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THE THESIS FOR THE DEGREE OF MASTER SCIENCE

**Study on sulfomethylation of kraft lignin
for use as a superplasticizer**

크라프트 리그닌의 유동화제 사용을 위한
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Abstract

Study on sulfomethylation of kraft lignin for use as a superplasticizer

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The large amount of kraft lignin has been produced from kraft pulping and incinerated to be converted to energy. However, kraft lignin has a possibility to be used as more value-added material via chemical modification. Lignosulfonate produced by sulfite pulping is used as a superplasticizer, but the production of lignosulfonate has been dwindled because sulfite pulping has been substituted to kraft pulping. Therefore, there are a lot of efforts to substitute lignosulfonate to kraft lignin via a variety of chemical modification.

In this study, sulfomethylation of kraft lignin was conducted by using formaldehyde and sodium sulfite in sodium hydroxide solvent with various reaction conditions. And then, final pH was adjusted with sulfuric acid (1 M) followed by centrifugation (12000 rpm, 15 min) to separate liquid and solid phases. Dried-solid sample was obtained by freeze-drying. Sulfomethylation of kraft lignin was conducted at final pH (7, 5 and 2), reaction temperature (80, 100 and 120°C), reaction time (1, 3, 5, 8 and 11 h), the dosage molar ratio of reagents (formaldehyde and sodium sulfite) to lignin (0.225, 0.45, 0.9 and 1.2:1). A particle charge detector (PCD) was utilized to measure charge

density of the sulfomethylated kraft lignin by using a titrant (polydiallyldimethylammonium, PolyDADMAC). By fourier-transform infrared (FT-IR) spectroscopy analysis, the changed functional group on lignin could be examined, and the different ratio of guaiacyl and syringyl group could be investigated by phosphorus-31 nuclear magnetic resonance (^{31}P -NMR). Furthermore, elementary analysis was utilized to compare the content of sulfonate. Through these analyses, the characteristics of sulfomethylated lignin under different reaction conditions were compared.

As a result of this study, the reaction condition for the highest charge density was determined as pH 5 for final pH, 100 °C for reaction temperature, 5 h for reaction time and 0.9:1 for the dosage molar ratio of reagents to lignin. On the other hand, the maximum fluidity of cement was obtained at pH 5 for final pH, 100 °C for reaction temperature, 3 h for reaction time and 0.45:1 for the dosage molar ratio of reagents to lignin. It was anticipated that more charge density made workability of cement increase, but the tendency between charge density and fluidity of cement was not corresponded. Moreover, there was not proportional tendency among the content of sulfur, charge density and fluidity of cement. According to similar studies, polycarboxylate which had high molecular weight, low charge density and longer chain structure was compared to sulfonated naphthalene formaldehyde condensate (SNFC), which had low molecular weight and high charge density. As a result, cement fluidity was better in case of polycarboxylate. Moreover, the separation of lignosulfonate with different molecular weight was carried out, and viscosity of cement paste was not proportional to molecular weight. Considering charge density and molecular weight were not in proportional relation with fluidity of cement, longer chain structure may have been regarded as the key factor for high fluidity of cement.

To investigate the influence of constituent unit of lignin in sulfomethylation, softwood kraft lignin (SKL) was sulfomethylated in same reaction condition and compared to hardwood kraft lignin (HKL). SKL which

had more guaiacyl group indicated higher charge density and fluidity of cement than HKL.

