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Synthesis, characterization and application of a dispersant based on rosin for coal-water slurry

Li Junguo *, Zhang Guanghua, Shang Ting, Zhu Junfeng

Key Laboratory of Additives of Chemistry & Technology for Chemical Industry, Ministry of Education, Xi'an 710021, China
College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China

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ABSTRACT

A rosin derivative and maleopimaric acid diethanolamide (MAD), was synthesized, characterized by FTIR and ^{1}H NMR, and applied as dispersant for the coal-water slurry (CWS) prepared from Chinese Shenfu coal. The CWS application performance investigation shows that the MAD dispersant has better abilities in reducing CWS viscosity and stabilizing the slurry than a commercial dispersant—sulfonated naphthalene-formaldehyde condensate (SNF). The physicochemical property investigation of the two tested dispersants shows that the adsorption amount of the MAD at coal-water interface is much larger than that of SNF, and the MAD has better wetting property than the SNF on the coal surface. It indicated that the excellent capabilities of MAD are related to the adsorption mode of standing upright on the coal surface. Based on the above, the mechanism of dispersion and stabilization of the CWS prepared from MAD dispersant is presented.

1. Introduction

In recent years, due to the rapid depletion of petroleum oil, the coal-water slurry (CWS), regarded as a promising alternative to petroleum, has received considerable attention [1–4]. A desirable CWS should have such properties, such as a high coal content for economic consideration, an excellent stability for storage, and a viscosity as low as possible for preparation, transportation and atomization. To achieve the demands, the selection of a dispersant plays an extremely important role [5–7]. Nowadays, many types of CWS dispersants, such as naphthalene sulfonate formaldehyde condensates, lignosulphonates, polyolefins, humates, polycarboxylates, sulphonated acetone-formaldehyde condensates and non-ionic surfactants, have been known [8–10]. However, most of the dispersants are pure chemicals and very harmful to environment, so it is essential to develop the environment-friendly CWS dispersants in the present background [11–13].

The rosin, an abundantly available and renewable resource, is obtained from the exudations of the pine trees which are extensively widespread in the world. The rosin acid is the main ingredient of rosin, and belongs to the monocarboxylic acid with a hydrophobic three-cycle skeleton. The rosin acid molecule has two reactive sites: the carboxyl group and latent conjugated unsaturation center, through which the hydrophilic groups could be introduced into the molecule. So rosin may be used to synthesize the CWS dispersants with amphiphilic structure.

In this study, the maleopimaric acid diethanolamide (MAD) was synthesized from rosin, maleic anhydride and diethanolamide by Diels–Alder addition and nucleophilic substitution reactions, and characterized by FTIR and ^{1}H NMR. The MAD was applied as dispersant for the CWS prepared from Chinese Shenfu coal, compared with a commercial dispersant—sulfonated naphthalene-formaldehyde condensate (SNF). The CWS application properties such as viscosity and stability, were investigated in the presence of MAD and SNF. The physicochemical characteristics of the two tested dispersants at coal-water interface, including contact angle and adsorption amount, were also studied. Based on the above results, the mechanism for dispersion and stabilization of the CWS from MAD is presented.

2. Experimental

2.1. Materials

Rosin was obtained from Wuzhou Rosin Ltd., industrial grade. Maleic anhydride, p-toluene sulfonic acid (PTSA) and diethanolamine, all analytically pure, were purchased from Nanjing Chemical Industry Inc., Tianjin Chemical Inc. and Shanghai Chuangxin Chemical Inc., respectively. Glacial acetic acid and potassium

* Corresponding author. Tel.: +86 15809252386.
E-mail address: kxrs863@163.com (J. Li).

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hydroxide were chemically pure and from Xi'an Chemical Inc. SNF was industrial product and supplied from Xianyang Chemical Company, all in China.

Shenfu coal from Shenfu, Shaanxi province in China, a kind of non-caking coal, was used in this study. Table 1 shows the results of the proximate and ultimate analyses of the coal. The coal was uninterruptedly comminuted in a dry ball mill to obtain coal powder, then the coal powder was screened and formed coal sample according to the multi-peak grade blending technology of Texaco. The particle size distribution of the coal sample was tested via a particle size analyzer (N4PLUS, Beckman Coulter, USA), and the result is reported in Fig. 1.

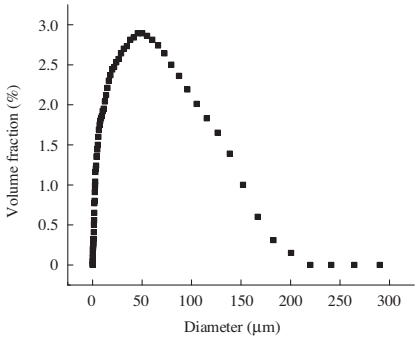

Fig. 1. Particle size distribution of coal sample.

