Preparation of Concrete Superplasticizer by Oxidation-Sulfomethylation of Sodium Lignosulfonate

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Modification of sodium lignosulfonate (SLS) via combined oxidation-sulfomethylation was employed to prepare concrete superplasticizer. It was found that the oxidation of SLS by peroxyacetic acid facilitated the subsequent sulfomethylation. After modification, both the molecular weight and sulfo group content were significantly increased, and thus the performance of SLS as water reducer was improved. With the water to cement ratio at 0.4 and 0.3% (w/w) modified SLS, the fluidity of cement paste could reach 185 mm, which was 15% higher than that with unmodified SLS. It was also comparable to the performance of commercial naphthalene superplasticizer under the same conditions.

Keywords: Sodium lignosulfonate; Concrete superplasticizer; Peroxyacetic acid; Black liquor

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INTRODUCTION

Water reducers (also known as concrete plasticizers) are special chemical products that can generate electrostatic repulsion, steric hindrance, or a lubrication layer among cement particles when added to a concrete mixture, thus improving the workability of the concrete. The main advantage of water reducers is to reduce water content (by 5 to 10%) in order to increase concrete strength (by up to 25%) for a given fluidity (Ouyang *et al.* 2006). Generally, the water reducing rate of a common water reducer (plasticizer) is under 12%, while the water reducing rate of superplasticizers is over 12% (Ji *et al.* 2012).

Lignosulfonate obtained from sulfite pulping spent liquor or prepared from sulphonation of alkali lignin at low cost can be used as a water reducer in the construction field. But the low water reducing capability (water reducing rate usually around 8%) hinders its large-scale application (Ouyang *et al.* 2006). Also, most of water reducers derived from fossil oil (*e.g.* naphthalene) are facing challenges due to the shortage of fossil fuel and global warming. Hence, it is of critical importance to ameliorate the performance of lignin-based concrete plasticizer (Matsushita and Yasuda 2005).

Up to now, many studies have been carried out to improve the water reducing capability of sodium lignosulfonate (SLS) via oxidation, sulfonation, or sulfomethylation (Pang *et al.* 2008; Goncalves and Benar 2001; Matsushita and Yasuda 2005), graft modification (Chakar and Ragauskas 2004), or ultrafiltration (Li *et al.* 2009; Jönsson *et al.* 2008; Toledano *et al.* 2010). It has been found that the molecular weight distribution (MWD) and the content of strong hydrophilic groups are key factors affecting the water reducing capability of the resulting SLS. In the present work, an industrial SLS was modified by means of peroxyacetic acid (PAA) oxidation and sulfomethylation. The effectiveness of modification was estimated, and the properties of the modified SLS were investigated as well.

EXPERIMENTAL

Materials and Methods

Table 1. Composition and Properties of Black Liquor

Density	pH	Solids* (%)	Organics* (%)	Inorganics* (%)	Hemicellulose* (%)	SLS* (%)
1.08	8.16	16.48	10.88	5.6	0.59	12.69
*Based on the weight of black liquor						

The black liquor was obtained from Tianhong paper industry Co. Ltd., Xinjiang, China. It was generated from alkali sulfite pulping of 80 wt% reed and 20 wt% wheat straw. The composition and properties of black liquor are listed in Table 1. The cement used was PO 42.5R Portland cement from Shanshui Co. Qingdao, China. PAA solution (18±1 wt%) was obtained from Laiyang Disinfectant Co. Qingdao, China.

Preparation of SLS Superplasticizer

The preparation of SLS included oxidation and sulfomethylation. The desired amounts of black liquor, PAA solution, and $FeSO_4$ were added into a flask (V = 500 mL) with a circulating water condenser, and then heated up to the required temperature (60ºC, 70ºC, 80ºC, 90ºC, and 100ºC, respectively) with an agitation of 800 rpm. Subsequently, the oxidation reaction took place for a required time (0.5 h, 1 h, 2 h, and 3 h, respectively). After that, the desired amount of formaldehyde and sodium sulfite was added to the solution and the sulfomethylation reaction was conducted under given conditions (different temperatures of 80ºC, 85ºC, 90ºC, 95ºC, and 100ºC and reaction times of 1 h, 2 h, 3 h, and 4 h for sulfomethylation were implemented, respectively). Upon completion, the solution was cooled to ambient temperature and spray-dried using a spray drier (FH-1500, Shanghai Gaoji, China).

