

Effect of Ozone Treatment on Softwood Soda Lignin-based Water Reducer Performance for Concrete

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A lignin-based water reducer for concrete was prepared from softwood soda lignin. The soda lignin and the lignin-polyethylene glycol (PEG) derivative were modified with ozone to improve their performance as water reducers. The performance of ozone-treated soda lignin was superior than untreated soda lignin and commercial lignosulfonate-type water reducers in the mortar flow test. The soda lignin treated with a high ozone charge showed better performance than lignin treated with a low ozone charge. The ozone treatment improved the performance of the lignin-PEG derivative water reducer as well. The lignin-PEG derivative water reducer with a longer PEG chain length showed better performance than that of the shorter PEG chain. The zeta potential of cement suspension with the ozone-treated soda lignin showed a higher negative value than the untreated soda lignin. The data of zeta potential analysis suggested that the electrostatic repulsion force of cement particles with the ozone-treated lignin would be larger than the untreated lignin.

Keywords: Softwood soda lignin; Polyethylene glycol; Ozone; Water reducer for concrete

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INTRODUCTION

A water reducer is a widely used concrete chemical admixture that can improve the workability of fresh concrete, which is made up of cement, water, sand, aggregates, and air. The fluidity of fresh concrete is improved when a water reducer is mixed with the concrete components because of its function as a cement dispersant. The water reducer can decrease the water amount in the cement to provide fluidity in the fresh cement which improves concrete strength (Kosmatka and Wilson 2011). Anionic surfactants prepared from anionic polymers such as lignosulfonate, naphthalene sulfonate, and polycarboxylate type are generally used as water reducers. Lignosulfonate, which is a by-product of the sulfite pulping process and recovered from spent sulfite liquor, is a biomass-based water reducer (Collepari 1996). Naphthalene and polycarboxylate types are synthetic polymers developed as high-performance water reducers, which show better fluidity than lignosulfonate-based water reducers (Sakai *et al.* 2006).

Lignin is the second most abundant biopolymer on earth (Argyropoulos and Menachem 1997). A large amount of black liquor, including lignin-derived substances, is produced as a by-product of the alkaline pulping process such as kraft and soda pulping. Studies have evaluated the potential of various kinds of herbaceous alkaline lignin as water reducers. Nadif *et al.* (2002) report that herbaceous soda lignin helps improve the mortar fluidity and shows a better cement dispersing performance than that of lignosulfonate. Chang and Chan (1995) developed a water reducer made from wheat straw soda lignin

sulfonated in black liquor, which has a similar effect on concrete as a lignosulfonate-type water reducer. Kalliola *et al.* (2015) report the property improvement of wheat straw soda lignin by oxygen treatment under alkaline condition improves water reducers.

Amphiphilic lignins prepared by a chemical conversion of various technical lignins with PEG (polyethylene glycol) have been applied as water reducer. Homma *et al.* (2010) report that amphiphilic lignins prepared from acetic acid lignin or kraft lignin with dodecyloxy-polyethylene glycol glycidyl ether bring a higher flow value of gypsum paste than lignosulfonate. Aso *et al.* (2013) report that amphiphilic lignin prepared from softwood kraft lignin with PEG diglycidylether or ethoxy (2-hydroxy)propoxy PEG glycidylether show higher cement dispersibility than lignosulfonate.

Japanese cedar soda lignin was shown to function as a water reducer and showed better performance than the commercial lignosulfonate water reducer type (Takahashi *et al.* 2014). The soda lignin-PEG derivative was prepared with the PEG mono-epoxide with a 50 mol chain length (the number of repeating units of ethylene oxide) showed better performance than those prepared with a shorter chain length (Takahashi *et al.* 2015).

A water reducer adsorbs on the surface of cement particle and disperses cement particles by electrostatic repulsion and/or steric repulsion. Since cement particles have a positive charge due to calcium ion, acidic groups of the water reducer molecules attach to the surface of cement particle and give the cement surface a slightly negative charge. This negative charge leads to electrostatic repulsion forces among cement particles (Kosmatka and Wilson 2011). The polymer chains of water reducer attached to the surface of cement particle bring steric repulsion among cement particles.

