Effects of Chemical Structure on the Properties of Carboxylate-Type Copolymer Dispersant for Coal-Water Slurry

Renfu Xu, Wei Zhuang, Qihui He, Jun Cai, and Baixing Hu
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

Jian Shen
College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210097, Jiangsu, China; and Research Center of Surface and Interface Chemistry and Engineering Technology, Nanjing University, Nanjing 210093, Jiangsu, China

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In this study, a series of carboxylate-type copolymer dispersants were prepared. The effects of chemical structures of the copolymer dispersants, including the molecular weight, kind, quantity and ratio of hydrophilic/hydrophobic groups, and side chain length, on the solid loading, apparent viscosity, zeta potential, rheological behavior, and stability of coal-water slurry (CWS) prepared from Dongtan, Yima, and Datong coals were systematically investigated. The dispersion performance of the copolymer can be improved by adjusting its chemical structures, and the dispersion mechanism was discussed. In addition, a high solid loading CWS with excellent stability toward settling can be achieved by means of the copolymer dispersant and carboxymethyl cellulose sodium salt (CMC-Na). Experiments have proved that the copolymer has the potential to be developed as a new high-effective dispersant for CWS. *AIChE J,* 55: 2461–2467, 2009
Keywords: chemical structure, copolymer, dispersant, coal-water slurry

Introduction

Since environmental problems associated with the increased use of energy are going to attract greater importance in the coming years, the efficient utilization of coal resource is an unavoidable trend at present and can play a very vital role on future energy policy. Advanced coal utilization technologies are urgently necessary to cater for the increasing use of energy and environmental demands and also to utilize the coal resources efficiently, economically, and cleanly.[1,2] One of such approaches is coal-water slurry (CWS) technology, which has been regarded as a promising fuel instead of petroleum oil because of the rapid depletion of the latter. The major reasons for investigating the suitability of CWS as a fuel are that these fuel slurries can be stored without the danger of coal-dust explosion, pumped, transported in pipelines, and combusted like residual fuel oil in an environmentally benign manner.[2–5]

Coal-water slurries are concentrated suspensions of fine coal in water. A practical CWS as a liquid fuel should have such properties as an appropriate yield value to maintain its stability during storage, a low apparent viscosity to accommodate CWS's spray for combustion, and a high solid content for economical use.[6–8] It is necessary for CWS to display excellent fluidity and stability suitable for its handling in preparation, storage, transportation, and combustion processes.[9,10]

The formation of CWS is greatly influenced by the surface chemistry of coal, which is determined by the coal nature, such as coal coalification degree, inherent moisture content,

Correspondence concerning this article should be addressed to B. Hu at baixinghu1010@yahoo.com

Table 1. Proximate and Ultimate Analyses of Three Coal Samples on Dry Basis

Component	Item	Coal Type		
		Dongtan	Yima	Datong
Proximate analyses	Ash (wt %)	10.10	24.67*	9.71
	Volatile matter (wt %)	34.26	28.90	26.80
	Inherent moisture (wt %)	2.16	2.71	4.76
	Calorific value (kJ/kg)	28.15	23.81	26.69
Ultimate analyses	C (wt %)	72.30	62.71	74.56
	H (wt %)	4.69	4.34	5.54
	N (wt %)	1.34	0.71	0.42
	S (wt %)	0.52	0.50	0.29
	O (wt %)	8.86	12.61	11.05

*Yima coal is directly taken from the colliery and the flotation process is not carried out.

ash content, coal surface wettability, O/C ratio, and porosity. Therefore, the coal properties should be considered in CWS preparation, and usually the applicability for the coals with different coalification degrees is used to evaluate the performance of a dispersant.[11,12]

There is a general consensus that the additive for CWS is a crucial factor in improving the properties of CWS.[13–17] It is well known that the fluidity of a CWS with a high coal concentration is largely affected by the nature of dispersant.[18] Dispersants adsorb on the particle surface, thus modifying the surface properties of coal particles. Many series of dispersants, such as sodium naphthalene sulfonate formaldehyde condensate, sodium polystyrene sulfonate, and nonionic surfactants, as well as lignosulphonate and humate, have been known as useful dispersants for the CWS.[6,19]

