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Investigation on the rheological and stability characteristics of coal–water slurry with long side-chain polycarboxylate dispersant

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A B S T R A C T

A novel comblike polymer, long side-chain polycarboxylate (LcPC), was designed as a dispersant for coal–water slurry (CWS) and synthesized in aqueous solution from the copolymerization of macromonomer polyethylene glycol-acrylate monoester(PA), sodium p-styrene sulfonate (SSS) and acrylamide (AM). PA was prepared by esterifying with polyethylene glycol (PEG200, 400, 600, 800, 1000, 2000) and acrylic acid (AA). The structure of LcPC was characterized. The performance of LcPC as dispersant for the low rank China coal–water slurry (i.e. Shenfu coal) was evaluated and the dispersion mechanism was also explored. Results showed that the dispersant was a polymer with long side-chains modified by $-ArSO_3Na$ and $-CONH_2$ groups. The CWS with LcPC displayed the better rheological and stability characteristics than the traditional dispersant in stock for the low rank China coal (i.e. the apparent viscosity and penetration ratio of CWS with 65 wt.% coal and 0.4 wt.% dispersant were 389 mPa·s and 82.0%, respectively). The properties of the CWS can be further improved in the presence of LcPC because of not only the better electrostatic force with the coal but also the stable steric hindrance of long side-chain.

1. Introduction

Coal water slurry (CWS), a type of novel fuel in the form of liquefaction of coal, is usually prepared by physical method. With advantages such as high solid concentration, lower transport cost, convenient transporting and handling similar with oil, CWS is regarded as one of the most promising alternatives for fuel oil and has received worldwide attention [1]. The technology for combustion of CWS has been developed for many years [2]. In China, the coal is mainly used for power generation on the basis of pulverized coal-fired technology which results in serious coal waste and environmental problems [3]. Therefore, advanced coal utilization technologies are urgently necessary to cater for the increasing use of energy and environmental demands [4,5].

Coal–water slurry (CWS) dispersant is a key factor to prepare fine coal–water slurry [6,7]. Currently, the CWS dispersants are categorized as: naphthalene sulfonate condensates with the high condensation, copolymers of acrylic acid and other acrylic monomers, polyolefin series, lignosulfonate, humic acid salts and sulfonated humic acid salts, carboxylic acid and phosphate salts, and non-ionic dispersing agent [8,9]. The polycarboxylate additives can be widely applied because they have flexible structures to change their molecular weight or molecular structures according to actual needs.

The traditional polycarboxylate CWS dispersant is of the non-ionic or anionic type. However, they have many weaknesses. The CWS which uses the traditional polycarboxylate dispersant has higher apparent viscosity and poorer stability [10,11]. Fortunately, as a novel comblike polymer, long side-chain polycarboxylate dispersant can be used to remedy the shortcomings. It can reduce the relative viscosity of CWS on the basis of higher solid content of CWS. So it has broad application prospects and environmental significance.

In this paper, a novel polycarboxylate (LcPC) dispersant for CWS with long side-chain ($m = 5$–45) and $-ArSO_3Na$ and $-CONH_2$ groups was synthesized, characterized and evaluated. It has been found that the apparent viscosity and stability of CWS with LcPC dispersant are better than the traditional dispersants in stock [12–14]. The good application performance is closely associated with its particular structure.

2. Materials and measurements

2.1. Materials

Polyethylene glycol-acrylate monoester (AA-PEG200, 400, 600, 800, 1000, 2000) was prepared from the esterification of polyethylene glycol (PEG 200, 400, 600, 800, 1000, 2000) and acrylic acid (AA) in our laboratory [15]. Sodium p-styrene sulfonate (SSS, industrial reagent, Nanjing Chemical Industry Corp., China) and acrylamide (AM, Xinyu Corp., China) were freshly distilled under vacuum. Potassium persulfate (KPS, Tianjin Chemical Corp., China) as catalyst was purified by recrystallization from warm water. Sodium hydroxide (Yaohua Corp., China) was freshly dissolved into 30 wt.% solution before use. Naphthalene dispersant and anionic polycarboxylate (copolymer of acrylic acidsodium and

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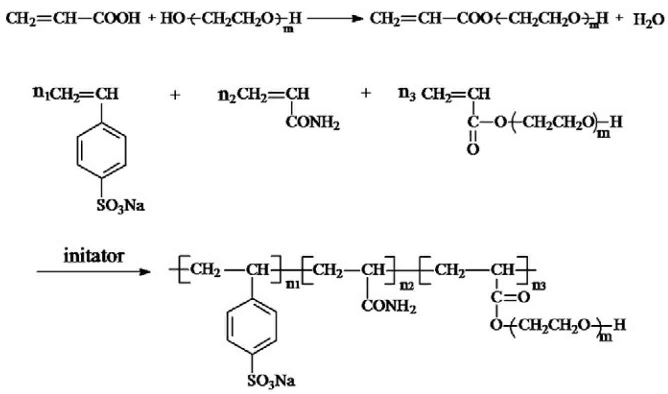

Fig. 1. Scheme of the polymerization reaction.(m = 5,9,14,18,23,45.)

allyl sulfonate) dispersant were supplied from Xianyang Chemical Company of China.