A polycarboxylate-type water reducer which is well known superplasticizer is composed of acrylic acid polymer grafted with a PEG side chain (Sakai *et al.* 2003). The polycarboxylate molecules attach to the cement particles through their adsorption sites of carboxyl groups. The steric repulsion force caused by the PEG side chains of the water reducer disperse the cement particles (Ohta and Uomoto 1997; Sakai *et al.* 2003; Li *et al.* 2005; Yoshioka *et al.* 1997). As cement particles can have a positive surface charge, especially in the absence of dispersants, the carboxyl group in the main molecule chain of the water reducer can work as an effective adsorption site for cement particles.

Ozone is a widely used oxidizing agent. In the pulp and paper industry, ozone has been applied as a bleaching agent to remove residual lignin in pulp. Ozone can react with both phenolic and nonphenolic types of lignin aromatic rings. Lignin aromatic rings react with ozone to form carboxyl groups during an ozone treatment (Hatakeyama *et al.* 1968; Kratzl *et al.* 1976; Kaneko *et al.* 1980, Mansson 1988).

With respect to the modification of industrial lignins, ozone treatment has been applied to introduce anionic functional groups such as carboxyl groups to lignin to change its chemical properties (Kaneko *et al.* 1980; Lee *et al.* 1991; Aimi *et al.* 2008). Detroit (1973) reports that the viscosity of cement slurry decreases when adding ozone-treated softwood kraft lignin derivatives prepared under alkaline conditions. In alkaline conditions, ozone self-degradation is accelerated (Kalmz 1986). A lower pH of the medium is preferred during ozone treatments to minimize ozone self-degradation. The carboxyl group is important in designing the molecule structure of a high-performance water reducer. Ozone treatment introduces functional anionic groups of carboxyl group to lignin.

In this study, the ozone treatment of softwood soda lignin and lignin-PEG derivatives under acidic conditions was investigated. The effect of the ozone treatment on the soda lignin-based water reducer performance with various ozone charges was evaluated using a mortar flow test.

EXPERIMENTAL

Soda Lignin Preparation

Soda lignin was prepared from the black liquor produced by soda-AQ cooking of Japanese cedar (*Cryptomeria japonica*). The cooking conditions to produce the black liquor were reported by Takahashi *et al.* (2014). The black liquor was adjusted to pH 2 using sulfuric acid. The soda lignin was separated from the black liquor by centrifugation at room temperature. The impurity compounds such as sodium sulfate and water-soluble compounds were removed from soda lignin by washing it with distilled water. The washed soda lignin was dried at room temperature.

Soda Lignin Modification with PEG

The PEG mono-epoxide (EPEG) was utilized for modifying the soda lignin. The EPEG was prepared from mono-methoxy PEG with repeating units of 50 mol and 90 mol ethylene oxide obtained from NOF Corporation Japan (Kanagawa, Japan) and Nippon Shokubai (Osaka, Japan), respectively. Then, 500 g of mono-methoxy PEG was dissolved into 500 g of tetrahydrofuran (THF), and 4.8 g or 10 g of sodium hydride (NaH) was added in 50 mol or 90 mol of the methoxy PEG THF solution, respectively. The epichlorohydrin of the four times molar quantity to the methoxy PEGs was added dropwise. The mixture was heated to reflux under N₂ at 70 °C for 3.5 h. After the reaction, distilled water was added to quench excess NaH. The reaction mixture was centrifuged to separate the NaCl by-product. The reaction mixture supernatant was concentrated by evaporation to remove THF. The concentrated mixture was added dropwise onto the mixture of diethyl ether and petroleum ether to precipitate EPEG. The precipitated EPEG was separated by filtration with a glass funnel and washed with ether to remove excess epichlorohydrin and dried under a vacuum. The prepared EPEG was analyzed by ¹H-NMR to check the degree of epoxidation.