**Key words: lignin, sulfomethylation, charge density, fluidity of cement,
lignin modification, anionic charge**

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Contents

1. Introduction.....	1
1.1. Lignin & technical lignin.....	1
1.2. Lignin as a superplasticizer.....	4
1.3. Obstacles of technical lignin.....	6
1.4. Objectives.....	7
2. Literature reviews.....	9
2.1. Precipitation of kraft lignin.....	9
2.2. Modification of kraft lignin.....	10
2.3. Sulfomethylation & sulfonation of technical lignin for a superplasticizer.....	11
3. Materials & methods.....	13
3.1. Materials.....	13
3.2. Sulfomethylation of kraft lignin.....	13
3.3. The measurement of fluidity of cement.....	15
3.4. Characteristics of sulfomethylated kraft lignin.....	15
3.4.1. Charge density analysis.....	15
3.4.2. Solubility of sulfomethylated kraft lignin in water.....	16
3.4.3. FT-IR spectrometer.....	16
3.4.4. Gel permeation chromatography (GPC).....	16
3.4.5. ³¹ P-NMR analysis.....	17
3.4.6. Elementary analysis.....	17
4. Results & discussion.....	19
4.1. Analysis of salts produced by side reaction.....	19
4.1.1. Comparison between SHKL with and without dialysis.....	19
4.1.2. The analysis of unreacted salts.....	25
4.2. Effect of each factor to charge density.....	27
4.2.1. Final precipitating pH.....	27
4.2.2. Reaction temperature.....	31
4.2.3. Reaction time.....	33
4.2.4. The dosage molar ratio of reagents to lignin.....	35

4.3. The reaction condition for the highest fluidity of cement.....	37
4.4. The relation among sulfur content, charge density and fluidity of cement.....	42
4.5. Comparison between SKL & HKL.....	48
4.5.1. Analysis of unreacted SKL & HKL.....	48
4.5.2. Comparison of unreacted and sulfomethylated SKL & HKL.....	53
4.6. Comparison between SHKL & commercial lignosulfonate.....	57
5. Conclusion.....	61
6. References.....	63

List of Tables

Table 1. Chemical properties of the technical lignin.....	3
Table 2. Elementary analysis results of product reacted without lignin, HKL, SHKL with and without dialysis.....	22
Table 3. Charge density and fluidity of cement for product reacted without lignin, SHKL with and without dialysis.....	23
Table 4. Charge density and solubility for SHKL at different final pH.....	29
Table 5. Charge density and solubility for SHKL at different reaction temperature.....	32
Table 6. Charge density and solubility for SHKL at different reaction time....	34
Table 7. Charge density and solubility for SHKL at different dosage molar ratio to lignin.....	36
Table 8. Charge density, fluidity of cement and molecular weight at different reaction temperature.....	39
Table 9. Charge density and fluidity of cement and molecular weight at different reaction time.....	40
Table 10. Charge density and fluidity of cement and molecular weight at different dosage molar ratio of reagents to lignin.....	41
Table 11. Solubility, charge density and fluidity of cement for SKL and HKL.....	51
Table 12. Comparison of the amount of each type of hydroxyl group for SKL and HKL by using ³¹ P-NMR.....	52
Table 13. Solubility, charge density and fluidity of cement for SSKL and SHKL.....	55
Table 14. Elementary analysis results of SHKL and commercial lignosulfonate.....	59
Table 15. Charge density and fluidity of cement for SHKL and commercial lignosulfonate.....	60

List of Figures

Figure 1. The mechanism of sulfomethylation of lignin.....	14
Figure 2. FT-IR spectra of the salts reacted without lignin, SHKL without dialysis and unreacted reagents obtained after dialysis.....	21
Figure 3. FT-IR spectra of SHKL with and without dialysis	24
Figure 4. FT-IR spectra of unreacted reagents obtained after dialysis, sodium sulfate, sodium sulfite and sodium thiosulfate.....	26
Figure 5. FT-IR spectra of SHKL at different final pH.....	30
Figure 6. The relation between the content of sulfur and charge density.....	44
Figure 7. The relation between the content of sulfur and fluidity of cement..	45
Figure 8. The relation between charge density and fluidity of cement.....	46
Figure 9. Model of train- and loop-formation for low and high molecular weight polymer.....	47
Figure 10. FT-IR spectra of SKL and HKL without sulfomethylation.....	50
Figure 11. FT-IR spectra of SSKL and SHKL.....	56
Figure 12. FT-IR spectra of SHKL and commercial lignosulfonate.....	58

List of Abbreviations

FT-IR	fourier-transform infrared spectroscopy
GPC	gel permeation chromatography
HKL	hardwood kraft lignin
³¹P-NMR	phosphorus-31 nuclear magnetic resonance
SHKL	sulfomethylated hardwood kraft lignin
SKL	softwood kraft lignin
SNFC	sulfonated naphthalene formaldehyde condensate
SSKL	sulfomethylated softwood kraft lignin

