Preparation and Evaluation of a Dispersant for Gypsum Paste from Acid Hydrolysis Lignin

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ABSTRACT: The preparation of dispersants with carboxyl groups from acid lignin (a byproduct in the saccharification process of woody materials that are renewable resources) was investigated, and their dispersion efficiency was evaluated. In this study, sulfuric acid lignin (SAL) was selected as a representative acid lignin. To convert SAL to water-soluble polymers, it was first subjected to phenolation with sulfuric acid to enhance its chemical reactivity. The introduction of a carboxy group was carried out with two methods. One was carboxymethylation with bromoacetic acid, and the other was the Mannich reaction with glycine, sarcosine, and iminodiacetic acid. The carboxymethylation product [carboxymethylated phenolized sulfuric acid lignin (CP-SAL)] with 1.4 carboxymethyl groups per phenolated phenylpropane lignin base unit was soluble in water. The Mannich reaction products were also soluble in water with a lower addition of carboxyl groups than that for CP-SAL. Surprisingly, all the prepared water-soluble polymers possessed a higher dispersibility for gypsum paste than commercial lignosulfate. This may be due to the higher molecular weights of acid lignin derivatives. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2508–2513, 2005

Key words: FTIR; renewable resources; water-soluble polymers

INTRODUCTION

We have become accustomed to consuming enormous amounts of fossil energy. However, it is predicted that these energy reserves will be depleted in about only 40 years if our consumption continues at this rate. Moreover, our use of fossil resources releases greenhouse gases that exacerbate global warming.[1] To maintain our present way of life, it is necessary to reduce our fossil energy consumption and to develop other energy alternatives.[2] Therefore, interest in the utilization of biomass energy has been growing because both its abundance and renewability give it the potential to replace fossil energy.

The saccharification of biomass is one of the more effective methods of producing an alternative energy source. A technique for the acid saccharification of woody materials has been developed for the production of ethanol and other industrial organic resources. However, this technique produces large quantities of less reactive acid lignin as a byproduct.

Acid lignin possesses a highly condensed structure due to intermolecular dehydrative condensation between benzylic carbons and aromatic nuclei.[3,4] Recently, the condensed aromatic nuclei of sulfuric acid lignin (SAL), a type of acid lignin with a diarylmethane structure, were selectively exchanged with phenol in the presence of a sulfuric acid catalyst.[5] As a result, the reactivity of phenolized sulfuric acid lignin (P-SAL) was enhanced by the addition of a reactive *p*-hydroxyphenyl moiety at the side-chain α position instead of condensed-type aromatic nuclei (Fig. 1). This allowed P-SAL to be easily converted by chemical reactions to functional materials.[6–10]

In this study, the preparation of dispersants with carboxyl groups for gypsum paste from P-SAL by two methods (carboxymethylation with halogenoacetic acid and the Mannich reaction with glycine, sarcosine, and iminodiacetic acid) was examined, and the dispersion efficiency of the prepared derivatives was investigated.

EXPERIMENTAL

Materials

Glycine, sarcosine, iminodiacetic acid, acetovanillone, and bromoacetic acid were obtained from Tokyo Kasei Kogyo (Japan), and commercial lignosulfonate (LS; Sanx P-252) was obtained from Nippon Paper Chemicals (Tokyo). Gypsum (Kosakuyo Sekko) was purchased from Toyo Matelan (Aichi, Japan).

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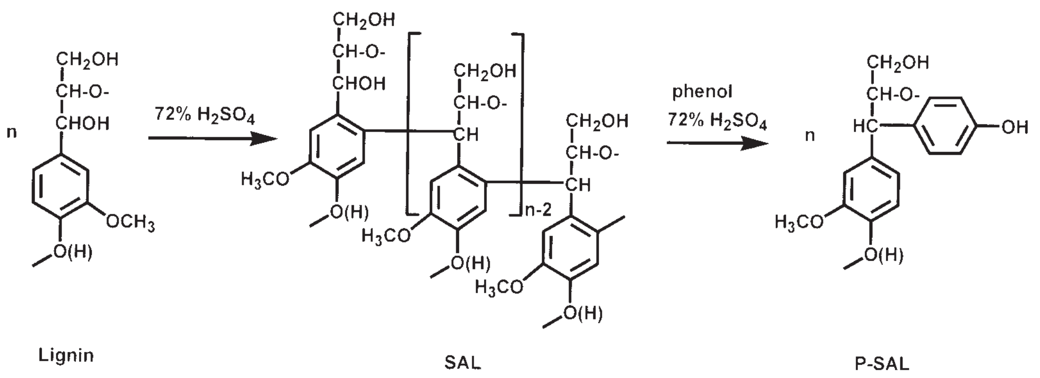

Figure 1 Formation of SAL and phenolation of SAL.