Polymer dispersants are generally added to CWS suspensions in order to control aggregation properties and obtain high solid loadings. Knowledge of the dispersion and stabilization mechanisms in coal-water suspensions is of critical importance. Many mechanisms of action and theories of polymer dispersants in suspensions have been discussed, for example, steric stabilization and rebridging, depletion, electrosteric effects, etc.[20] After the dispersant is adsorbed by coal particles, electrostatic stabilization of coal particles in water may be obtained through repulsion of overlapping diffuse double layers when coal particles approach each other. In suspensions with moderate solids loadings electrostatic stabilization of coal particles may be sufficient, but it can be ineffective when the solids content is increased and the particles are forced together mechanically.[21]

Steric hindrance effect is believed to play an important role in the stabilization of suspension systems with high solids loadings. In sterically stabilized systems, flocculation is prevented since the total energy interaction is repulsive also at very short distances provided that the particle surfaces are covered with polymer. The steric repulsion originates from free energy changes due to interactions between adsorbed polymer chains as the coal particles are brought together.

The dispersion of coal particles in water using charged homopolymer dispersants has been investigated extensively, but few previous studies on copolymers as dispersant for CWS have been reported. Several literatures reported the effects of copolymer dispersant chemical structure on the properties of CWS, but systematical studies on the dispersion mechanism of copolymer dispersant, and the rheological behavior and stability of CWS prepared from the copolymer dispersant could not be found.[22,23] In recent years, copolymer polyelectrolytes have gained more and more attention due to its excellent dispersing abilities.[24–26] Compared to homopolymers, copolymer dispersants present the advantage to have different functional groups, which can play different roles in CWS processing.[27] The chemical structure of copolymer dispersant can be easily adjusted by changing monomer proportions and polymeric reaction conditions, which would make the performance of copolymer dispersant improved for different types of coal used in CWS.

In this article, a series of carboxylate-type copolymer dispersants were prepared. The effects of chemical structures of the copolymer dispersants, including the molecular weight, kind, quantity and ratio of hydrophilic/hydrophobic groups, and side chain length, on the solid loading, apparent viscosity, rheological behavior, and stability of CWS prepared from three Chinese coals were systematically investigated. Based on the results, the dispersion and stabilization mechanisms were discussed.

Experimental Materials and Methods

Materials

Dongtan, Yima, and Datong coal samples taken from different areas of China were used. The proximate and ultimate analyses of three coal samples are given in Table 1.

The raw coal was crushed in jaw and roll type crushers to obtain particles of sizes less than 3 mm, respectively. Then, the crushed particles were comminuted in a bill mill to obtain samples by controlling of milling time, loading, mill speed, etc. The particle size distributions of the coal samples were determined by LS-CWM (2) type particle sizer produced by Omec Science and Technology Ltd., Zhuhai of China. The particle size distributions of three coal samples are shown in Figure 1. As seen from Figure 1, because of experimental conditions and coal self-characteristics, Datong coal contains significant amount of coarser particles than the others. In CWS technology, it is well known that the small coal particles may enter the voids between the larger coal

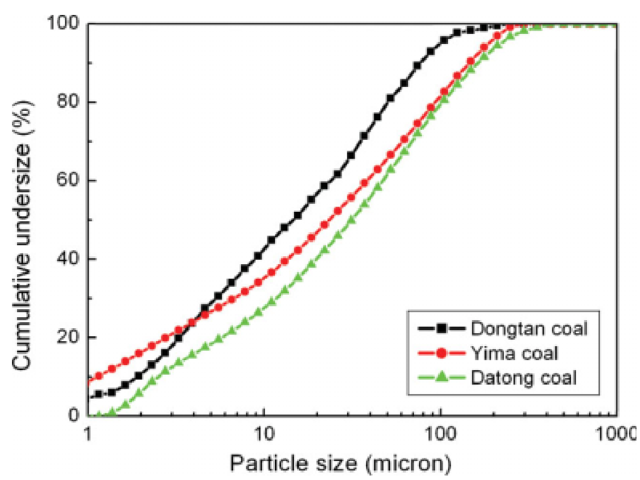

Figure 1. Particle size distributions for Dongtan, Yima, and Datong coal samples.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