1. Introduction

1.1. Lignin & technical lignin

Lignin is a natural and the second bountiful organic polymer in plants. It is obtained approximately 50 million tons from industry (Mai et al., 2000) and takes up 20-35% of the weight of plants. Lignin principally consists of hydroxyl-phenylpropane units that are *p*-coumaryl, sinapyl and coniferyl alcohols and is categorized into two generous groups, with ether (C-O-C) linkages and carbon-carbon (C-C) linkages. The former are separated into β -O-4, α -O-4, 4-O-5 and the latter are separated into 5-5, β -5, β -1, β - β , prominently. These linkages make lignin have complex and heterogeneous structures. However, although lignin is the most prominent component followed by cellulose, the amount of lignin used in industry was just 2% for commercialization in 2005. Thus, various researches and technical developments have been conducted to use extra technical lignin efficiently (Kubo & Kadla, 2005). Despite of low efficiency of using technical lignin, the attractive properties of lignin, such as high abundance, antioxidant property, biodegradable and amphiphilic properties, have a potential for being utilized in various areas (Thakur et al., 2014).

The properties of technical lignin appear differently according to the origin of biomass as well as pulping processes (Table 1). Furthermore, they can be derived from a variety of pulping processes or treatments of biomass (Vishtal & Kraslawski, 2011). Therefore, researches of lignin with different functional groups and structures should be conducted to be used properly. Kraft lignin, which accounts for 85% of technical lignin obtained around the world (He & Fatehi, 2015), is obtained from black liquor by adding strong mineral acid, such as H₂SO₄, in kraft pulping process (Sjöström, 1993). Kraft pulping, using “white liquor” composed of sodium hydroxide and sodium

sulfide, is the preminent process in pulp industry. During this process, lignin is eliminated from cellulose, and black liquor with lignin is produced (Chakar & Ragauskas, 2004). Kraft lignin has a lot of phenolic group in its structure because many β -aryl ether and enol ether linkages are cleaved during pulping process (He & Fatehi, 2015). Meanwhile, lignosulfonate is originated from sulfite pulping by using sulfite liquor that consists of calcium hydrogen sulfite and sulfur dioxide (Sjöström, 1993). Lignosulfonate has anionic charges due to sulfonate group which makes it have high solubility in water (Aro & Fatehi, 2017). For this reason, lignosulfonate, which has a colloidal properties, is able to be utilized for an adhesive agent, plasticizer and a dispersant and so on (Sjöström, 1993). Organosolv lignin is produced by organosolv pulping with acid or alkali treatment, which is an important biorefinery process for biomass (Rinaldi et al., 2016). Organosolv lignin has more α -ether than β -ether bonds in alkali treatment, and has more β -ether bonds than α -ether bonds in acid treatment (Sun et al., 1997). During organosolv process, lignin is isolated via solubilization, which separates lignin with less changed structure. Soda lignin is derived from soda pulping process which is treated by sulfur-free liquor. It is more similar to original lignin than kraft lignin or lignosulfonate in view of non-sulfur content (Vishtal & Kraslawski, 2011). Especially, side chain structures and many hydroxyl groups are dwindled during soda pulping (Wormeyer et al., 2011).

Table 1. Chemical properties of the technical lignin (Vishtal & Kraslawski, 2011)

Parameter	Kraft lignin	Lignosulfonate	Organosolv lignin	Soda lignin
Ash (%)	0.5-3.0	4.0-8.0	1.7	0.7-2.3
Polydispersity (M_w/M_n)	2.5-3.5	4.2-7.0	1.5	2.5-3.5
Molecular weight, M_w (g/mol)	1,500-5,000 (up to 25,000)	1,000-50,000 (up to 150,000)	500-5,000	1,000-3,000 (up to 15,000)
Sulfur (%)	1.0-3.0	3.5-8.0	0	0
Nitrogen (%)	0.05	0.02	0-0.3	0.2-1.0
Carbohydrates (%)	1.0-2.3	-	1-3	1.5-3.0
Acid soluble lignin (%)	1-4.9	-	1.9	1.0-11