Synthesis of model compound I

Model compound **I** was synthesized from acetovanillone by reduction after phenolation.[11]

Carboxymethylation of compound I

To a stirred mixture of 100 mg of compound **I** and 0.6 mg of NaOH in 10 mL of 80% aqueous methanol, 230 mg of bromoacetic acid was slowly added, and the mixture was heated to 60°C. After 10 h, another 350 mg of bromoacetic acid was added to the reaction mixture, and the reaction continued for 10 h more. Then, 15 mL of distilled water was added to the reaction solution and extracted with ethyl acetate after acidification with 2*M* HCl. The extracted solution was dried with sodium sulfate and concentrated under reduced pressure. The reaction product was dissolved in a small quantity of methanol and methylated with diazomethane. The products were purified by silica gel column chromatography eluted with *n*-hexane and acetone (3:1 v/v) to yield compounds **II**, **III**, and **IV** at concentrations of 15.1, 2.1, and 6.1%, respectively.

Compound **II**

^{1}H-NMR ($CDCl_3$, δ): 1.58 (3H, d, $J = 7$ Hz; CH_3), 3.77 (3H, s; CH_3 of methyl ester), 3.78 (3H, s; OCH_3), 3.82 (3H, s; OCH_3), 4.04 (1H, q, $J = 7$ Hz; CH), 4.66 (2H, s; CH_2), 6.95–6.74 (3H, m; aromatic H), 6.62 (2H, d, $J = 9$ Hz; aromatic H), 7.12 (2H, d, $J = 9$ Hz; aromatic H). ^{13}C-NMR ($CDCl_3$, δ): 22.2 (CH_3), 43.6 (CH), 52.2 (OCH_3), 55.3 (OCH_3), 55.9 (OCH_3), 66.7 (CH_2), 111.9, 113.8, 114.4, 119.4, 128.6, 138.7, 141.5, 145.6, 149.6, 158.0, 169.9 (C═O).

Compound **III**

^{1}H-NMR ($CDCl_3$, δ):1.59 (3H, d, $J = 7$ Hz; CH_3), 3.80 (3H, s; CH_3 of methyl ester), 3.82 (3H, s; OCH_3), 3.85 (3H, s; OCH_3), 4.05 (1H, q, $J = 7$ Hz; CH), 4.61 (2H, s; CH_2), 6.69–6.79 (3H, m; aromatic H), 6.83 (2H, d, $J = 9$ Hz; aromatic H), 7.13 (2H, d, $J = 9$ Hz; aromatic H).

Compound **IV**

^{1}H-NMR ($CDCl_3$, δ):1.57 (3H, d, $J = 7$ Hz; CH_3), 3.78 (3H, s; CH_3 of methyl ester), 3.80 (3H, s; CH_3 of methyl ester), 3.82 (3H, s; OCH_3), 4.04 (1H, q, $J = 7$ Hz; CH), 4.61 (2H, s; CH_2), 4.66 (2H, s; CH_2), 6.70–6.74 (3H, m; aromatic H), 6.83 (2H, d, $J = 9$ Hz; aromatic H), 7.12 (2H, d, $J = 9$ Hz; aromatic H). ^{13}C-NMR ($CDCl_3$, δ): 22.2 (CH_3), 43.6 (CH), 52.2 (OCH_3), 52.3 (OCH_3), 55.9 (OCH_3), 65.5 (CH_2), 66.7 (CH_2), 112.0, 114.4, 114.6, 119.4, 128.7, 139.9, 141.2, 145.7, 149.6, 156.2, 169.8 (C═O), 169.9 (C═O).