The soda lignin was dissolved in 0.8 M NaOH aqueous solution to a concentration of 200 g/L. Table 2 lists the charged weight ratio of EPEG to soda lignin for preparing lignin-PEG derivatives with 50 mol and 90 mol PEG chain lengths. The prepared EPEG was added to the lignin solution in a beaker, and the mixture solution was heated at 70 °C while mixing for 3 h. After heating, the reaction mixture solution was cooled in an ice bath.

The reaction mixture solution contained the lignin-PEG derivative and the unreacted EPEG with soda lignin. The unreacted EPEG did not contribute to cement dispersion. Therefore, the reaction mixture solution (lignin-PEG derivative solution) was directly applied to the mortar flow test. The weight ratio of PEG and lignin moiety in the lignin-PEG derivative was calculated based on the amount of the reacted phenolic hydroxyl group (Takahashi 2015).

Ozone Treatment of Soda Lignin and Lignin-PEG Derivative

The ozone treatment of lignin samples was conducted under an aqueous condition with pH 4 to 5 at room temperature. The pH value of all lignin sample solutions was adjusted with 3 M HCl. For the soda lignin sample, 30 g of soda lignin powder was dissolved in 600 mL of dioxane/water (1/1, v/v). For the lignin-PEG derivative, the reaction mixture solution was directly applied to the ozone treatment. The ozone was generated from oxygen by an ozone generator (ED-OG-R6, Ecodesign, Saitama, Japan). The ozone concentration was measured by iodometric titration. Oxygen with an ozone concentration of 2.4% was bubbled into the lignin sample solution in a gas-washing bottle equipped with

10% KI solution in a trap bottle on the downstream at a flow rate of 0.5 L/min at room temperature. The trapped ozone in the outgoing stream, which did not react with the sample, was measured by iodometric titration to calculate ozone charge of the lignin. The ozone charges were 0.4 or 0.8 mol per one unit of the lignin aromatic ring (the molecular weight of one lignin unit was assumed to be 180) for the soda lignin sample and 0.8 mol for the lignin-PEG derivative sample. After the ozone treatment, the pH of ozone-treated solution decreased. The solution pH was adjusted to pH 5 by 3 M NaOH aqueous solution.

The ozone-treated soda lignin samples were placed in a flask of a rotary evaporator to remove the solvent. The dried ozone-treated soda lignins were dissolved into the NaOH solution before the mortar flow test. The ozone-treated lignin-PEG derivative solutions were directly applied for the mortar flow test.

Mortar Flow Test

The prepared lignin-derived samples (soda lignin, lignin-PEG derivatives, and ozone-treated lignin samples) and a commercial lignosulfonate-type water reducer (LS) (Pozzolith No.8, Pozzolith Solutions Ltd., Kanagawa, Japan) were subjected to the mortar flow test of JIS R5201 (1997). Portland cement obtained from Taiheiyo Cement Corporation (Tokyo, Japan) and ISO standard sand were used in the mortar flow test. The mortar consisted of 500 g of cement, 1350 g of sand, and 250 g of water. The fresh mortar was prepared by mixing water, cement, and sand mechanically with the help of a mixer for 4 min. The flow cone was filled with the fresh mortar right after preparing the mortar. Then, the flow cone was lifted away to allow the mortar to flow. The diameter of mortar (mortar flow value) was measured.

Analysis

The lignin contents in the soda lignin and lignin-PEG derivatives were evaluated by the UV method (Lin and Dence 1992). The absorption coefficient at 280 nm of 30.3 L/g·cm was used to calculate the UV lignin sample content (Takahashi *et al.* 2014). The phenolic hydroxyl group content in the soda lignin and lignin-PEG derivative samples was measured by the ionization difference method (Takahashi *et al.* 2015). The carboxyl group content in the lignin was measured by the conductive titration method (Kaneko *et al.* 1980).

The zeta potential of cement suspension containing soda lignin or ozone-treated soda lignin was determined using a zeta potential analyzer (nano Partica SZ-100 HORIBA, Ltd., Kyoto, Japan) at 25 °C. The cement suspension was prepared by mixing 0.1 g of cement and 50 g of distilled water with the lignin samples in a 100 mL glass beaker. The additive amount of lignin samples was 0.15% of the cement. The suspensions were mixed with a magnetic stirrer for 4 min and dispersed for 30 sec with an ultrasonic bath. The suspensions were transferred into a disposable cell of the zeta potential analyzer.