1.2. Lignin as a superplasticizer

A superplasticizer, same as a dispersant or dispersing agent, is used to enhance the mechanical properties of polymers, proteins, dye, cement and oil (Horoz et al., 2004). Some specific purposes to use a superplasticizer are to lower the viscosity of concrete, to decrease moisture content of cement mixture and to give electrostatic repulsion (He & Fatehi, 2015). To use the dispersing agents in industry, the ability of them should be estimated by investigating chemical components, molecular weight and charge density. However, there are problems that dispersing agents from nature, such as starches and alginates, are main materials for aggregation controller because of conflicts to food problem. Besides, it has some defects such as low efficiency, low heat durability and crushing with food (Amjad, 2001). Moreover, a naphthalene sulfonic acid dispersant based on petroleum chemicals is commonly used, but it has some critical disadvantages as weakness by heat, harmfulness and expensiveness. Therefore, other alternative resources as dispersing materials excepting from food and harmful chemicals should be found.

Because lignin is amphiphilic and relatively easy to modify functional group by using chemicals, it has been preferred to use as a superplasticizer. Also, lignin as a bio-based material is able to decrease surface tension in a suspension or a colloid. It causes splitting of insoluble particles preventing aggregation. These are the principal reasons why lignin is tried to be utilized as a dispersing agent (Calvo-Flores et al., 2015). First of all, the production of lignosulfonate was restricted worldwide because sulfite pulping has dwindled gradually. Meanwhile, the huge amount of kraft lignin are produced from kraft pulping process (Kouisni et al., 2012). Generally, by-products of pulping, such as kraft lignin, are underestimated because of their low solubility in organic solvent and heterogeneous

molecular weight. After chemical modification of these by-products to overcome limits by attaching sulfite and carboxylate, they can be used as a superplasticizer more effectively. They take advantages not only on reducing expenses in industry, but also on environmental aspects. Sulfomethylation and carboxylation of lignin are common methods to give hydrophilicity to lignin. This property makes lignin more affiliate to cement particles and give more zeta potential to this particles. Therefore, fluidity of cement caused by the modified lignin can be improved due to enhancement of electrostatic repulsion.

1.3. Obstacles of technical lignin

Lignosulfonate, a by-product from sulfite pulping, has been mainly used as a superplasticizer in industry. However, the profit efficiency is not reasonable for commercialization because precipitation of lignosulfonate in acid condition is very limited, so separation of sugar and lignosulfonate with high yield is difficult (Fatehi & Chen, 2016). Moreover, the amount of lignosulfonate from sulfite pulping is not sufficient because of challenging filtration and fractionation (Areskogh, 2011). Besides, lignosulfonate has few sulfonate group that is one of the important factors for high zeta potential of cement particles (He & Fatehi, 2015). Additionally, suitable method for polymerizing of lignosulfonate for high molecular weight has not revealed recently (Areskogh, 2011). Because of these limitations, other alternatives and bio-based dispersants need to be developed. Specifically, to substitute lignosulfonate to an effective bio-based superplasticizer, modification of functional groups in technical lignin should be investigated. A change into anion groups such as sulfonate, carboxylate and phenolic hydroxyl group could be the main examples.

Large amounts of technical lignin, such as kraft lignin, organosolv lignin, soda lignin and so on, are manufactured via different pulping processes and they have the potential for valuable products. However, use of them as raw technical lignin are not efficient, so many researches have recently studied to utilize them as a bio-based dispersing agent, which is substituting petroleum-based materials via various modification. Through these processes, technical lignin is able to become high-valued products.

1.4. Objectives

Kraft lignin obtained from kraft pulping is the most abundant technical lignin. However, its application is not well-developed, and almost of the kraft lignin is used to generate energy by incineration with low efficiency. Therefore, application of kraft lignin needs to be investigated because of their large amount of production and the potentials for various applications. Using raw kraft lignin in industry is not easy to handle due to their low reactivity and heterogeneous structures, so it should be treated with chemical reaction for various applications such as sulfonated lignin, carbon fibers, fertilizers, activated carbon and so on. Sulfomethylation, the way to improve anionic properties on the lignin, is one of the promising techniques to increase the value of kraft lignin. It affects the charge density that is related to dispersion of cement particles caused by adsorption, and is the one of the crucial factors for a superplasticizer.