SAL

SAL was prepared from red pine (*Pinus densiflora* Sieb. et Zucc) by a treatment with 72% sulfuric acid according to the Klason method.[12]

Phenolation of SAL

A mixture of 1.0 g of SAL and 6.3 g of phenol in 15 mL of 72% sulfuric acid was stirred at 60°C for 6 h. After quenching by dilution with 560 mL of water, the suspension was boiled for 3 h. The solids were filtered out and thoroughly washed with warm water to yield 1.2 g of P-SAL. The molecular weight of P-SAL per phenolated phenylpropane lignin base unit (C_9–C_6) was estimated to be 275.[5]

Carboxymethylation of P-SAL

To a solution of 400 mg of P-SAL and 0.16 g of NaOH in 80% aqueous methanol, bromoacetic acid was slowly added, and the mixture was stirred at 60°C, as shown in Table I. After the reaction, 2*M* HCl was added to the reaction mixture to pH 3, and the mixture was dialyzed with a cellulose tube (molecular-weight cutoff = 3500) to remove excess reagents. The reaction products were lyophilized to yield carboxymethylated phenolized sulfuric acid lignin (CP-SAL).

TABLE I
Carboxymethylation of P-SAL

	Reaction conditions		Product		
				Molecular weight	
	Bromoacetic acid (mg)[a]	Time (day)	COOH/C_9–C_6	M_n ($\times 10^4$)	M_w ($\times 10^4$)
CP-SAL 1	114 × 3	3	0.8	1.3	2.4
CP-SAL 2	114 × 5	5	1.0	1.1	1.7
CP-SAL 3	114 × 10	10	1.4	1.0	1.4

[a] Bromoacetic acid was added every day.

Mannich reaction of P-SAL

P-SAL was reacted with formaldehyde and amines in 10 mL of 0.5*N* NaOH at 60°C under various conditions shown in Table II. The Mannich reaction products (GP-SAL, SP-SAL, and IP-SAL) were yielded by dialysis and freeze-dried.

Molecular weight distribution

The molecular weight distribution was measured with a Sepharose CL-6B (51 × 1.8 cm) with 0.5*N* NaOH as an eluent and a UV detector (280 nm). Sodium poly(styrene sulfonate)s [weight-average molecular weight (M_w) = 1.8×10^3 to 1.0×10^5] were used as standards.

Evaluation of dispersibility

An evaluation of the dispersibility of the samples was conducted as follows.[13] The requisite quantity of the additive was dissolved in 88 mL of water at 20°C. A 110-g sample of gypsum was added to the solution, and the solution was stirred for 15 s; afterwards, the resultant gypsum paste was poured into a ring-shaped container (diameter = 50 mm, height = 50 mm) set on a glass plate. After 10 s, the ring-shaped container was removed to allow the gypsum paste to spread out on the glass plate.

The final diameter (ϕ_{final}) was measured, and the flow value was defined with the following equation:[14]

$$\text{Flow value} = \frac{\phi_{\text{final}} - \phi_{\text{in}}}{\phi_{\text{in}}} \times 100$$

where ϕ_{in} is the initial diameter (50 mm).

The measurement of each sample was carried out at least three times, and the average was calculated. The flow value, measured as a blank without any additives, was 113.

Measurement of the carboxyl group content

The measurement of the carboxyl group content of CP-SAL was performed by the titration, with 0.25*N* HCl, of 30 mg of each prepared SAL derivative in 0.5*N* NaOH. In the Mannich reaction products, the carboxyl group content was determined by its nitrogen content as measured by elemental analysis.

Spectrometry

The ^{1}H- and ^{13}C-NMR spectra of the lignin model compounds in deuterochloroform were recorded on a Varian Gemini 2000 300-Hz spectrometer. Deuterium oxide was used as a solvent when the spectra of CP-SAL were measured. Fourier transform infrared (FTIR) spectra were recorded on a Horiba FT-720 spectrophotometer with a KBr disc.

TABLE II
Mannich Reaction of P-SAL

	Reaction conditions				Product		
		Dosage[a]				Molecular weight	
	Amine	Amine (mg)	HCHO (mg)	Time (days)	COOH/C_9–C_6	M_n ($\times 10^4$)	M_w ($\times 10^4$)
GP-SAL 1	Glycine	270 × 3	108 × 3	3	0.5	1.5	2.1
GP-SAL 2	Glycine	270 × 3	108 × 3	6	0.9	1.3	2.4
SP-SAL 1	Sarcosine	320 × 3	108 × 3	3	0.6	1.1	1.7
SP-SAL 2	Sarcosine	320 × 3	108 × 3	6	1.2	1.2	2.5
IP-SAL 1	Iminodiacetic acid	479 × 3	108 × 3	1	0.5	0.9	2.0
IP-SAL 2	Iminodiacetic acid	479 × 3	108 × 3	3	1.0	1.3	2.6

[a] Bromoacetic acid was added every day.

