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Synthesis and evaluation of a novel dispersant with jellyfish-like 3D structure for preparing coal–water slury

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HIGHLIGHTS

- A novel dispersant for coal–water slurry, TAA, was developed and characterized.
- TAA was synthesized by grafting copolymerization of tannic acid and acrylic acid.
- TAA presents in CWS as a unique jellyfish-like 3D structure.
- TAA demonstrates superior slurry-making performance compared to SDS and PSS.
- Made with renewable resources and S/N-free, TAA is environmentally friendly.

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ABSTRACT

TAA, a new dispersant for making coal–water slurry (CWS), has been synthesized by grafting copolymerization of oxidized tannic acid (TA) and acrylic acid (AA). ^{1}H NMR and FTIR tests revealed that TAA has a unique jellyfish-like 3D molecular structure, in agreement with experimental evidences from contact angle and zeta potential measurements. The surfactivity of TAA in aqueous solution was characterized using a surface-tension meter. The rheological properties and static stability of CWS containing 66 wt.% coal with 0.3 wt.% TAA dosage were examined and compared with slurries prepared with two commercial dispersants, i.e. sodium dodecyl sulfate (SDS) and sodium polystyrene sulfonate (PSS). TAA showed excellent slurry-making performance due to its special 3D structure, with polar and non-polar sites in the bottom plane exhibiting affinity to those on the coal particle surfaces to build strong interactions. CWS prepared with TAA showed good stability and favorable rheological properties compared with slurries prepared with SDS and PSS. The present work provides a new approach to the development of high-performance and environmentally friendly S/N-free dispersants from renewable resources.

1. Introduction

Coal–water slurry (CWS), a type of coal-based fluidized fuel prepared by physical method, consists of about 65 wt.%–70 wt.% coal, 29 wt.%–34 wt.% water, and 1 wt.% dispersant [1–4]. A practical CWS should display a high coal content, appropriate yield stress and low apparent viscosity for storage, transportation and burning process [5–8]. Since it is unstable thermodynamically, so flocculation and sediment easily appears when it is stored. Many researches realize the viewpoint that the dispersant plays a more crucial role for the properties of CWS among many factors such as coal properties [9] and particle size [10], because the surface properties of coal will be greatly changed due to the existence of interactions between the coal particle and dispersant so as to improve the stability and rheological behavior of CWS [11,12]. Therefore, many types of dispersants have been synthesized and evaluated [13–15]. According to the molecular structures of dispersants in CWS, they can be classified as two groups: one is one-dimensional linear structure whose hydrophobic ends and polar head groups are together as a straight line, such as naphthalene sulphonate formaldehyde condensate (NSF) [16], dodecyl benzenesulfonic acid sodium salt, and sodium dodecyl sulfate (SDS); the other one is two-dimensional planar structure molecular, which contains many hydrophobic groups and polar groups such as sodium polystyrene sulfonate (PSS), comblike polymer produced by copolymerization of macromonomer polyethylene glycol-acrylate monoester, sodium p-styrene sulfonate and acrylamide [4].

Recently, non-S/N-containing dispersants such as polycarboxylate series have been paid more attention [4,5,17,18]. However,

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their assemblies in CWS belong to above linear or planar structures and the interactions between the dispersant and coal is still weak [19,20]. The desired structure as a dispersant should meet such a requirement that acting sites from dispersant can match well with that of the coal surface although there are some polar groups such as O/S/N-contained species besides a great deal of hydrophobic groups on coal surface. However, the hydrophobic ends of traditional dispersants contain only some hydrophobic groups. Obviously, it is necessary to design a new structure for the dispersant, which contains both hydrophobic sites and polar sites at the same end. In order to achieve this aim, the dispersant with a three-dimensional molecular structure containing polar and hydrophobic groups at one end for CWS should be developed. In view of this idea, we organized a kind of environmental friendly polymer dispersant by renewable resources–tannic acid and acrylic acid (AA), displaying jellyfish-like 3D structure.

Tannic acid (TA), a kind of typical hydrolysable tannin with high molecular weight of 1701, is widely present in leaves, seeds, and flowers of plants and has a large number of phenolic hydroxyl groups and aromatic rings in its planar structure [21]. That is to say, it contains both hydrophobic aromatic rings and polar hydroxyl groups. These characteristics are very close to that of the coal surface, indicating that there exist maximum interactions between TA and coal particles. If we graft some long side chains with AA on its planar structure, these side chains tend to parallelly align in CWS due to the electrostatic repulsion and steric hindrance. Obviously, hydration films may be easily built on the outside of coal particles. This facilitates to reduce the viscosity and increase the stability of CWS. In this work, TA-based dispersant with jellyfish-like 3D structure (TAA) for CWS was designed and synthesized by grafting copolymerization with AA. The physicochemical properties of CWS with TAA, such as rheology and stability, were investigated and compared with that with SDS and PSS. The dispersing and stabilizing mechanism of TAA on coal/water interface was also discussed. Obviously, the cost of dispersant production will be greatly reduced due to the usage of cheap biomass raw materials. In addition, TAA is very environmentally friendly without containing N/S elements. More importantly, the study provides a new strategy for developing a new dispersant for CWS.

