and after absorbing dispersant PC-St were depicted by XPS in Fig. 9. Compared with blank coal sample, the intensity of C and Si peaks on the surface of coal after absorbing PC-St decreased and the intensity of O and Na increased. Since the content of O and Na in PC-St was higher than that of coal and the content of C was lower than that of coal, the content of O and Na on the coal surface increased while the content of C decreased. Though there was no Si in PC-St, Si element was still detected on the coal surface due to the thin absorbed layer. With Si as the characteristic element, the adsorption layer thickness could be calculated by determining the intensity of photoelectron Si2p across the absorbed layer. As demonstrated in Fig. 10, the intensity of photoelectron Si2p on the surface of coal particles decreased significantly because of the encapsulation effect. The adsorption layer thickness was calculated based on the integration of the peak area (as shown in Table 5). The adsorption layer thickness of PC-St on Shenhua coal was 7.57 nm, thinner than that of PC1000 (6.60 nm), because starch contained a large number of carboxyl groups after oxidation. It was easier for the carboxyl groups in the side chain and anions in the main chain to anchor on cationic mineral salts on the surface of coal particles, PC-St provided better hydrophilic modification on coal and formed thicker adsorption film. Better steric hindrance among coal particles was also provided by PC-St to effectively reduce agglomeration, preventing the increase of apparent viscosity. Therefore, it could be concluded that PC-St was an effective dispersant for CWS to keep good stability.

4. Conclusion

Two kinds of polycarboxylate dispersants with different side chains were synthesized, and the molecular structures were demonstrated by FT-IR and 1H NMR. It was found that economically accessible PC-St using starch as the side-chain had better dispersibility. When the dosage of PC-St was 0.4 wt%, the maximum concentration of coal water slurry (CWS) could reach 66.5%.

Therefore, the natural starch could replace expensive polyether and be used to modify polycarboxylate dispersant to obtain starch-g-polyacrylic acid PC-St dispersant. Compared with polycarboxylate dispersant PC1000, PC-St dispersant displayed greater saturated adsorption, higher absolute value of Zeta potential and adsorption film thickness on the surface of Shenhua coal. It can play a dual role in achieving efficient dispersion of coal particles by providing good steric hindrance and electrostatic repulsion. At the same time, the surface of coal particles was hydrophilically modified through adsorption. The Gibbs free energy of the slurry was decreased and the stability of the slurry was simultaneously improved.

Acknowledgement

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