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Synthesis and super retarding performance in cement production of diethanolamine modified lignin surfactant

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HIGHLIGHTS

- Diethanolamine modified lignin (DML) has been synthesized and firstly used for the production of Portland cement.
- DML is effective in the improvement of grindability and particle size distribution, and mechanical properties of the produced cements.
- In contrast to lignin, both the initial and final setting times of tested cements with DML increased obviously.

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ABSTRACT

The diethanolamine modified lignin (DML) was synthesized by lignin, chloromethyloxirane and diethanolamine, and firstly used for the production of Portland cement. Cement mortars were tested for the standard consistency, setting times and mechanical properties. The results showed that DML improved the grindability and particle size distribution efficiently, and the cement mortars made with DML exhibited excellent mechanical properties. In contrast to unmodified lignin, it was found incidentally that DML not only had excellent grinding performance, but also showed strong and unique retarding effect. The retarding mechanism mainly attributed to steric hindrance of molecular structure and electrostatic interactions of anchoring groups adsorbed on the surface of cement during the hydration process, and just the synergistic effects retarded further hydration of cement.

1. Introduction

Cement as one of the most important construction materials has been widely used in various industrial and civil buildings. However, cement has already been regarded as energy/resource-consumed and unfriendly environment materials. Cement is made by heating limestone in kiln in a process known as calcination, whereby carbon dioxide is liberated from the calcium carbonate, and the resulting hard substance(calcium oxide or quicklime) called as "clinker", then clinker is ground with small amount of gypsum into powder to make Ordinary Portland Cement (often referred to as OPC). Among the cement producing process, about approximate two thirds of the electrical energy used in cement plant is utilized for grinding clinkers [1–4]. As a result, even if a small gain in grinding efficiency not only has a large impact on the operating cost, but also cut the emission of greenhouse gases, toxic gases and dusts.

Grinding is one of the most inefficient unit operations in various industries where fine particles are produced by grinding, viz. mineral, cement, pigment, metal powder, etc. In particular, in the cement industry huge amounts of clinker, coal and other raw materials are need for grinding. It has already been proved that grinding aids sometimes referred to as grinding additives are one of the most effective measures to maximize energy saving and improve grinding efficiency in the cement grinding process [5,6]. Small percentages of grinding aids can effectively improve the performance of the mill, reduce the particle size and increase the specific surface area of the cement under the same grinding condition. Grinding aids are certain surface active chemicals, a variety of materials have already been used as grinding aids, such as triethanolamine (TEA), triisopropanolamine (TIPA), glycol, glycerol, organic acetates, and calcium sulfate [7,8]. Two important mechanisms (Rebounder's strength reduction theory and Mardulier's particle dispersion theory) have been suggested in order to explain the action of various grinding aids [9]. However, the action mechanisms of grinding aids which remarkably improve the grinding efficiency with small adding

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amount have not been understood perfectly. Therefore, if actually using some new compounds and chemicals as grinding aids at the present technical level, empirically determining the variety and quantity of the compounds and chemicals based on experimental data is very important.

As renewable material, lignin is a constituent of all plants, including annual plants and wood, and is second in the natural abundance in the organic world after cellulose [10]. Meanwhile, lignin is unusual because of its heterogeneity and lack of a defined primary structure. Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000. It is relatively hydrophobic and aromatic in nature [11]. However, through chemical modification of the active groups (phenolic hydroxyl, carboxyl and hydroxyl) in lignin molecular, a variety of lignin-based high value-added fine chemicals and polymer materials have been produced and widely used in oil well additives, cement and concrete additives, dyestuff dispersants, agricultural chemicals and other industrial binders [12–15].

As one kind of the most important polymeric surfactants, lignin and its derivatives especially the lignosulfonates have been widely used as concrete additives owing to its advantages including easily available, low cost and environmental friendliness [15,17]. Lignosulfonates are also used as auxiliary components for cement grinding aids. However, the poor grinding and strength enhancing performance has limited their further application in the cement and concrete field. In order to make more effect use of lignin and its derivatives, researchers have done lots of works, and mainly concentrated on physical or chemical modification to improve its water solubility and surface activity [18,19].

During the study on lignin modification and cement additives we found incidentally that by proper chemical modification lignin had excellent grinding performance and strong retarding effect. The overall goal of this present work is to synthesize the diethanolamine modified lignin and research its effect on grindability and cement performance including standard consistency, setting times and compressive strengths. To the best of our knowledge, this is the first report about the usage of diethanolamine modified lignin as cement grinding aids. As known, lignin is one kind natural macromolecular material; because of the active epoxy group the diethanolamine modified lignin system has many side reactions such as epoxy ring opening reaction with hydroxyl and methoxy group. Therefore, this paper mainly focused on the grinding performance and effect of DML on cement properties.