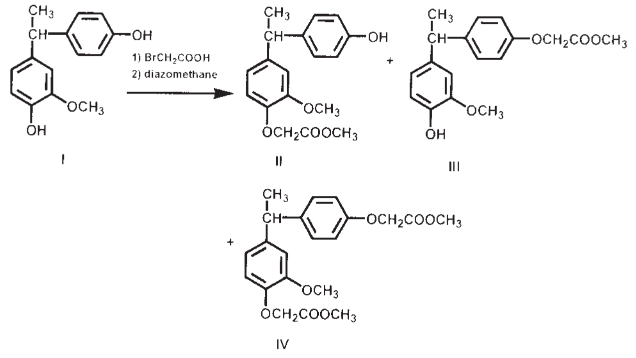

Figure 2 Carboxymethylation of compound **I**.

RESULTS AND DISCUSSION

Carboxymethylation of model compound I

The introduction of a carboxyl group by carboxymethylation with halogenoacetic acid has been widely used to obtain industrial materials (e.g., carboxymethylated cellulose), whereas Lang and Schweers[15] applied the reaction to organosolve lignin and kraft lignin to modify their characteristics. It was thought that the halogenoacetic acid might react with phenolic compounds at the phenolic hydroxyl groups and induce carboxymethyl groups. Because P-SAL possesses a reactive *p*-hydroxyphenyl moiety introduced at the side-chain α position (Fig. 1), carboxymethylation with halogenoacetic acid may occur, resulting in water-soluble polymers.

To elucidate the chemical reactivity of P-SAL with halogenoacetic acid, the reaction of a model compound of P-SAL was studied. Model compound **I** was selected for P-SAL. Three compounds (**II–IV**) resulted from the carboxymethylation products of **I** (Fig. 2). Compounds **II** and **III** possessed one carboxymethyl group in the guaiacyl and *p*-hydroxyphenyl units, respectively. Compound **IV** had two carboxymethyl groups each in the guaiacyl and *p*-hydroxyphenyl units. The yield of **II** was higher than that of **III**, and this indicated a higher reactivity for the guaiacyl nucleus than for the *p*-hydroxyphenyl unit.

Carboxymethylation of P-SAL

We attempted the carboxymethylation of P-SAL on the basis of our model-compound experiments. The considerable reaction of carboxymethylation is shown in Figure 3. We used the same 80% aqueous methanol used in the model-compound experiment. The reaction conditions and properties of the reaction products (CP-SAL) are shown in Table I. The increase in the quantity of the reaction reagent and the prolongation of the reaction time resulted in an increase in the number of introduced carboxymethyl groups. The solubility of CP-SAL in water was significantly related to the number of such groups. CP-SAL (CP-SAL 3) with 1.4 carboxymethyl groups per C_9–C_6 was soluble only in water.

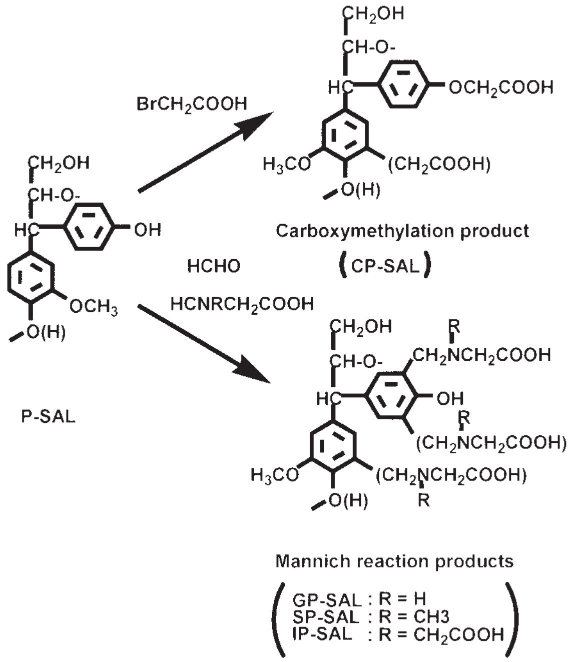

Figure 3 Conversion of P-SAL to the dispersant with the carboxyl group.

The FTIR spectra of CP-SAL are shown in Figure 4. Comparing CP-SAL with P-SAL, we found that the peak near 1600 cm^{-1} was increasing, and this suggested the introduction of carboxyl groups. In the ^{13}C-NMR spectrum of CP-SAL, signals appeared at 67.8 and 177.8 ppm due to methylene and carboxyl carbon, respectively, suggesting the introduction of the carboxymethyl group into P-SAL.