particles, and less water is required to fill the interparticle voids. Furthermore, the smaller particles filling the gaps between larger particles can even act as a lubricant, in turn leading to higher relative mobility of the coal particles in the suspension and consequently to lower the viscosity. Therefore, such particle size distribution is disadvantageous to obtain high solid loading for Datong coal slurry.

Two different chemicals were used as dispersants: naphthalene sulfonate formaldehyde condensate (NSF) and carboxylate-type copolymer, which is a sulfonated copolymer of styrene, maleic anhydride, and methyl-terminated allyl alcohol polyoxyethylene ether. The chemical structure of the copolymer is shown in Figure 2.

As shown in Figure 2, the copolymer contains ionizable carboxylic and sulfonic groups along the backbone and charge-neutral polyethylene oxide (PEO) side chains.

Carboxymethyl cellulose sodium salt (CMC-Na, weight average molecular weight: 7.6×10^4), which is a water-soluble polymer produced by Suzhou of China, was used as a stabilizer. The dosages of dispersant and stabilizer were based on dry coal, unless otherwise stated.

CWS preparation

The CWS preparation procedure was identical for all samples tested. Distilled water was weighed into a 400 ml beaker, and the selected dispersant and stabilizer were dissolved in predetermined dosages. The weighed coal sample was slowly poured into the beaker and the contents were stirred by a propeller-type agitator for 20 min after addition of all the coal. The coal concentration was accurately determined from the weight loss measured after drying in an oven at 105°C for 2 h. Before testing, a slurry sample was always thoroughly mixed by stirring to ensure homogeneity.

Viscosity and rheology measurements

The apparent viscosity of CWM was measured using NXS−11A rotary viscometer made in Chengdu of China, which was equipped with a circulating water bath. The geometry of NXS-11A viscometer was a rotational concentric cylinder (rotor-cylinder) system. There were five sets of rotor-cylinder measure systems (A, B, C, D, and E) for different viscosity ranges. At a constant temperature of 25°C, measures were performed using B system and required sample volume was 60 ml. For B system, cylinder inner diameter and rotor outer diameter were 4 and 3.177 cm, respectively, and the gap size between rotor and cylinder was about 0.41 cm. Based on the computer program, the apparent viscosity at 28.38 s^{-1} shear rate would be obtained. The measured apparent viscosity in the article was corresponding to this shear rate, unless otherwise stated.

The shear-dependent rheological properties of the samples were determined by changing the shear rate then acquiring the resulting apparent viscosity as a function of shear rate.

Zeta potential measurements

The zeta potential of coal particles was measured on Zetasize 3000 HS (Malvern, UK). The ionic strength of a dilute suspension (2 wt %) was maintained at 10^{-3} M using NaCl. After pH value of the suspension was adjusted to 9.0 by a small amount of HCl or NaOH solution, the sample was ultrasonicated for 15 min. Both solutions of NSF and copolymer are alkaline, and the CWSs prepared from these two dispersants exhibit alkalinity. To conveniently compare the performance of NSF and copolymer dispersant, the pH value was set to 9.0. Each sample was repeatedly measured three times and the value reported was the mean value.

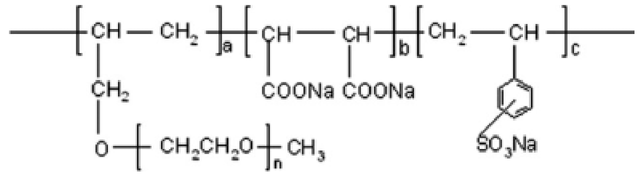

Figure 2. The chemical structure of copolymer.