2. Experimental

2.1. Materials

Lignin was obtained from Gaotang Duoyuan Co. Ltd. (Shandong, China). Dihydroxybenzene, chloromethyloxirane, diethanolamine (DEA), triethanolamine (TEA) and triisopropanolamine (TIPA) were all analytical grades, and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Deionized water was used throughout the following work. All other reagents were analytic grade without further purification.

Cement clinker was supplied by Lunan China United Cement Company, China. The composition of the clinker used is reported in Table 1. Its mineralogical phases, which were determined by XRD analysis, are given in Fig. 1. XRD analysis conditions: using a Japan RIGAKU D/MAX-1200 X-ray powder diffraction, voltage current of 30 mA, 40 kV, closed type copper target X-ray source, and graphite crystal interference device.

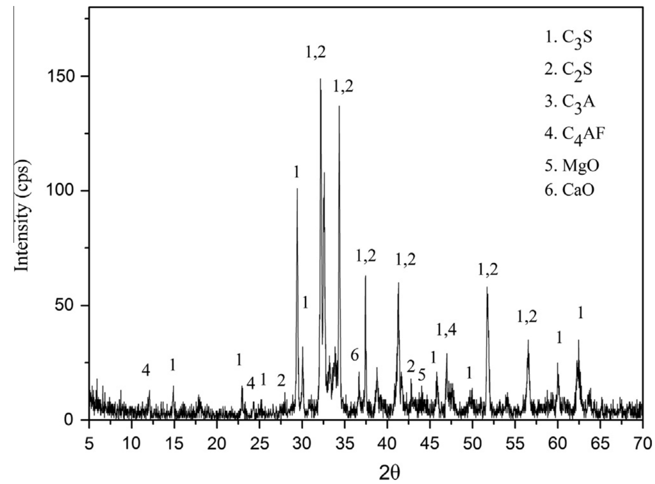

Fig. 1. XRD diffraction of the cement clinker used.

2.2. Synthesis of DML

DML was prepared from lignin, chloromethyloxirane and diethanolamine. Appropriate amount of distilled water, lignin and sodium hydroxide were placed in a three-necked flask equipped with reflux condenser, feeding inlet and thermometer, stirred and made lignin completely dissolved, a small amount of dihydroxybenzene was added. When the temperature rose to 90 °C, chloromethyloxirane was added dropwise for 1 h, refluxed for 2 h, then added diethanolamine, rose to 110 °C and reacted for 4 h. The diethanolamine modified lignin surfactant was precipitated with 30% HCl solution, and then washed with anhydrous ethanol to remove the unreacted epichlorohydrin, diethanolamine and other impurity ions. The sample obtained was dried at 60 °C for 24 h in a vacuum oven, and the DML was obtained.

2.3. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5100 spectrometer by KBr sample holder method in the fundamental region of 400–4000 cm^{-1}. The evaluation of carbon and nitrogen content was tested by MICRO element analyzer, Elementar Vario, Germany. Distribution of particle size was tested by WS5-RODOS laser particle size analyser, System Partikel Technik, Germany. Measurement of surface tension was tested by K100 automatic surface tensiometer, DKSH China.

The grinding evaluation of DML was carried out by intergrinding Portland cement clinker and gypsum (95% clinker, 5% gypsum, weight percent), in a 5 kg laboratory rotating ball mill for 25 min, using steel balls as grinding medium. Make sure to keep the mill in the same working conditions, first grinding 4.75 kg clinker and 0.25 kg gypsum as reference cement (Ref.), then grinding 4.75 kg clinker and 0.25 kg gypsum with different grinding aids, and each grinding aid was added to the mill in accordance with 0.01%, 0.02%, 0.03%, 0.04% and 0.05% (weight percent of solid content to clinker and gypsum). The determination of the standard consistency (% w/w, weight percent of actual amount of water required to cement) and the setting times of the cement pastes were determined according to the China Standard GB/T 1346–2001 (Test methods for water requirement of normal consistency, setting time and soundness of the Portland cements) and GB/T 26748–2011 (Cement grinding aids). The compressive strength measurements were conducted at the ages of 3, 7 and 28 days in accordance to GB/T 17671–2005 (Method of testing cements – Determination of strength, ISO method).

3. Results and discussion

3.1. FT-IR and element analysis

In this paper using lignin as raw material, through chemical modification introducing hydrophilic groups, synthesized one kind

Table 1
Chemical analyses and mineral composition of the cement clinker.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	f-CaO	Loss	∑
Composition (%)	21.73	5.11	3.32	65.63	2.81	0.21	0.57	0.38	99.19