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Research article

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

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ABSTRACT

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 ^{1}H NMR. The dispersants were used for Shenhua 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.

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 naphthalene 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

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Table 1
Analyses of Shenhua coal samples in dry basis.

Items	Content (wt%)
Mt	11.97
Mad	3.67
Ad	10.08
Vd	33.96
Cd	55.9
Hd	4.55
Od	12.17
Nd	0.97
St.d	0.24

chain [7]. 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, electrified 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 [14]. The mixtures was stirred and heated to 90 °C for 30mins 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 ^{1}H 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_2O.

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].

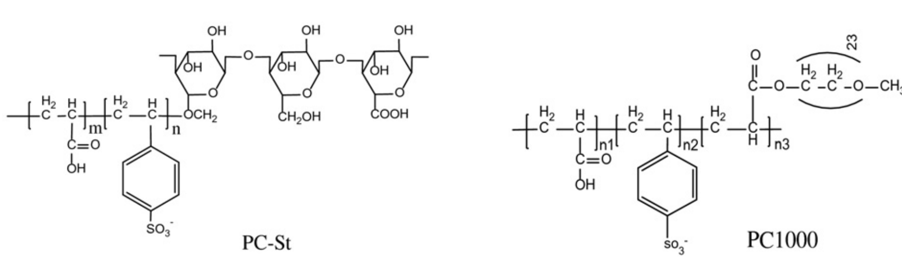

Fig. 1. Two different side chain structure of the molecular structure of polycarboxylate dispersant.