2.2. Synthesis of MAD

In a reactor flask equipped with a temperature controlled electric heating device, a motor stirrer, a thermometer and a reflux condenser, 70 g rosin was melted at 180 °C under N_2 for 2 h. The temperature was lowered to 120 °C, then 11.5 g maleic anhydride, 2 g PTSA and 45 mL glacial acetic acid were added in the flask, and the reaction was carried out at this temperature for 5 h. At the end of the reaction, the reaction temperature was lowered below 5 °C, and a white powder, maleopimaric anhydride (MA), was obtained. The powder was filtered, washed several times with glacial acetic acid, and dried at 60 °C in vacuum to constant weight 10 g MA prepared, 9.6 mL diethanolamine and 0.4 g potassium hydroxide were added to another flask and stirred to react at 160 °C under N_2 for 4 h. The mixture was cooled down to room temperature, then a certain amount of deionized water was added in, and the MAD product was acquired with a mass concentration of approximately 30%.

2.3. Methods

2.3.1. FTIR analysis

The FTIR spectra within a range of 4000–400 cm^{-1} were recorded on a German Bruker VECTOR-22 spectrophotometer. The MAD and MA were repeatedly purified with acetone and then dried in vacuum to constant weight. The spectra were obtained employing potassium bromide pellet technique.

2.3.2. ^1H NMR analysis

The ^1H NMR spectra were measured on a 400 MHz spectrometer (ADVANCE III, Bruker, Germany) using TMS (i.e., tetramethylsilane) as the internal standard, D_2O as the solvent and the probe temperature of 298.5 K.

2.3.3. Viscosity measurement

The viscosity measurement was performed by using a rheometer (AR-2000, TA Instrument Company, USA). The CWS was agitated at 1200 r/min for 5 min before measurement. The temperature was kept within 25 ± 1 °C. The measured viscosity value is the apparent viscosity.

Table 1
Proximate and ultimate analyses (%, by weight) of Shenfu coal sample.

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C
M_{ad}	A_d	V_{daf}	C	H	N	O_{diff}		
7.68	4.59	33.01	82.55	4.69	0.91	11.59	0.26	0.0568

Note: [a]diff means by difference; daf means dry and ash-free basis; M_{ad} means moisture (air-dried basis); A_d means ash (dry basis); V_{daf} means volatile matter (dry and ash-free basis); $S_{t,d}$ means the total sulfur (dry basis).

2.3.4. Static stability test

The CWS prepared was poured into a glass cylinder (3 cm in diameter; CWS layer 15 cm in height). The top of the cylinder was sealed and the CWS was stored at room temperature for a definite period. The static stability of the CWS was evaluated by applying the rod penetration method [14].

2.3.5. Contact angle measurement

The contact angle was measured by applying the static drop method employing a drop shape analyzer (Easydrop, Kruss Company, Germany). The surface of small lump coal was burnished smoothly before the measurement. The static contact angle was obtained from the water droplet on coal surface, and then the photograph of the coal-water interface was taken. The mean value of the contact angle, which was measured ten times, is adopted in this study.

2.3.6. Adsorption amount measurement

In adsorption test, the CWS was prepared with 10% (by weight) of coal and known concentration of a dispersant. The slurry was stirred at 1200 r/min for 10 min, then centrifuged, and the supernatant was used for determining the dispersant equilibrium concentration, employing an UV–vis spectrophotometer (UV-265FW, Shimadzu Corp., Japan). The concentration of the dispersant in the solution was determined from the absorbance at 240 nm according to a predetermined calibration curve. The adsorption amount was calculated as follows:

$$\Gamma = [(c_o - c_t + c_{blank}) \times V]/m \quad (1)$$

where Γ is the adsorption amount per unit mass coal, mg/g; c_o and c_t the initial and final mass concentrations of the dispersant, mg/L; c_{blank} the mass concentrations of the blank sample, mg/L; V the total volume of the solution, L; and m the mass of the coal sample, g.

3. Results and discussion

3.1. Chemical structure

Fig. 2 presents the FTIR spectra of MA and MAD. It is observed that both spectra show the bands in the vicinity of 3446, 2952 and 2867 cm^{-1} related to $\nu_{O\text{-}H}$, ν_{as} and ν_s of —CH_2— group, respectively. The three bands in the Curve *b* are much stronger than those in the Curve *a*, which attributed to the introduction of diethanolamine containing more —OH and —CH_2— groups. In the Curve *a*, the characteristic bands of MA could be seen at 1843 and 1778 cm^{-1} (double band of anhydride group) as well as 1695 cm^{-1} ($\nu_{c=O}$ of —COOH group). As expected, the characteristic absorption band of amide group at 1622 cm^{-1} corresponding to $\nu_{c=O}$, appears in the Curve *b*, which demonstrates that diethanolamine has been indeed attached to MA via chemical bonds.