Characterization

Hemicellulose content of black liquor

The black liquor was hydrolyzed by 4% sulfuric acid at 121ºC for 30 min. The hemicellulose was degraded into sugar monomers. The hydrolyzate was filtered with a 0.22 μm filter before analysis with a high performance liquid chromatography (HPLC) system (Model 1200, Agilent, USA) equipped with a Sugar Pak 1 column (300 mm × 6.5 mm) and refractive index detector. The column was operated at 80°C with 0.05 g/L EDTA-Ca-2Na solution as the mobile phase at a flow rate of 0.5 mL/min, and the quantitative analysis was performed using a calibration with external standards of known concentration. A blank experiment was carried out by using xylose to calculate the loss during the acid hydrolysis process.

SLS content in black liquor

Solutions at different concentrations (0.4, 0.2, 0.1, 0.04, and 0.02 mg/mL) of SLS (reagent grade, Aladdin, China) were prepared. The absorbency of samples was measured by ultraviolet and visible spectrophotometer (752N, Shanghai Jingke, China) at a wavelength of 280 nm. The content of SLS in sample solution could be obtained according to the standard curve of concentration – absorbency.

Fluidity of cement paste

The fluidity of cement paste was determined according to the Chinese National Standard of GB 8077-2000; 300 g cement, 120 g water, and 0.9 g superplasticizer were added into paste blender, and stirred for 4 min. Subsequently, the paste was rapidly poured into the truncated flow cone mold (base diameter of 10 ± 0.05 cm, top diameter of 7 ± 0.05 cm, and height of 6 ± 0.05 cm) on the glass plate.

Once the cone was lifted, the fresh cement paste collapsed and spread. The paste was allowed to flow on the glass plate for 30 seconds. The maximum diameter of the spread, d_1, and the diameter perpendicular to it, d_2, were measured. The average value, $(d_1 + d_2)/2$, was as the fluidity of cement paste. Three replicates for each sample were carried out, and the average was reported.

Molecular weight distribution (MWD) of SLS

The molecular weight and its distribution of SLS were characterized by Gel Permeation Chromatography (GPC) (HELEOS System, Wyatt, USA) with 0.1 mol/L $NaNO_3$ as mobile phase, and the flow rate was 1.00 mL/min. The differential detector and laser detector were used. Standard sodium polystyrenesulfonates with molecular weight of 3600, 6500, 15450, 41000, and 145000 were utilized for calibration.

Sulfonation degree (SD) of SLS

The anion exchange resin (717) and cation exchange resin (732) were immersed in 1 to 3 mol/L NaOH and 1 to 3 mol/L HCl respectively for 10 h, and then washed to neutral pH with deionized water. The solution of SLS passed through the anion exchange resin first in order to remove inorganic acid of low molecular weight, and then passed through the cation exchange resin so that the sodium lignosulfonate was transformed into lignosulfonic acid. Subsequently, the solution was titrated by NaOH standard solution of 0.04 mol/L, and detected by a conductivity meter (DDS-307, Shanghai Jingke, China). The sulfomethylation degree was calculated according to the following formula,

$$SD = \frac{N_{NaOH} \cdot V_{NaOH}}{W_{SLS}} \tag{1}$$

where SD is the sulfonation degree (mmol/g); N_{NaOH} is the concentration of NaOH standard solution (mol/L); V_{NaOH} is the consumed volume of NaOH standard solution (mL); and W_{SLS} is the weight of sodium lignosulfonate (g).

FTIR analysis

A Nicolet 6700 FTIR Spectrometer (Thermo, USA) was used to obtain the spectra of SLS. The sample was prepared through KBr pellet, and the weight ratio of KBr to SLS product was 100:1. Spectra were collected at a resolution of 4 cm^{-1} in the range of 500 cm^{-1} to 4000 cm^{-1}, and 32 scans per sample were conducted.

^{1}H-NMR analysis

An AVANCE-III 600 MHz instrument (Bruker, Switzerland) was used to characterize the functional groups of SLS; 10 to 20 mg SLS was dissolved in 0.5 to 0.6 mL D_2O, and DSS (4, 4-dimethyl-4-silicon generation amyl sulfonate) was used as internal standard.