Static stability measurements

The evaluation of static stability was based on the CWM Quality Testing Methods (CCUJ Unified Methods, Center for Coal Utilization, Japan, 1994). The static stability of slurry could be estimated according to the particles sedimentation velocity. The average static sedimentation velocity could be determined after the slurry sample statically held for 7 days. Details on the operation for measurement of CWS static stability could be found in the reference.[15]

Results and Discussion

The effect of the molecular structure of copolymer on slurryability

Molecular Weight. The molar ratio of styrene, maleic anhydride, and methyl-terminated allyl alcohol polyoxyethylene ether, the sulfonation degree, and the PEO side chain length were fixed at 1:1:3, 100%, and 23 (unless otherwise stated), respectively, based on our search results from optimal dispersion of calcium carbonate aqueous suspension and fresh cement paste, and the molecular weight (M_W) of copolymer (weight-average molecular weight, procured from gel permeation chromatography) varied from the initiator concentration. The relationship between the apparent viscosity of CWS and copolymer molecular weight is given in Figure 3. For each sample, a constant Dongtan coal loading of 68.0% was used. As seen in Figure 3, an optimum range of molecular weight between 40,000 and 60,000 g/mol was indicated. It is disadvantageous to dispersion ability of copolymer when the molecular weight is too low or high.

It is well known that the amount of ionizable carboxylic and sulfonic groups increases with an increase in the copolymer molecular weight. After coal particles adsorbed the copolymer dispersant, the electrostatic repulsion between coal particles can be large. So the reduction of CWS viscosity occurs with increasing the copolymer molecular weight. The increase of viscosity of CWS prepared with high molecular weight copolymer is due to the increase of water viscosity resulting from the solution of copolymer dispersant. In addition, the flocculation between coal particles will be promoted because the bridging adsorption becomes possible when the molecular weight of copolymer is larger, which causes an increase in CWS viscosity.

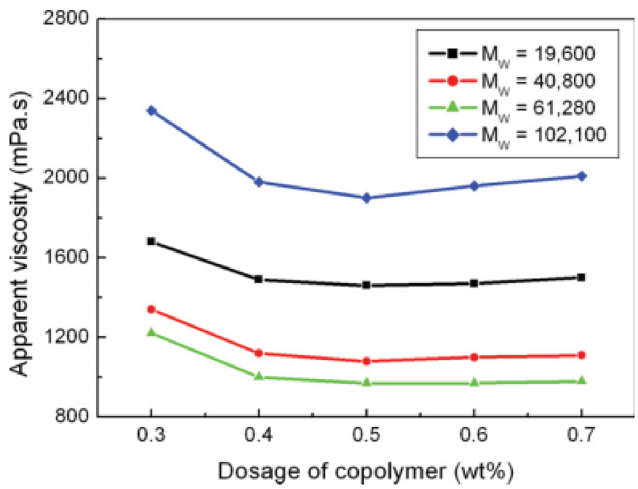

Figure 3. Effect of the dosage of copolymer on apparent viscosity of Dongtan CWS under different molecular weights.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Also, there exists the optimal dosage, suggesting a saturation adsorption, to minimize the apparent viscosity of CWS. A further addition of polymer dispersant slightly increases the viscosity. Two factors account for this phenomenon. First, the increase of the counter-ion density (Na^+) will compress electric double layers and reduce the relatively long-range electrostatic repulsive force. Secondly, the structure of the adsorbed polymer dispersant on particle surface will be compressed by the negative charge (COO^-, SO_3^-) in free polymers. The compression of adsorbed structure of polymer reduces the short-range steric repulsive force between particles. Both reducing mechanism of long-range electrostatic and short-range steric repulsive force prompted the formation of large aggregates in the suspension and increased the suspension viscosity.[20]

PEO Side Chain Length. In the above-mentioned range of molecular weight, copolymers with different PEO side chain length were used for the study. The PEO has degrees of polymerization of 9, 23, 45, and 68 corresponding to copolymer molecular weight of 55,610, 61,280, 53,300, and 54,270, respectively. Under the condition of 0.5% copolymer dosage, the effect of PEO length on the apparent viscosity of CWS is given in Figure 4. To exhibit good fluidity and practicability, the apparent viscosity of CWS is usually set to about 1000 mPa s, and the solid loading of three slurry samples is 68.0, 66.8, and 65.3%, respectively. It is observed that the apparent viscosity exhibits the minimum value when PEO length is 23. Also, the viscosity of Datong CWS is insensitive to PEO length, which is possibly relative to coal self-characteristics.