RESULTS AND DISCUSSION

Ozone Treatment of Softwood Soda Lignin

Soda lignin was treated with 0.4 and 0.8 mol of ozone on one lignin unit of C6-C3 structure. Table 1 lists carboxyl group contents of the soda lignin and ozone-treated soda lignins. The carboxyl group contents of the soda lignin were increased by the ozone treatment. The content increased approximately twofold on the treatment with 0.8 mol of ozone charge. Select carboxyl group derivatives such as ester type of carboxyl group and

muconic acid type could be produced by the lignin ozone treatment (Kaneko *et al.* 1980). To check the presence of the carboxyl group derivatives, the soda lignin treated with 0.8 mol of ozone charge was saponified with 0.1 M NaOH solution at room temperature overnight. After the saponification, the amount of consumed alkaline was measured by a titration with 0.1 M HCl to estimate the carboxyl group derivatives amount. Saponification test data suggested that the carboxyl group derivatives of 0.35 mol per one lignin unit of C6-C3 structure were formed by the ozone treatment. Due to fresh concrete being an alkaline substance, the carboxyl group derivatives such as ester type of compound could change to the carboxylate group within the fresh concrete.

Table 1. Carboxyl Group Content of Soda lignin (SL) and Ozone-Treated Soda Lignins (SL-Z1 and SL-Z2) and Zeta Potential of the Cement Suspension with a Sample

Sample	Ozone Charge on Lignin (mol/one lignin aromatic ring)	Carboxyl Group Content (mol/ one lignin aromatic ring)	Zeta Potential of Cement Suspension with a Sample (mV)
SL	-	0.23	-4.5
SL-Z1	0.4	0.30	-5.7
SL-Z2	0.8	0.42	-7.7

Water Reducer Performance of Ozone Treated Soda Lignin

The soda lignin and ozone-treated soda lignins were subjected to the mortar flow test to evaluate their performance as a water reducer. Higher mortar flow values represent better performance as water reducer. Figure 1 shows the mortar flow value plotted with the additive amount of samples on cement in the mortar flow test. The ozone-treated soda lignins brought a higher mortar flow value than SL and LS at the same additive amount on the cement.

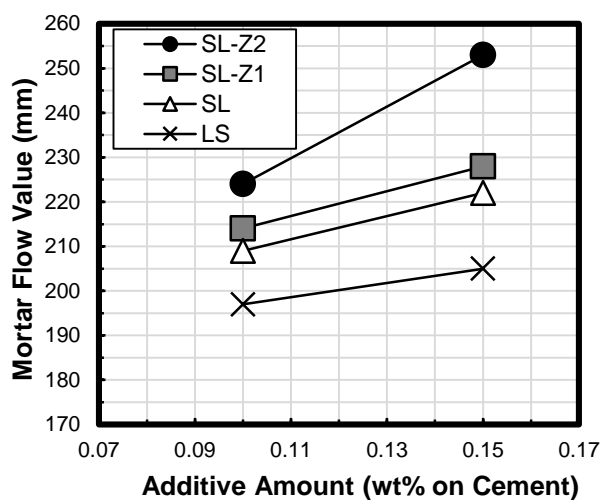


Fig. 1. Relationship between mortar flow value and additive amount of soda lignin (SL), ozone-treated soda lignins (SL-Z1 and Z2), and the commercial lignosulfonate-based water-reducing admixture (LS)

Anionic groups help adsorb water reducer on the surface of cement particle. When the water reducers adsorb on cement particles, they give repulsion forces such as the electrostatic repulsion force to repulse the cement-water reducer complexes (Sakai *et al.* 2003). A higher absolute value of the cement particle zeta potential brings better cement dispersibility (Daimon and Roy 1979). As listed in Table 1, the zeta potential of cement suspension with the ozone-treated soda lignin showed more negative potential than the untreated soda lignin. The force of electrostatic repulsion among cement particles with the ozone-treated soda lignins would be larger than the untreated lignin.