RESULTS AND DISCUSSION

Effect of Chemical Dosage on the Performance of Modified SLS as Water Reducer

The performance of SLS as water reducer was determined by the fluidity of cement paste (Chandra and Bjornstrom 2002), and the dosage was 0.3% on the basis of the weight of cement. As shown in Fig. 1a, the fluidity of cement paste was improved by about 7.6% as the dosage of PAA increased from 10% to 30%. This is because in the oxidation step, more reactive points of the SLS were exposed so that more sulfonic groups could be introduced to SLS in the subsequent sulfomethylation step, thus improving the performance of SLS. In this way the electric potential on the particle surface of cement was enhanced by strongly electrostatic repulsion, and thereby the dispersibility of cement was improved (Zhao *et al.* 2005). However, the fluidity was slightly decreased when the dosage of PAA was over 30%. This is due to the fact that the over degradation of SLS decreased its molecular weight and the amount of active groups of SLS, which was not beneficial for the subsequent sulfomethylation.

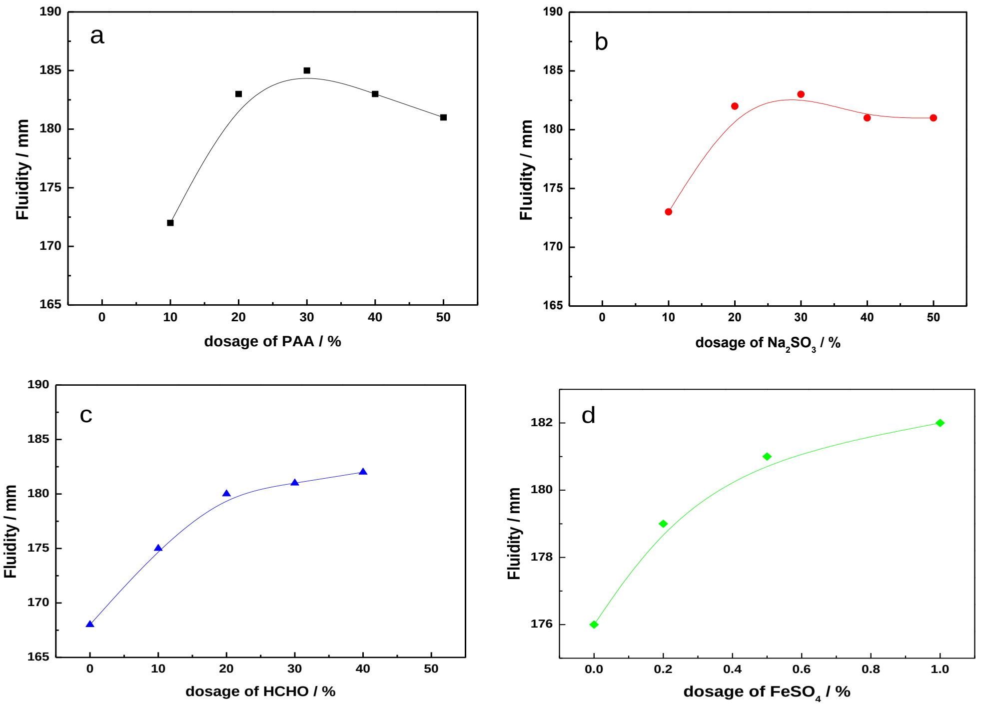

Fig. 1. Effect of chemical dosage on the performance of modified SLS. a: 1 h oxidation at 80 ºC; 2 h sulfomethylation at 90 ºC with 30% Na_2SO_3 and 15% HCHO; b: 1 h oxidation at 80 ºC with 30% PAA; 2 h sulfomethylation at 90 ºC with 15% HCHO; c: 1 h oxidation at 80 ºC with 30% PAA; 2 h sulfomethylation at 90 ºC with 30% Na_2SO_3; d: 1 h oxidation at 80 ºC with 30% PAA; 2 h sulfomethylation at 90 ºC with 30% Na_2SO_3 and 15% HCHO. All dosages were based on the dry weight of SLS.

Figure 1b shows that, with the increase of Na_2SO_3 loading from 10% to 30%, the fluidity of cement paste was increased, while it was basically steady as the dosage of Na_2SO_3 was higher than 30%.