Mannich reaction of P-SAL

The Mannich reaction occurs between a carbon with a higher electron density and an immonium ion formed

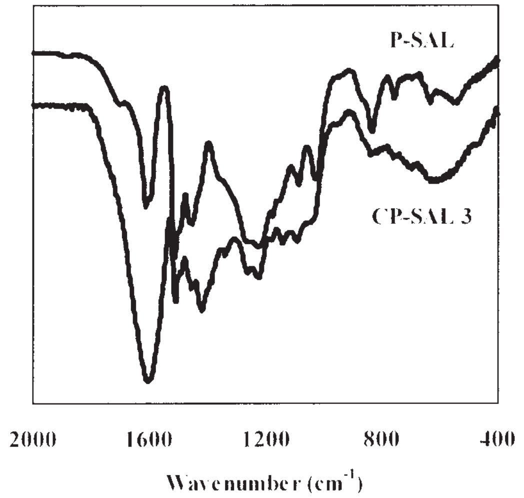

Figure 4 IR spectra of P-SAL and its carboxymethylation product.

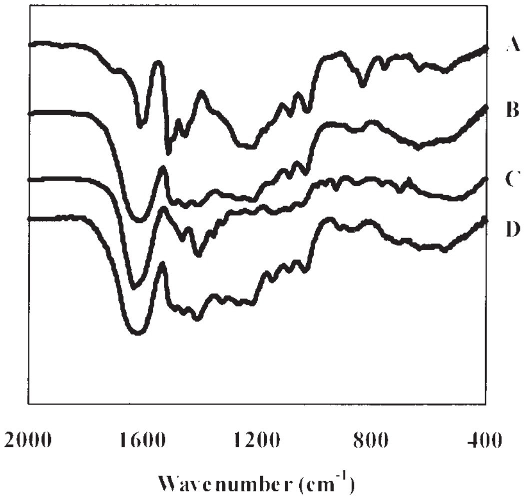

Figure 5 IR spectra of P-SAL and the Mannich reaction products: (A) P-SAL, (B) GP-SAL 2, (C) SP-SAL 2, and (D) IP-SAL 2.

from formaldehyde and an amine. Therefore, an aminomethyl group in the Mannich reaction can be introduced at the ortho position of a phenolic hydroxyl group. In thiolignin, it can be introduced at the 5-position of guaiacyl nuclei.[16] In our previous article, we confirmed the introduction of an aminomethyl group into P-SAL at the ortho position of the guaiacyl and/or *p*-hydroxyphenyl units, using our model compound **I**.[9] In this study, the Mannich reaction was carried out with glycine (GP-SAL), sarcosine (SP-SAL), and iminodiacetic acid (IP-SAL) as amines to obtain the carboxylated derivatives (Fig. 3).

The reaction conditions and properties of the Mannich reaction products of P-SAL are shown in Table II. All the products were soluble in water. There were few differences in the molecular weights of the Mannich reaction products, which proved to be almost the same as those of CP-SAL. In comparison with CP-SAL, fewer introduced carboxyl groups of the Mannich reaction products turned out to be soluble in water. This difference may be due to the presence or absence of a phenolic hydroxyl group because CP-SAL was generated while the phenolic hydroxyl group diminished, whereas the Mannich reaction products retained it.

The FTIR spectra of the Mannich reaction products are shown in Figure 5. As with CP-SAL, the peak near 1600 cm^{-1} due to the carboxyl group increased in the Mannich reaction products.

Dispersibility of the prepared SAL derivatives

In this experiment, the dispersibility of the prepared materials was determined by the flow of gypsum paste in the presence of the additives measured with small-scale testing equipment. It is well known that the fluidity of gypsum paste is related to the dosage of the dispersant.[13] The relationship between the flow value and the dosages of commercial LS and a prepared derivative (IP-SAL 1) is presented in Figure 6. LS is a water-soluble supernatant with 6.3% sulfur. As expected, similarly to the flow value of commercial LS, that of IP-SAL increased with an increase in the dosage. Moreover, IP-SAL 1 had a higher dispersion efficiency than LS.