2. Experimental

2.1. Materials

TA was of analytical grade and purchased from Tianjin Shentai Corp., China. AA (Tianjin Shentai Corp., China) was freshly distilled under vacuum. Potassium persulfate (KPS, Tianjin Chemical Corp., China) and sodium bisulfite (Tianda Corp., China) as redox catalysts were purified by recrystallization in warm water. About 30 wt.% of sodium hydroxide solution was prepared freshly. SDS and PSS on behalf of one-dimensional linear dispersant and two-dimensional planar dispersant respectively, were tested for comparison with TAA.

The coal used in the experiments was obtained from Taiyuan Coal Gasification Company (Shanxi Province, China) [11]. The results of both proximate and ultimate analysis of the coal are listed in Table 1. Raw coal was dried at 105 °C for 48 h, and then it was crushed and sieved with different meshes. The coal sample used for CWS was prepared according to the multi-peak grade blending technology of Texaco. And the size distribution of coal particles is shown in Fig. 1.

2.2. Preparation

2.2.1. Synthesis of TAA

The typical process was conducted as follows: approximately 100 g distilled water and 10 g TA were first placed in a 250 mL three-necked flask equipped with a reflux condenser and two pressure-equalizing dropping funnels. When the reactant was heated to 80 °C, 1 mL H_2O_2 was dropped into flask with a stirring speed of 400 rpm, and the reaction was maintained for 0.5 h. Subsequently, 8.50 g AA was added drop-wise into the flask through pressure-equalizing dropping funnel. Afterward the aqueous solution of KPS and sodium bisulfite (the mass ratio of KPS and sodium bisulfite was 4:1) were separately dropped into the flask. The polymerization reaction lasted for 3 h at 80 °C and cooled to room temperature [4,18]. Next, the produced brown mixture was neutralized to pH = 8 through adding 30 wt.% of NaOH solution. And a brown transparent TAA solution was obtained and evaporated by rotary evaporator to remove the solvent. At last, it was washed by ethanol to obtain the product (TAA). Fig. 2 describes the flow chart for the synthesis of TAA. Similar procedures were previously reported by others authors [20,22–25].

2.2.2. Preparation of CWS

80 g coal particles were slowly added in a glass beaker containing predetermined quantities of distilled water and dispersant. The mixture was continuously stirred by a helical ribbon mixer at 1200 rpm to ensure the homogenization of CWS during the addition of coal particles; finally, the prepared slurry was allowed to stand for 5 min to release any entrapped air before determining its characteristics.

2.3. Measurement

2.3.1. FTIR and ^1H NMR analysis

Potassium bromide (KBr) discs were used to analyze the sample by FTIR spectrophotometer (BRUKER TENSOR 27). The spectra were obtained with the following parameters: resolution, 4 cm^{-1}; scan frequency, 32 Hz; and scan range, 400–4000 cm^{-1}.

The chemical structures of TA and TAA were also characterized by ^1H NMR analysis recorded on a 600 MHz spectrometer (ADVANCE III, Bruker, Germany) with tetramethylsilane as the internal standard. Additionally, D_2O was applied as a solvent.

2.3.2. Inherent viscosity of TAA

In the study, the inherent viscosity of TAA was measured by the Ubbelohde viscometer with a diameter about 0.8 mm under 25 °C ± 0.1 °C. The stopwatch was used to record the flow time,

Table 1
Proximate and ultimate analysis of the coal.

Proximate analysis (wt.%)				Ultimate analysis (wt.%)[c]					C/O
M_{ad}[a]	A_d[b]	V_d[b]	FC_d[b]	C_d	H_d	O_d	N_d	$S_{t,d}$	
1.17	10.45	26.33	63.22	71.68	4.78	10.79	1.19	1.41	6.64

[a] M_{ad} denotes the moisture content on an air-dried basis.
[b] A_d, V_d and FC_d denote the ash, volatile and fixed carbon contents on a dried basis, respectively.
[c] Ultimate analysis is also on a dried basis.