2.2. Preparation

2.2.1. Synthesis of long side-chain polycarboxylate dispersant

Appropriate amounts of distilled water, sodium bisulfite (1.0 wt.% of the total mass of monoesters) and polyethylene glycol-acrylate monoester AA-PEG (200, 400, 600, 800, 1000, 2000) were placed in a 250-ml three-necked flask equipped with a reflux condenser, feeding inlet and thermometer. The reactants were stirred with 600 rpm and heated at a certain temperature under 50 °C. And then reaction monomers, such as SSS, AM and KPS were separately added drop-wise into reactor at about 80 °C. And the mixture was allowed to react at 80 °C for about 3 h. After that, the mixture was cooled to 50 °C and sodium hydroxide solution of 30 wt.% was added under fast stirring (500 rpm) until the pH rose to 7–8 [16–19]. Finally, the LcPC copolymer, a brown transparent liquid, used for the additive of CWS was obtained. The scheme of the reaction was described in Fig. 1.

2.2.2. Synthesis of coal–water slurries

A Shenfu coal that has been pulverized by a dry ball mill was used in this study. The Shenfu coal is not bonding and has low degree of metamorphism. The results of coal quality analysis were given in Table 1.

The coal powder was slowly mixed in a pot containing a certain known quantity of dispersant and deionized water. The contents were continuously stirred by a mixer during the addition of coal, and then the stirring of the slurry was continued for another 10 min at 1200 rpm to ensure the homogenization of CWS. The slurry so prepared was left for the study of its characteristics. According to the multi-peak grade blending technology of Texaco, the particle size distribution of Shenfu coal sample is shown in Fig. 2.

2.3. Measurements

2.3.1. FTIR studies

Fourier transformer infrared (FTIR) spectra in the range of 4000–400 cm^{-1} were recorded on German Brucker EQUI NX55 FTIR spectrophotometer. The polymer prepared was repeatedly purified with acetone and dried warmly to constant weight. The spectra were obtained from the pressed disk of polymer and KBr.

Table 1
The properties of Shenfu coal.

Shenfu coal sample		Content (%)
Proximate anal. (wt.%)	Moisture content	7.68
	Ash	4.59
	Volatile	33.01
Ultimate anal. (wt.%)	Carbon content	82.55
	Hydrogen content	4.69
	Oxygen content	11.59
	Nitrogen content	0.91
	Sulfur content	0.26

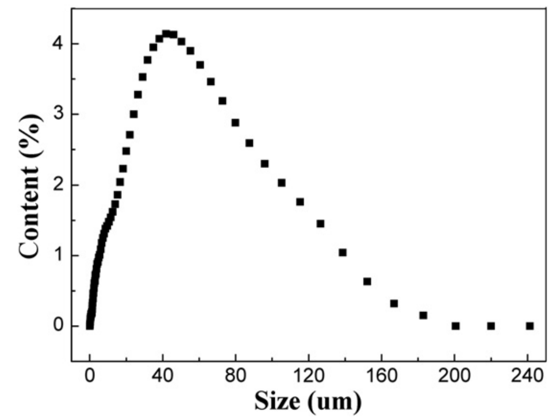

Fig. 2. Particle size distribution of Shenfu coal sample.

2.3.2. Viscometric measurements

The apparent viscosity and shear stress of CWS with shear rate (0–100 s^{-1}) were tested by rheometer (the United States, TA, AR-2000), under the condition of temperature 25 °C.

2.3.3. Static stability measurements

The CWS was stored for 168 h (i.e. 7 days) in a test tube of 50 ml before the stability measurements. The stability was evaluated by the glass rod penetration test (penetration ratio, %) [20,21].

2.3.4. Coal particle size and Zeta potentials

Coal particle size and Zeta potentials were tested by Zetasizer Nano ZS (Malvern Instruments). A serial of 65.0 wt.% CWSs were prepared with different dosages of three kinds of dispersants. After the CWSs were laid for 24 h and centrifugalized for 30 min, the upper solutions of CWSs were taken to measure Zeta potentials.

3. Results and discussion

3.1. Structure of long side-chain polycarboxylate dispersant

Infrared spectra of long side-chain polycarboxylate dispersant are depicted in Fig. 3. Analysis results of spectra are as follows: A typical spectrum shows the −OH group stretching vibration absorption bond at 3413 cm^{-1} and 2873 cm^{-1}. Two peaks at 1105

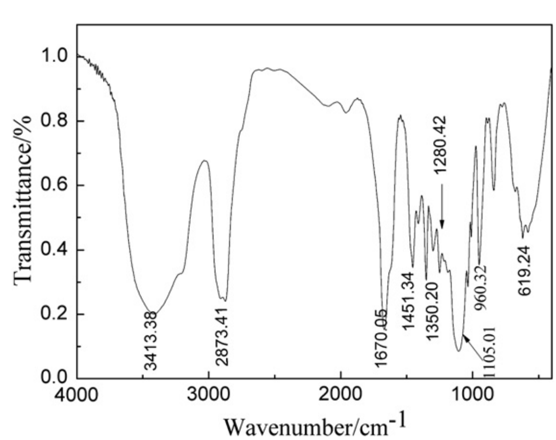

Fig. 3. FTIR spectrogram of long side-chain polycarboxylate dispersant (m = 14).