Also, as shown in Fig. 1c, the fluidity was improved by 7.5% when the dosage of HCHO increased from 0% to 20%. This is because the addition of HCHO can introduce hydroxymethyl groups to benzene rings in lignin so that more sulfonic groups can be introduced to lignin during sulfonation (Matsushita and Yasuda 2005), as shown in Fig. 2. However, an excessive dosage (above 20%) of formaldehyde was not needed, as it could make the hydroxymethylated lignin further condensed as a result of aldol condensation and disproportionation reactions.

In addition, $FeSO_4$ can be used as a catalyst in the oxidation process, as it can enhance the oxidation reaction in the constructed redox system with PAA. The appropriate dosage of $FeSO_4$ was 0.5 %, as shown in Fig. 1d.

Therefore, the suitable dosages of PAA, Na_2SO_3, HCHO, and $FeSO_4$ were 30%, 30%, 20%, and 0.5%, respectively. Under such conditions, the fluidity of cement could reach 185 mm, while it was only 161 mm by using unmodified SLS.

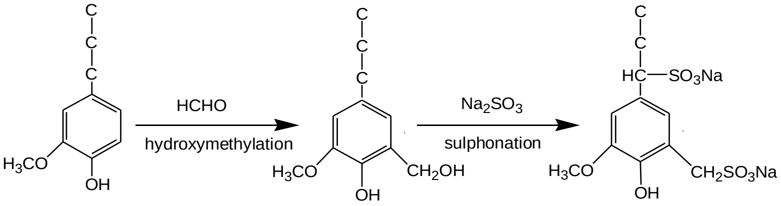

Fig. 2. Sulfomethylation of lignosulphonates base on guaiacyl propane units

Effect of Reaction Temperature on the Performance of Modified SLS as Water Reducer

The effects of reaction temperature of oxidation and sulfomethylation on the performance of SLS as water reducer were investigated respectively. As can be seen from Fig. 3, appropriately elevating temperature in both oxidation and sulfomethylation step can significantly improve the performance of the modified SLS, while an overheating would result in the degradation of macro molecular of lignin.

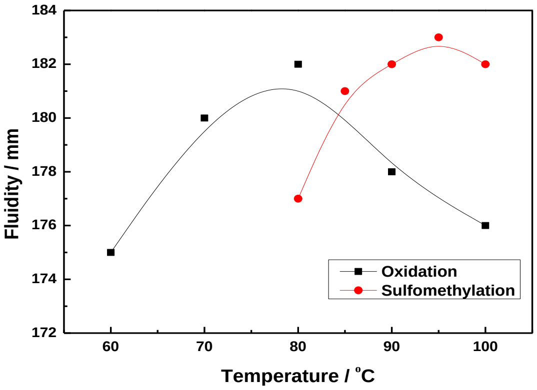

Fig. 3. Effect of reaction temperature on the performance of modified SLS (to study the effect of oxidation temperature on the performance of modified SLS, sulfomethylation was at 90°C for 2 h with 30% Na_2SO_3 and 20% HCHO; to study the impact of sulfomethylation temperature on the performance of modified SLS, oxidation was at 80°C for 2 h with 30% PAA and 0.5% $FeSO_4$; the corresponding fluidity when using unmodified lignosulfonate is 161 mm.)

Experiments (Fig. 3) showed that the temperature of sulfomethylation was higher than that of oxidation, and the suitable temperatures for oxidation and sulfomethylation were 80 ºC and 95 ºC, respectively.

Effect of Reaction Time on the Performance of Modified SLS as Water Reducer

Figure 4 exhibits the effect of reaction time of oxidation and sulfomethylation on the performance of modified SLS. It can be seen that the fluidity of cement was increased with the extension of reaction time to a plateau both for oxidation and sulfomethylation, and the appropriate oxidation and sulfomethylation times were 2 h and 3 h, respectively.