It is possible to obtain steric hindrance effect if the polymer chains stretch out from the particle surface. This depends on the configuration of the polymer on the coal particle surface. The copolymer backbones that contain carboxylic and sulfonic groups are adsorbed on coal particles surface as the anchor groups, and the PEO side chains will protrude out into the bulk solution, which would provide steric repulsion, because water is a good solvent for PEO chain segments.[21]

In the design of steric stabilization chains, the polymerization degree of PEO chain is an obviously important parameter, with too low a polymerization degree causing dispersion instability, and too high a polymerization degree giving reduced performance, probably because of a tendency for the chains to ''fold back'' on to themselves or bridging flocculation between particles.[28]

Kind and Quantity of Hydrophilic Group. In this section, a copolymer dispersant was selected, whose molecular weight and PEO length are 61,280, and 23, respectively, according to above experimental results.

There are two hydrophilic groups, carboxylic and sulfonic groups, along the copolymer backbone. To investigate the effects of kind and quantity of hydrophilic group on the dispersion capability of copolymer, the molar ratio between styrene and maleic anhydride segments varied from different proportions of two monomers in the copolymerization reaction. Under the circumstance of 0.5% copolymer dosage, the relationship between the molar percent of maleic anhydride (the fraction of the number of maleic anhydride repeating units to the total number of styrene and maleic anhydride repeating units in the copolymer structure) and apparent viscosity of CWS is given in Figure 5. It is revealed from Figure 5 that there exists a minimum viscosity value for each of three slurry samples when the molar fraction of maleic anhydride is between 45 and 55%.

It is well known that the dissociation of a styrene sulfonate repeating unit can generate a negative charge, and two negative charges will be generated from the dissociation of a maleic anhydride repeating unit. Thus, the negative charges along the copolymer backbone increase with the increase of maleic anhydride molar fraction. When the molar fraction of maleic anhydride increases up to about 45%, electrostatic repulsion between coal particles that adsorb the copolymer dispersant increases and the apparent viscosity of CWS rapidly decreases. But the molar fraction of maleic anhydride exceeds 55%, the adsorption affinity between coal particle and copolymer is weakened due to high charge density.

The above copolymers were sulfonated by excessive oleum during a long reaction time and could be thought to

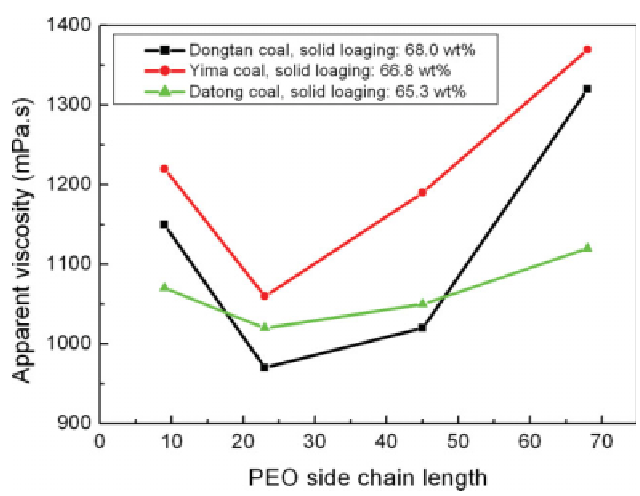

Figure 4. Effect of PEO side chain length on the apparent viscosity of CWS.