As shown in Fig. 1, the ozone-treated soda lignins with an ozone charge 0.8 mol (SL-Z2) brought a higher mortar flow value than that with 0.4 mol (SL-Z1). Table 1 shows the zeta potential of cement suspension with the samples. The SL-Z2 cement suspension showed a larger negative value than SL-Z1. These results indicated that the soda lignin on introducing a higher carboxyl group content exhibited better performance than the lower carboxyl group due to larger negative charge attributed to the carboxyl group.

Performance of the Lignin-PEG Derivatives

Table 2 lists the chemical modification conditions of the soda lignin with EPEG and the phenolic hydroxyl group content and PEG contents of the prepared lignin-PEG derivative. To evaluate the effect of PEG content in the derivatives, four types of lignin-PEG derivatives with various PEG contents were prepared in each series of PEG chain lengths.

Table 2. Preparation of a Lignin-PEG Derivative with 50 and 90 mol PEG Chain Lengths: Modification Conditions of Soda Lignin, PhOH Group Content, and PEG Content of Lignin-PEG Derivatives

Sample	Modification Condition		Lignin-PEG Derivative	
	EPEG (EO) mol	EPEG/Lignin (Weight Ratio)	PhOH Group Content* (mmol/g Lignin)	PEG Content (wt%)
50-1	50	19/81	2.57	7
50-2		46/54	2.29	42
50-3		66/34	1.87	62
50-4		76/24	1.53	71
90-1	90	24/76	2.52	23
90-2		55/45	2.39	46
90-3		68/32	2.13	65
90-4		88/12	1.46	82

Note: *PhOH group content of soda lignin 2.60 mmol/g

Figures 2 and 3 shows the dispersibility plotted with the additive amounts of the lignin-PEG derivative on the cement in the mortar flow test. The dispersibility is the percentage of the improved mortar flow value based on the plain mortar flow value.

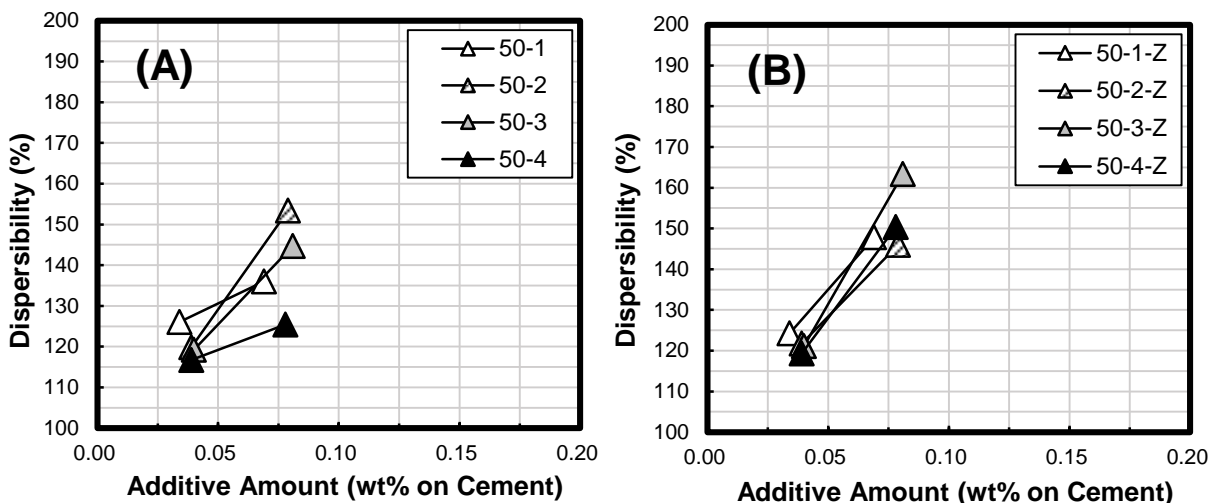


Fig. 2. Dispersibility of lignin-PEG derivatives of the 50 mol PEG chain length series; (A) plain samples and (B) ozone-treated samples