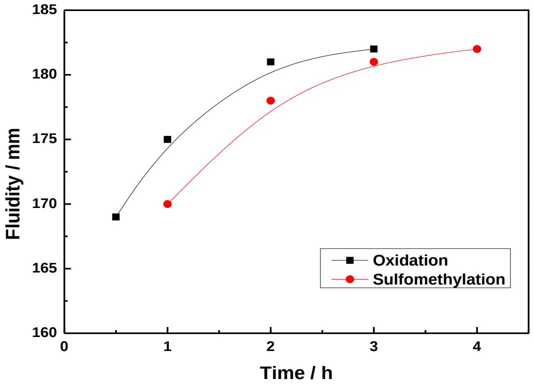

Fig. 4. Effect of reaction time on the performance of modified SLS (to study the effect of oxidation time on the performance of modified SLS, sulfomethylation was at 90 ºC with 30% Na_2SO_3 and 20% HCHO; to study the impact of sulfomethylation reaction time on the performance of modified SLS, oxidation was at 80 ºC with 30% PAA and 0.5% $FeSO_4$; the corresponding fluidity when using unmodified lignosulfonate is 161 mm.)

MWD and SD of SLS

The molecular weight and distribution are key factors that affect the performance of SLS products. It was proved that a suitable molecular weight was beneficial to the improvement of water reducing capability and dispersibility of SLS (Zhou *et al.* 2006, Matsushita and Yasuda 2005). The structure of SLS derived from pulping was quite different from native lignin. For instance, SLS possesses a lower relative molecular weight and a wider MWD. The SLS with higher molecular weight has a larger steric repulsive force. As can be seen from Table 2, both M_w and M_n of modified SLS were much larger than that of unmodified SLS, and the polydispersity index (PDI) of SLS was decreased from 2.01 to 1.12 after modification. This was mainly due to the condensation reactions during oxidation (Zhao *et al*. 2005).

Table 2. Molecular Weight Distribution and Sulfonation Degree

SLS product	M_w	M_n	PDI	R_h(w) (nm)	SD (mmol/g)
Unmodified	2378	4767	2.01	3.2	0.65
Modified*	23650	26400	1.12	3.8	1.45

* Conditions: oxidation at 80 ºC for 1 h with 30% PAA and 0.5% $FeSO_4$; sulfomethylation at 90ºC for 2 h with 15%HCHO and 30%Na_2SO_3. All based on the dry weight of SLS.
R_h(w) is the weight hydrodynamic radius obtained from GPC by ViscoStar-II viscometer (Wyatt Corporation).

In addition, the hydroxymethylation and crosslinking of formaldehyde also led to condensation of SLS (Gosselink *et al.* 2004). Thereby the average molecular weight was increased and MWD of SLS became more homogeneous after modification. However, the molecular size of modified SLS in terms of diameter (hydrodynamic radius) was only slightly larger than that of unmodified SLS, as presented in Table 2.

Sulfonation degree (SD) is a direct indicator for evaluating the performance of sulfonation effect. The higher the SD of SLS, the more sulfo groups; thus the better workability of SLS could be obtained (Matsushita and Yasuda 2005). As shown in Table 2, the SD of modified SLS was more than twice higher than that of unmodified SLS. That is because after oxidation the steric hindrance of lignin was reduced due to the lignin degradation, such as the removal of methoxyl and phenolic hydroxyl on aromatic ring unit, which led to an easier bonding between sulfonic groups and lignin during sulfonation, and thus the dispersibility and the fluidity of cement paste were promoted.

FTIR Spectra of SLS

The FTIR spectra of unmodified and modified SLS are presented in Figs. 5a and 5b. The strong and broad band at around 3433 cm^{-1} is characteristic of the OH group or phenolic compounds (Ibrahim *et al.* 2004). The peaks at 2940 cm^{-1} to 2930 cm^{-1} are associated with C-H stretching of methyl or methylene groups. The peak at 1589 cm^{-1} can be attributed to the aromatic functionality in lignin, and the characteristic peaks of benzene ring skeletal vibration appear at 1508 cm^{-1}. C-H deformation and C-H in-plane deformation peaks can be observed at 1415 cm^{-1} and 1354 cm^{-1} due to the methylene group (Sahoo *et al.* 2011). The peak at 1200 cm^{-1} can be attributed to C-O stretching of phenol and C-O deformation of methoxyl group. Its enhancement probably was caused by oxidation (Kamoun *et al.* 2003). The absorption peak at 1046 cm^{-1} of modified SLS attributing to sulfonic acid groups was much stronger than that of unmodified SLS, and this is in agreement with the SD analysis. In Fig. 5b, a peak at 928 cm^{-1} can be attributed to carboxyl groups, which is likely due to the degradation and oxidation of lignin.