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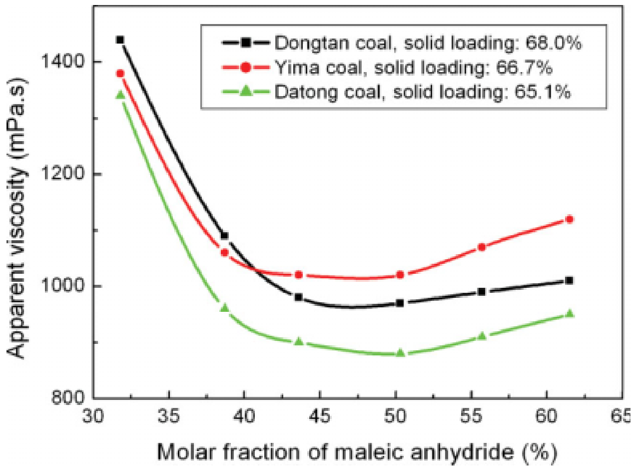

Figure 5. Relationship between the molar percent of maleic anhydride and apparent viscosity of CWS.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

obtain a complete sulfonation. The sulfonation degree (molar percent of sulfonic group to styrene unit) could be adjusted by changing oleum dosage, reaction time, and temperature. The relationship between the sulfonation degree and the apparent viscosity was investigated with 0.5 wt % copolymer (the molar ratio of styrene to maleic anhydride was 1:1) used. The results are shown in Figure 6.

As shown in Figure 6, the apparent viscosity of CWS rapidly decreases when the sulfonation degree increases up to about 75%. It is because, with the increase of sulfonation degree, the quantities of negatives capable of giving to coal surfaces and resulting electrostatic repulsion between coal particles will increase. However, when the sulfonation degree is more than 75%, its effect on the viscosity is small. For high sulfonation degree, the adsorption of copolymer is hampered by the electrostatic repulsion between highly negative charged copolymer and coal particles. In the case of Yima coal, the viscosity slightly increases with the sulfonation degree over 75%. This can be related to the surface characteristic of Yima coal.

Based on the relationships between chemical structures and dispersion capability, the copolymer with molecular weight of 61,280, PEO side chain length of 23, maleic anhydride molar fraction of 50.3%, and sulfonation degree of 100% was used in the following tests.

Dispersion Mechanism. The zeta potential as a function of NSF and copolymer dosage is shown in Figure 7.

It is observed that the net surface charge of coal particles is negative, and the incorporation of dispersant causes a decrease of zeta potential as a consequence of the adsorption of the anionic polymer on the particle surface. In general, the zeta potential decreases first with increasing dispersant concentration, and then reaches a plateau of approximately −70 and −35 mV when the amount of dispersant increases to about 0.6 wt % for NSF and 0.4 wt % for copolymer, respectively. The value at the plateau accounts for the amount of dispersants required for the formation of saturated adsorption on the particle surface. The critical dosage for NSF is greater than that for copolymer and the absolute value of zeta potential at plateau for suspensions with copolymer is much less than that with NSF.

The changes in apparent viscosity of Dongtan CWS (solid loading: 68.0 wt %) corresponding to NSF and copolymer dosage were examined, respectively, and the results are presented in Figure 8.

One could note that a steep decrease in viscosity is observed at low dispersant dosages followed by a plateau or slight viscosity increase with further increasing dispersant dosages. The viscosity minimum in the dispersant demand profile corresponds to the optimum dispersant level. Thus, it is established from the study that the optimum dosages of NSF and copolymer in CWS formulation should be 0.6 and 0.4–0.5 wt %, respectively. The results are in good agreement with those from the zeta potential curves mentioned earlier. Compared with NSF, copolymer requires a less amount to reach a minimum viscosity and approached value,

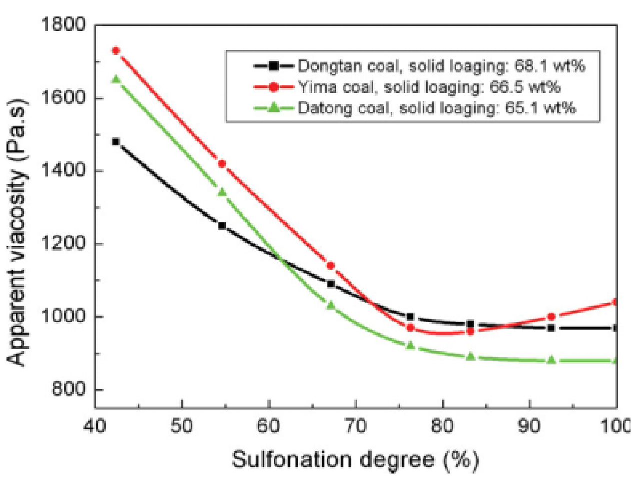

Figure 6. Relationship between the sulfonation degree and apparent viscosity of CWS.