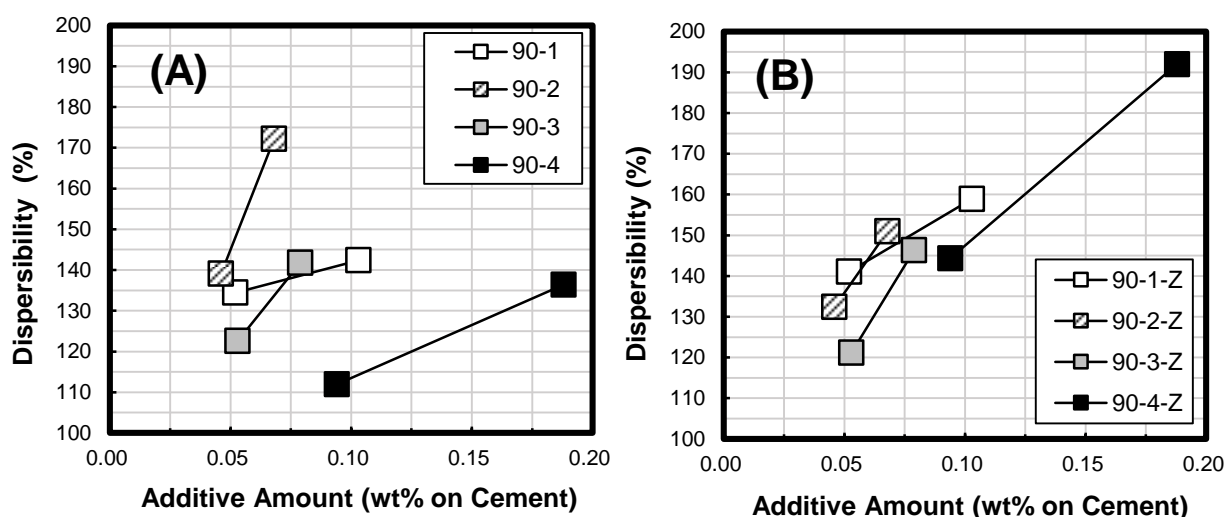


Fig. 3. Dispersibility of lignin-PEG derivatives of the 90 mol PEG chain length series; (A) plain samples and (B) ozone-treated samples

The mortar flow value without any additive was 161 and 151 mm in the 50 mol series test (Fig. 2) and 90 mol (Fig. 3) series test, respectively. As shown in Fig. 3(A), the performance of the lignin-PEG derivative with the PEG chain length of 90 mol on the mortar was in the following order: 90-2 > 90-1 \approx 90-3 > 90-4. The 90-2 sample with a PEG content of 46% showed the highest dispersibility in the 90 mol PEG series. However, the lignin-PEG derivatives (90-3 and 90-4) with further increasing PEG content showed lower dispersibility than the 90-2 sample. Increasing the PEG introduction amount to the soda lignin decreased the residual phenolic hydroxide group amount, which could be one of the adsorbing sites of the cement particle surfaces (Takahashi *et al.* 2015). As shown in Fig. 2(A), in the 50 mol PEG chain length series, the best dispersing performance was the 50-2 sample with a PEG content of 42%. In the 90 mol PEG chain length series, the best dispersing performance was the 90-2 sample. Both 50-2 and 90-2 samples had a similar

PEG content level of approximately 40 wt%.

A previous study reports the improved performance in 10, 25, and 50 mol of the PEG chain length (Takahashi *et al.* 2015). In this paper, the longer PEG chain of 90 mol type was prepared to evaluate the cement dispersion performance. Comparing the dispersibilities of lignin-PEG derivative with 90 mol and 50 mol PEG chain length at the same additive amount on the cement, the data of 90 mol chain length (90-2) showed 1.2 times better dispersibility than the 50 mol chain length of 50-2. These results supported the idea that a longer PEG chain is appropriate for developing a high-performance water reducer based on softwood soda lignin (Takahashi *et al.* 2015).