In this study, it was intended to investigate the suitable sulfomethylation condition by using formaldehyde and sodium sulfite for the application as a superplasticizer. Some functional groups could be added by sulfomethylation to make more anionic properties. After these processes, sulfomethylated kraft lignin was mixed with cement, and the fluidity of cement was analyzed to estimate the possibility for a superplasticizer. Moreover, charge density of the products was measured, and functional groups and degree of sulfomethylation was determined to reveal how much these factors affect charge density related to an effective dispersant.

Specifically, the aims of this study are:

1. To evaluate the impact of sulfomethylation to increase charge density which is one of the important factors for a superplasticizer.
2. To analyze sulfomethylated products concerning their anionic

functional groups and charge density to reveal the relation among these factors and fluidity of cement.

3. To figure out condition of sulfomethylation for kraft lignin to maximize fluidity of cement.

2. Literature reviews

2.1. Precipitation of kraft lignin

According to various precipitation methods, kraft lignin which has different properties, such as molecular weight, functional groups and surface morphology, can be produced. If kraft lignin with various characteristics can be utilized efficiently by using each specific property, waste of them in industry can be decreased.

Hermiati et al. conducted two-step precipitation of kraft lignin by using hydrochloric acid and ethanol. They made pH of black liquor approximately 12 followed by adding ethanol into the black liquor to precipitate sugars. After these processes, acid was continued to add up by pH 2. From two-step treatment, they obtained the higher amount of precipitated kraft lignin and the lower ash content compared to the process without addition of ethanol. Moreover, they investigated the removal of sugar did not influence the lignin structure and surface morphology of the lignin. Some dirt on the surface was found, and there were few pores on the surface. It meant isolation of kraft lignin by using hydrochloric acid was not efficient owing to not completely removed non-lignin components. (Hermiati et al., 2016)

Zhu and Theliander precipitated kraft lignin by using sulfuric acid under different temperatures and ionic strengths. They investigated the amount of precipitated kraft lignin augmented at lower pH and temperature, and higher ionic strength. Moreover, the amount of phenolic hydroxyl groups increased with decreasing yield of kraft lignin and increasing molecular weight of precipitated kraft lignin. Besides, the amount of methoxyl groups increased with lowering precipitation yield. In other words, the tendency of the changes by precipitation yield in the content of methoxyl and phenolic hydroxyl groups was opposite. (Zhu and Theliander, 2015)

2.2. Modification of kraft lignin

The production of kraft lignin via kraft pulping has increased consistently, while almost of the kraft lignin has been incinerated to use as energy. Therefore, various modifications of kraft lignin have been studied to make valuable chemicals.

Dua et al. investigated the Mannich reaction for modification of kraft lignin. Mannich reaction is the process to attach the alkyl-substituted amine on aromatic ring in lignin. It is expected to increase hydrophilicity, dispersing ability and positive charge of lignin in acid solution (Dua et al., 2013).

Kalliola et al. tried to investigate how lignin is functionalized by excessive O₂ treatment in sodium hydroxide solution. The result showed that there was no change in functional groups, but the condensation of kraft lignin by 5-5 radical coupling was examined. This reaction was a relatively simple way to increase molecular weight of kraft lignin by 5-5 coupling without unnecessary functionalizing process (Kalliola et al., 2014).

Kim et al. showed that modification of kraft lignin by using tetrahydrofuran and γ -butyrolactone as a reagent and sulfuric acid as a catalyst. In case of tetrahydrofuran modification, aliphatic and non-condensed phenolic hydroxyl groups were not reacted. In contrast, the content of carboxyl groups and β -O-4 alpha hydroxyl groups decreased. In case of γ -butyrolactone modification, hydroxyl groups in aliphatic and non-condensed phenolic structure were mainly reacted. Moreover, small amount of β -O-4 alpha hydroxyl groups was decreased. This study supposed that the reaction using tetrahydrofuran or γ -butyrolactone can functionalize selectively in kraft lignin (Kim et al., 2016).