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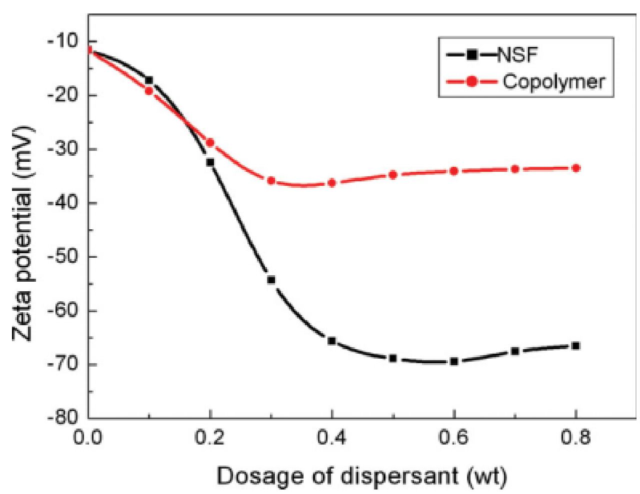

Figure 7. Effect of dispersant dosage on the zeta potential of Dongtan coal particle.

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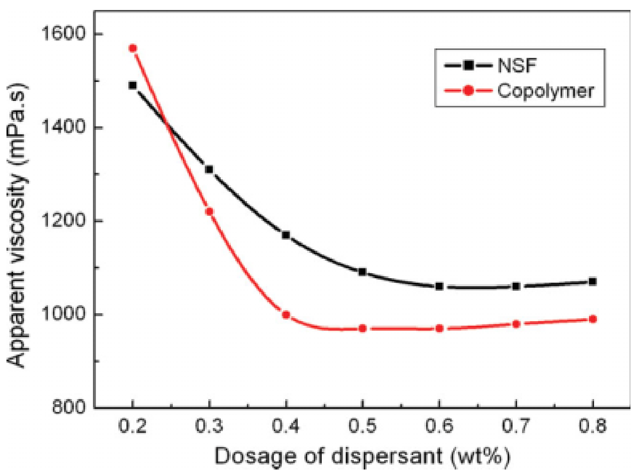

Figure 8. The apparent viscosity of Dongtan CWS as a function of NSF and copolymer dosage.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

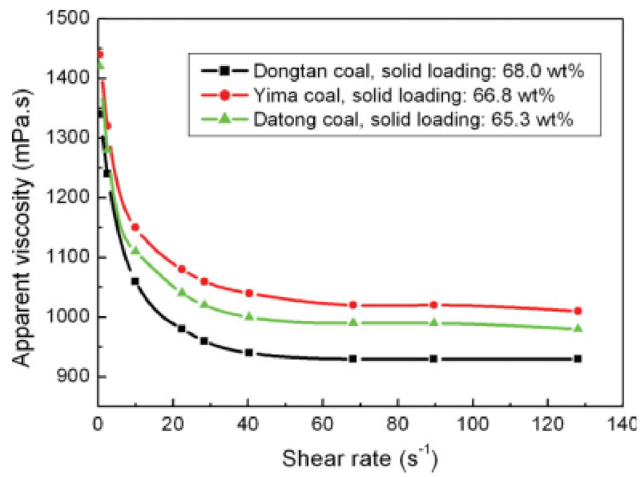

Figure 9. Effect of shear rate on the apparent viscosity of slurries.

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and it exhibits excellent dispersion performance. The different dispersion actions, induced by these two chemicals, account for this difference.

