Fuel 190 (2017) 221–228

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Dispersion performance and mechanism of polycarboxylates bearing side chains of moderate length in coal-water slurries

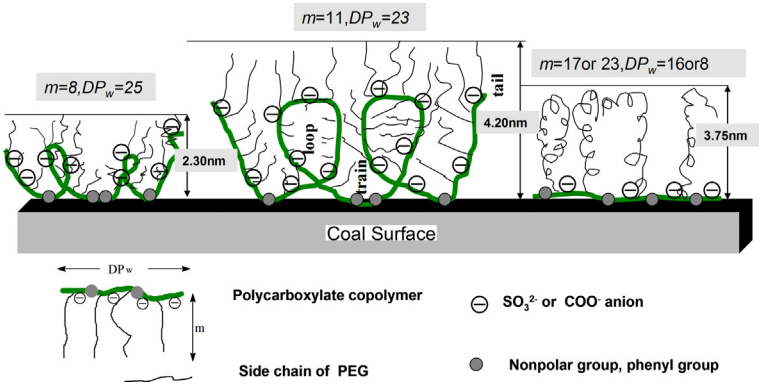
Junfeng Zhu *, Pei Wang, Yuanbo Li, Junguo Li, Guanghua Zhang

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

HIGHLIGHTS

- Polycarboxylate with moderate length side chain shows excellent dispersion property.
- Dispersion relies on polycarboxylate adsorption thickness and density on coal.
- Both length of main chain and side chain can affect polycarboxylate adsorption.
- Adsorption layer thickness was measured to monitor polycarboxylate adsorbing on coal.
- Efficient dispersant can be screened by length ratio of main chain to side chain.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 June 2016
Received in revised form 4 October 2016
Accepted 5 November 2016
Available online 11 November 2016

Keywords:
Polycarboxylate dispersant
Length of side chain
Adsorption behavior
Dispersion performance
Coal-water slurry

ABSTRACT

The side chain structures of polycarboxylates are of great importance for their dispersion performance. The impacts of side chain length (length of polyethyleneglycol PEG, *m* ranging from 8 to 23) of the polycarboxylates on their dispersion performances and adsorption behaviors were investigated systematically to clarify the governing dispersing mechanism. The study reveals the length of side chain affects main chain polymerization degree (DP_w) of polycarboxylates, density of charge groups and adsorption in coal-water interface. Dispersion performances of polycarboxylates in coal-water slurry depend on their adsorption density and the adsorption layer thickness on the coal. The shorter side chain is beneficial to increase adsorption density. However, the longer side chain is good for increasing adsorption layer thickness. Specifically, the polycarboxylate with side chains of moderate length ($m = 11$) has the thickest adsorption layer and the highest adsorption density to result in its excellent dispersion performance. This information indicates that a balance between main chain length and side chain length should exist. So the polycarboxylate with the moderate length ratio of main chain to side chain can be designed as a highly efficient dispersant for low rank coal-water slurries.

1. Introduction

In industrial practice, the rheology of coal-water slurry is a critical factor to affect its storage, transportation and atomization. In order to meet industry needs, high-quality coal-water slurry (CWS) has not only a high concentration of slurry but also an ideal shear thinning effect [1,2]. Therefore, to prepare the CWS with low viscosity and ideal stability is necessary for industrial application, and it may be a feasible solution developing a dispersant with both viscosity-reducing performance and stabilizing ability for CWSs [3,4].

* Corresponding author.
E-mail address: zjfeng123123@163.com (J. Zhu).

http://dx.doi.org/10.1016/j.fuel.2016.11.025
0016-2361/

Comb-like polycarboxylates with polyethyleneglycol (PEG) segment have been extensively used as polymeric dispersants in the concrete mixtures industry [5,6], due to their special properties compared to traditional polyelectrolyte dispersants. Recently, comb-like polycarboxylates have also been proven to be effective robust dispersants for the high-concentrated coal-water slurry system [7,8].

In our previous research, we found that side chain of polycarboxylate played the primary role on the stabilization mechanism [7]. However, what is the effect regularity of side chain length on polycarboxylate adsorption in the interface of coal and water? In order to make CWS better dispersion and rheological behavior, how many PEG segments (m) polycarboxylate should bear? Aiming at solving these questions, a series of polycarboxylates bearing pendent groups was synthesized using esterified macromer MPEGAA with different lengths of PEG segments. Main chain polymerization degrees (DP_w) of polycarboxylates and density of charge groups vary as the length of side chain varies. The dispersion, rheological properties and zeta potential of coal-water slurries incorporating the polycarboxylates with different lengths of side chain were evaluated. Meanwhile, the adsorption density and adsorption layer thickness of polycarboxylates in coal-water interface were established by ultraviolet–visible light absorption spectra (UV) and X-ray photoelectron spectroscopy (XPS). The effects of PEG length in the polycarboxylates on the dispersion and rheology of concentrated CWS and their interface adsorption were investigated systematically. The information produced can help developing relationships between structure and property and illustrating the mechanism of the polycarboxylate dispersants. Comparing the dispersion and rheological behavior of CWSs with the polycarboxylates adsorption in coal-water interface, the polycarboxylate with the moderate length ratio of main chain to side chain (DP_w/m) will be screened to serve as the dispersant for low rank coal-water slurries.