2.3. Sulfomethylation & sulfonation of technical lignin for a superplasticizer

Sulfonation of technical lignin is mainly utilized to use lignin as a superplasticizer that needs high charge density. Therefore, many researches have tried to increase anion groups by using different chemicals to increase charge density via sulfonation (Dekker, 1994).

Ouyang et al. studied sulfonation of alkali lignin after oxidation and hydroxymethylation using hydrogen peroxide, iron sulfate and various amount of formaldehyde under different temperatures. Oxidation and hydroxymethylation was conducted to increase the reactivity of alkali lignin for sulfonation. Sulfonation of alkali lignin with different amount of sodium sulfite was conducted. And then, the amount of adsorption, zeta potential and fluidity of the cement paste were measured. In this study, they concluded that degree of sulfonation and dispersibility increased with the augmentation of the oxidation temperature. Moreover, the amount of formaldehyde of 40 wt% based on alkali lignin showed the maximum of sulfonation degree and dispersibility. Moreover, they compared zeta potential of the commercial lignosulfonate with sulfonated lignin. It showed that sulfonated lignin had higher zeta potential than the lignosulfonate which means better dispersion effect of sulfonated lignin (Ouyang et al., 2009b).

He and Fatehi estimated the relation between the sulfonation degree and fluidity of cement. Softwood kraft lignin (SKL) was oxidized by nitric acid with different temperatures and times. After oxidation, they sulfonated lignin with sodium hydroxide, formaldehyde and sodium metabisulfite under different temperatures and time. And then, they investigated the adsorption of lignin on cement particles and the fluidity of the cement paste mixed with sulfonated kraft lignin. According to their study, oxidation before sulfonation made sulfonated lignin have more charge density which caused the higher

electrostatic repulsion, so the fluidity of cement augmented. Moreover, the sulfonation degree augmented to a certain extent with increase of formaldehyde amount, and then decreased. However, too much amount of sodium metabisulfite and increasing temperature decreased sulfonation degree. Consequently, charge density and fluidity of cement paste was increased with the augment of the sulfonation degree. (He & Fatehi, 2015).

Huang et al. used sweet gum tree lignin that is acquired after auto-hydrolysis and enzymatic hydrolysis by using sodium hydroxymethylsulfonate that was formed by formaldehyde and sodium sulfite. They targeted to investigate a maximum content of water-soluble lignosulfonate from enzymatic hydrolysis residue by differentiating the charge of sodium hydroxymethylsulfonate. As a result, 2 mmol/g of enzymatic hydrolysis residue was the optimum concentration of sodium hydroxymethylsulfonate for the maximum sulfur content that was a mark of sulfomethylation (Huang et al., 2016).

3. Materials & methods

3.1. Materials

HKL (Moorim Pulp & Paper) and SKL (Domtar) were used as starting materials which were by-products of kraft pulping using sodium hydroxide and sodium sulfide. Formaldehyde (35%) and sulfuric acid (95%) were purchased from SAMCHUN chemical (Pyeongtaek, South Korea), and sodium sulfite was purchased from SHINYO PURE chemicals CO., LTD (Osaka, Japan). NaOH was purchased from Junsei chemical Co., Ltd (Tokyo, Japan).

3.2. Sulfomethylation of kraft lignin

Sulfomethylation of kraft lignin was conducted in 500ml three-neck round bottom glass flask with condenser. A 5 g of kraft lignin was reacted with formaldehyde and sodium sulfite and 250 ml of 0.5 M sodium hydroxide at 150 rpm. The reaction was conducted under different molar ratios of formaldehyde and sodium sulfite to lignin (0.225, 0.45, 0.9 and 1.2:1), temperature (80, 100 and 120 °C) and reaction time (1, 3, 5, 8, 11 h). And then, it was cooled down at room temperature followed by adding sulfuric acid to reduce pH of solution under different final pH (2, 5 and 7). Dialysis tubing process was conducted by using dialysis membranes (H1, Cellu-Sep[®], USA) for 6 h, exchanging water per 3 h. After acidification or dialysis of reacted lignin solution, liquid and solid parts were separated by centrifugation at 12,000 rpm for 15 min. Freeze-drying was conducted to obtain a solid-state sulfomethylated lignin. After the process, sulfomethylated kraft lignin was obtained and the mechanism of reaction was shown as Figure 1A (Pang et al., 2008) and 1B (Ouyang et al., 2009a).