The polyelectrolyte may lay flat on the surface as a pancake, which it is likely to do if the surface coverage is low, or it may coil up in mushrooms if the net charge is low. When the net charge and adsorbed amount is high, the polyelectrolyte chain will adsorb in trains on the surface and loops protruding out into the solution. The latter configuration would provide both electrostatic and steric repulsion.[29] NSF has naphthalene rings in its molecules that are highly affinitive with coal surfaces having polycyclic aromatic property. When used as a dispersant, NSF is flatly adsorbed on particle surfaces, and only the electrostatic repulsion effect can be expected.[30] The copolymer contains ionizable carboxylic and sulfonic groups along the backbone which could provide electrostatic repulsion, and charge-neutral PEO side chains which should provide steric repulsion.

From the results of zeta potential measurement, the electrostatic repulsion between coal particles with NSF used is greater than that with copolymer used when each optimal amount has arrived. However, the copolymer has more excellent dispersion ability than NSF, which owes to the steric hindrance effect. As far as copolymer is considered, steric repulsion is believed to play an important role in the dispersion of CWS systems.

Rheological Behavior. The application property of CWS is influenced significantly by its rheological behavior. Generally, one aims at a pseudo-plastic system with sufficiently high low shear viscosity (to prevent sedimentation) and low high shear viscosity for ease of application.[31]

The effect of shear rate on the apparent viscosity of three slurry samples is illustrated in Figure 9. For each sample, a constant amount of 0.5% copolymer was used. As it is seen in Figure 9, the slurries exhibit shear-thinning or pseudo-plastic behavior with an apparent viscosity decreasing with increasing shear rate.

Static Stability. The effects of dispersant type and CMC-Na on the sedimentation velocities of three slurry samples are reported in Table 2. It is observed that the average sedimentation velocity is markedly decreased and the static stability is improved when CMC-Na is used as a stabilizer. Under the condition of addition of 0.02 wt % CMC-Na, the slurry prepared with the copolymer dispersant displays more excellent stability than that prepared with NSF. Besides, though the addition of CMC-Na will inevitably increase the viscosity of CWS, in the case of the slurry prepared with the copolymer, this effect is relatively lower. Thus, a high solid loading CWS with excellent stability toward settling can be

Table 2. Effects of Dispersants and CMC-Na on Static Sedimentation Velocities of Dongtan, Yima, and Datong Coal-Water Slurries

Coal Sample	Coal Concentration (wt %)	Dispersant	CMC-Na Stabilizer (wt %)	Viscosity (mPa s)	Sedimentation Velocity (%/d)
Dongtan	68.0	0.5 wt % copolymer	0	970	1.43
		0.5 wt % copolymer	0.02	1220	0.13
		0.6 wt % NSF	0.02	1450	0.19
Yima	66.8	0.5 wt % copolymer	0	1060	1.87
		0.5 wt % copolymer	0.02	1370	0.22
		0.6 wt % NSF	0.02	1580	0.35
Datong	65.3	0.5 wt % copolymer	0	1020	2.06
		0.5 wt % copolymer	0.02	1190	0.31
		0.6 wt % NSF	0.02	1310	0.54

expected by means of the copolymer dispersant and appropriate stabilizer.

Conclusions

In the investigation of the effects of the copolymer dispersant, CMC-Na stabilizer on the properties of CWS prepared with Dongtan, Yima, and Datong coal samples, the following results are obtained:

By adjusting the chemical structure of the copolymer dispersant including the molecular weight, kind, quantity and ratio of hydrophilic/hydrophobic groups, and side chain length, its dispersion performance can be improved for different types of coal used in CWS.

The dispersing mechanism of the copolymer is that, after being adsorbed onto the coal particles surface, the electrostatic and steric (or electrosteric) repulsions can be simultaneously created. Moreover, steric repulsion plays an especially important role in the dispersion of CWS suspension.

A high solid loading CWS, with excellent stability and fluidity suitable for its handling in preparation, storage, transportation, and combustion processes, can be achieved by means of the copolymer dispersant and appropriate stabilizer. The copolymer has the potential to be developed as a new high-effective dispersant for CWS.

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