Performance of the Ozone Treated Lignin-PEG Derivatives

The lignin-PEG derivatives were treated with ozone under acidic medium conditions. The ozone was charged for 0.8 mol on one lignin C6-C3 unit of the lignin-PEG derivative. Table 3 lists the carboxyl group contents of the lignin-PEG derivatives and their ozone treated samples. As shown, the ozone treatment increased the carboxyl group content in the lignin-PEG derivatives. Figure 4 shows a presumed chemical structure of the ozone-treated lignin-PEG derivative. As the ozone treatment produced carboxyl groups, the ozone treated lignin-PEG derivative had the PEG chain as well as carboxyl groups in one molecule.

Table 3. Carboxyl Group Content of Untreated and Ozone-Treated Lignin-PEG Derivatives

Sample	Carboxyl Group Content (mmol/g lignin-PEG derivative)	
	Untreated	Ozone-Treated
50-1	1.39	1.73
50-2	0.76	1.52
50-3	0.51	0.97
50-4	0.38	0.93
90-1	1.08	1.84
90-2	0.76	1.39
90-3	0.48	1.20
90-4	0.26	0.67

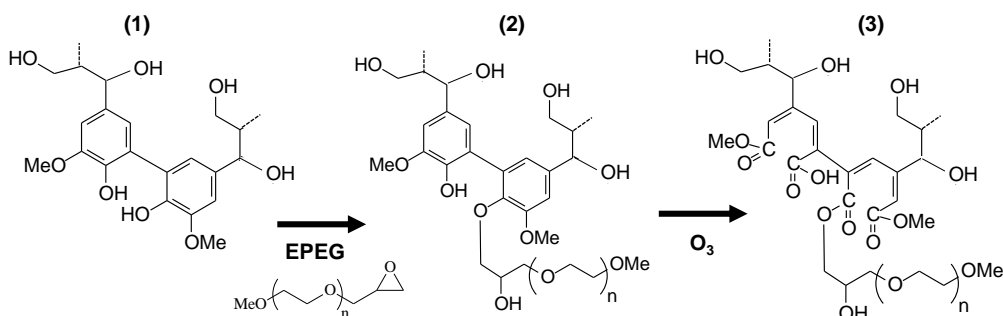


Fig. 4. Presumed chemical structures; (1) unmodified lignin, (2) lignin-PEG derivative, and (3) ozone-treated lignin-PEG derivative

Figures 2 and 3 show the dispersibility plotted with the additive amount of the ozone-treated lignin-PEG derivatives. For the 90 mol PEG chain length series, the performance of the ozone-treated samples was estimated by the slope of the line in Fig. 3(B) in the following order: 90-1-Z \approx 90-2-Z > 90-3-Z > 90-4-Z. However, the ozone

treatment did not work for the 90-2 sample. The ozone treatment improved the performances of the 90-1, 90-3, and 90-4 samples. For the 50 mol PEG chain length series, the ozone treatment improved the performance of the 50-1, 50-3, and 50-4 samples. However, this treatment did not work for the 50-2 sample (Fig. 2). The results suggested that the ozone treatment could be effective in improving the following two types of lignin-PEG derivatives: lignin-PEG derivative with relatively smaller PEG content such as 90-1 (PEG content 23%) and lignin-PEG derivatives with relatively higher PEG content such as 90-3 and 90-4 (PEG content 65% and 82%, respectively). In contrast, the performance of ozone-treated lignin-PEG derivatives of 90-2 and 50-2 did not change much. As the performance of these two samples might already be at the highest level, the ozone treatment could not show apparent improvement in the mortar flow test.

CONCLUSIONS

1. The ozone treatment was applied to improve the softwood soda lignin-based water reducer. The mortar flow test showed that the water reducer performance of ozone treated soda lignin was higher than that of untreated soda lignin and commercial lignosulfonate-based water reducer.
2. The negative zeta potential value of the cement slurry with the ozone-treated soda lignin was larger than that of the untreated soda lignin. Cement particles would be dispersed more by the electrostatic repulsion force due to the ozone-treated soda lignin with higher amount of carboxyl groups.
3. To develop a high-performance soda lignin-based water reducer, soda lignin was modified with polyethylene glycol (PEG), which could introduce steric repulsion, then applied to the ozone treatment. The ozone treatment improved the performance of lignin-PEG derivative type of water reducer.

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