Figure 7 shows the dispersion efficiencies of all the prepared water-soluble SAL derivatives at a 0.1% dosage. This suggests that all the prepared samples possessed a higher efficiency than LS. It is well known that the dispersion efficiency of a dispersant is significantly affected by its molecular weight related to the steric repulsive force and by its ionicity influenced by the electrostatic repulsive force of the dispersant. Uchikawa et al.[17] reported that the steric repulsive force had a greater effect than the electrostatic repulsive force on the fluidity of cement paste. In this study, the molecular weight of prepared lignin derivatives (M_w = 1.7–2.6 × 10^4) was higher than that of LS (M_w = 5.8 × 10^3), and this suggests that the difference in the molecular weights may be one of the reasons for the high efficiency of the prepared polymers.

In GP-SAL and SP-SAL, the dispersion efficiency decreased with an increase in the number of introduced aminomethyl groups, whereas in IP-SAL it increased. Although we found no reason that completely explains this, it may be due to a major effect of the differences in the chemical structure [e.g., the high chelating effect of —N(CH_2COOH)$_2$]. To explain this result, we have to conduct further research into the mechanism underlying dispersibility.

CONCLUSIONS

The preparation of dispersants with carboxyl groups from SAL was investigated. First, to enhance its chemical reactivity, SAL was phenolized with sulfuric acid as a catalyst, and this resulted in a decrease in the molecular weight and the introduction of the *p*-hydroxyphenyl nucleus. To introduce carboxyl groups,

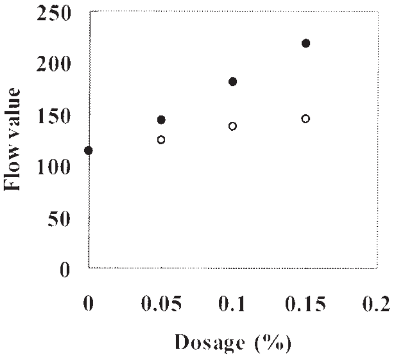

Figure 6 Flow values of IP-SAL 1 and commercial LS (0–0.15%): (●) IP-SAL 1 and (○) commercial LS.

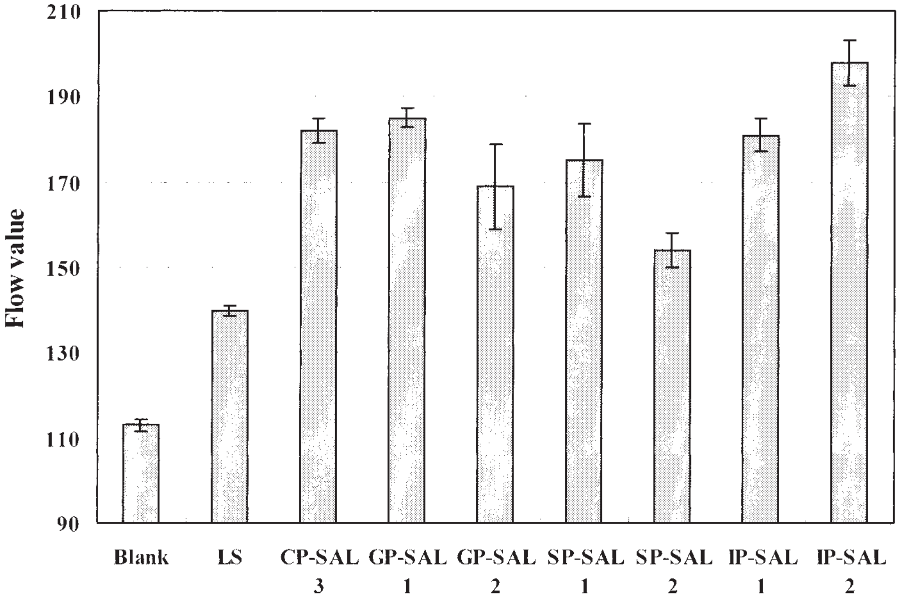

Figure 7 Flow values of prepared water-soluble SAL derivatives at a 0.1% dosage.

two applications were studied. One was carboxymethylation with haloacetic acid, and the other was the Mannich reaction with glycine, sarcosine, and iminodiacetic acid. The carboxymethylation product with 1.4 carboxymethyl groups per C_9–C_6 was soluble in water. The Mannich reaction products were soluble in water with a lower number of carboxyl groups than that of carboxymethylated derivatives. All the prepared water-soluble SAL derivatives possessed a higher dispersion efficiency for gypsum than commercial LS. This may be due to the higher molecular weights of the prepared derivatives in comparison with that of commercial LS.

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