2. Materials and measurements

2.1. Materials

Methoxy poly(ethylene oxide) (MPEG) with different molecular weights (M_w = 350, 500, 750, 1000) was purchased from Jiangsu Haian Chemical Reagent (China); sodium *p*-styrenesulfonate (SSS), acrylic acid (AA) and *p*-toluene sulfonic acid were purchased from Tianjin Chemical Reagent (China); A commercial dispersant sulfonated naphthol-formaldehyde (SNF) was employed as reference dispersant from Xianyang Chemical additives company in China. Binchang coal used in this study was from Binxian, Shannxi province of China. The coal is a low rank coal with high ratio of oxygen to carbon and internal water. It contains 5.71 wt% moisture, 10.58 wt% ash, 23.59 wt% volatile matter, and other elements. The results of coal quality analysis were given in Table 1.

Table 1
Proximate and ultimate analyses of Binchang coal sample on air dried basis.

	Item	Content
Proximate analyses	Moisture (wt%)	5.71
	Ash (wt%)	10.58
	Volatile matter (wt%)	23.59
	Fixed carbon (wt%)	60.12
Ultimate analyses	Carbon (wt%)	67.84
	Sulfur (wt%)	0.36
	Hydrogen (wt%)	3.97
	Oxygen (wt%)	10.86
	Nitrogen (wt%)	1.04
	Oxygen/carbon ratio (wt%)	0.16
	Surface area (m^2/g)	6.667

2.2. Preparation

2.2.1. Synthesis of polycarboxylate with pendent groups

A series of poly(AA)-co-poly(SSS)-co-poly(MPEGAA) polycarboxylate copolymers (herein after called $PC_{m=8}$, $PC_{m=11}$, $PC_{m=17}$ and $PC_{m=23}$) with various length of PEG branch-chains (m = 8, 11, 17, 23) was synthesized by free radical polymerization of sodium *p*-styrenesulfonate (SSS), acrylic acid (AA) and methoxypolyethyle neglycol-acrylic acid (MPEGAA) [9]. Esterified macromer of MPEGAA (MPEGAA 350, 500, 750, 1000) were first synthesized by catalytic esterification reaction between MPEG and the AA in the presence of *p*-toluene sulfonic acid as the catalyst [10]. The synthesis process of the polycarboxylate dispersants was shown in Fig. 1.

2.2.2. Preparation of coal-water slurries

Depending on the *multi-peak grade blending technology* for Texaco gasification, the Binchang coal particles used in this study were pulverized via a dry XM-4 planetary ball mill (Foshan Branch of Guangdong Ceramics Company). The size distribution of Binchang coal particles was determined via the particle size analyzer (BT-9300Z, Dandong, China). The result was presented in Fig. 2. The average size of volume for the coal particles is about 25.35 μm. The D50 for the coal particles is about 18.21 μm. The D90 is about 59.93 μm. Then, the coal particles were gradually mixed in a beaker containing a certain quantity of dispersant and deionized water. The dispersant (solid content calculated by 30 wt%) was added into coal-water mixture at a dosage of 0.4 wt % (based on the quantity of dry coal). The mixture was continuously stirred for 10 min at 1200 rpm to ensure the homogenization of CWS [11].

2.3. Measurements

2.3.1. Characterization of polycarboxylate

The crude synthesized polycarboxylate was purified by anhydrous ether and dried at 60 °C under vacuum to the constant weight. Fourier transformer infrared (FTIR) spectrum was obtained from the pressed disc of polycarboxylate and KBr [12]. The ^{1}H NMR spectrum of the polycarboxylate was measured on a 400 MHz spectrum (Bruker AVANCE-400 MHz NMR Spectrometer, USA) using TMS (i.e. tetramethylsilane) as the internal standard, D_2O as the solvent and the probe temperature was kept constant at 295.5 K [13]. The PC molecular weight M_w, polymerization degree DP_w, distribution and pendent groups content were collected using GPC_{max} + TDA305 Viscotek TDAmax gel chromatography system (British Malvern instrument company). 0.1 mol L^{-1} $NaNO_3$ solutions flowing at a rate of 1 mL min^{-1} and at a temperature of 35°C was used as the mobile phase. The internal standards were polyethylene oxides [14].

2.3.2. Viscometric measurements

The apparent viscosity of coal-water slurries was tested by rheometer (the United States, Brookfield, R/S-SST Plus), at 25 °C. In order to comply with the needs of the coal gasification industry, the CWSs were prepared at a high solid content of 65 wt% and the polycarboxylate dispersants (solid content calculated by to be 30 wt%) were added into coal-water slurries at a dosage of 0.4 wt % (based on the mass of dry coal). After thorough mixing for about 30 min, the slurries were transferred directly into the measuring fixtures. In order to obtain the flow curves and thixotropy information of the slurries, the shear rate was increased from 0 to 100 s^{-1} in 3 min then returned back to 0 in another 3 min [15]. The viscosity value at a shear rate of 100 s^{-1} was used as the apparent viscosity of the suspension, unless otherwise stated.