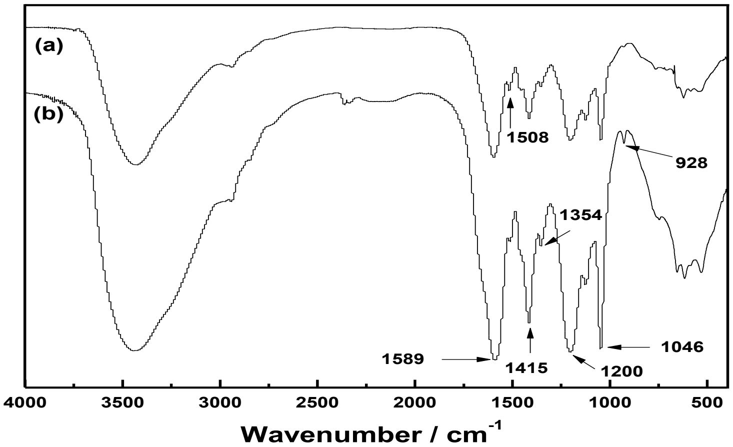

Fig. 5. FTIR spectra of SLS (Modified at optimized condition), (a) unmodified (b) modified

^{1}H-NMR Spectra of SLS

Figure 6 presents 1H-NMR spectra of unmodified and modified SLS. As can be seen, the peak at 8.4 ppm can be assigned to the H of phenolic hydroxyl, and its enhancement in Fig. 6b reveals the increase of amount of phenolic hydroxyl groups due to the cleavage of ether bond and demethylation (Chakar *et al.* 2004). Compared to unmodified SLS, the peak at 7.2 ppm attributable to the H of aromatic or vinyl groups, is much weaker, probably due to the breakage of aromatic ring or the oxidation of C=C bond. The peak at 4.4 ppm in Fig. 6b is related to the H in the groups of -CH_2-O- (Zhao *et al.*, 2005), most probably resulting from condensation after modification. The peak at 3.9 ppm corresponds to the H of methoxyl groups, and its weakness after modification is caused by demethoxylation. The peak at 3.3 ppm was associated with the proton of D_2O. In addition, the peak at 1.6 ppm, which can be attributed to hydrogen atom resonance adsorption on methyl or methylene, is weakened after modification.

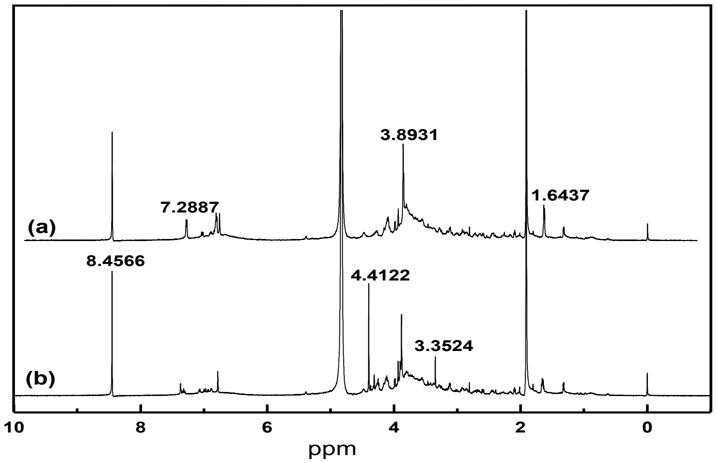

Fig. 6. ^{1}H-NMR spectra of SLS (Modified at optimized condition), (a) unmodified (b) modified

CONCLUSIONS

In this study, SLS oxidation by PAA followed by sulfomethylation, was studied to improve the performance of SLS as a superplasticizer. The results showed that, under the suitable conditions (oxidation at 80ºC for 2 h with 30% PAA and 0.5% $FeSO_4$; sulfomethylation at 95 ºC for 3 h with 20% formaldehyde and 30% Na_2SO_3), the fluidity of cement with 0.3% dosage of modified SLS can reach 185 mm, which is significantly higher than that with unmodified SLS. Thus, PAA oxidation and sulfomethylation would be an efficient way to improve the performance of SLS, and the improvement of the water reducing capability of the modified SLS is attributed to the increase of molecular weight and sulfo group content after modification.

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