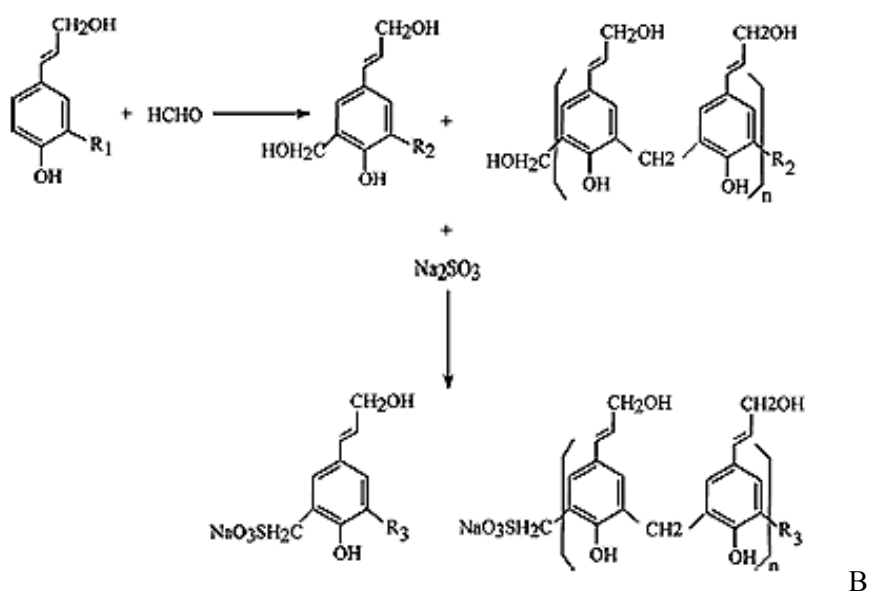
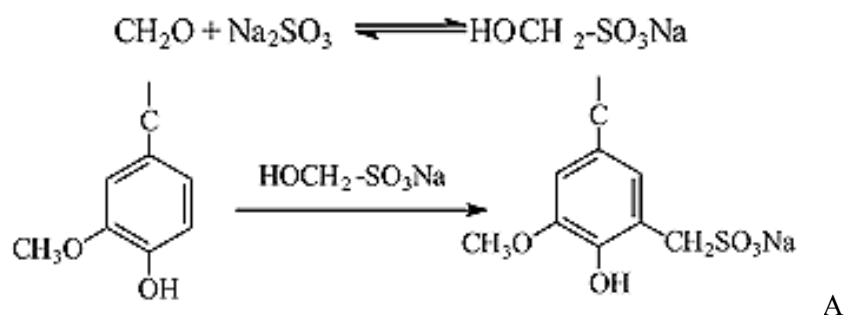


Figure 1. The mechanism of sulfomethylation of lignin (Ouyang et al., 2009a; Pang et al., 2008).

3.3. The measurement of fluidity of cement

The 1.2 g of SKL was mixed with a 600 g of masonry cement mortar (Sampyo, Korea) and 96 g of water by using a cement paste blender for 4 min (slow for 1 min, and fast for 3 min). After mixing them, the mixture was poured on a flow table composed with a conical frustum shape mold with a top diameter of 70 ± 0.5 mm and a base diameter of 100 ± 0.5 mm. After the paste was poured into the mold by approximately 3/4, the paste was pressed 25 times by using cuboid stick. And then, the mold was totally filled with the paste followed by being pressed 25 times with the cuboid stick. The mold was removed, and the flow table was dropped 25 times. As the paste was dropped, it spread out on the flow table. After finishing dropping the flow table, the changed diameter was measured 3 times to calculate average diameter.

3.4. Characteristics of sulfomethylated kraft lignin

3.4.1. Charge density analysis

After sulfomethylation of kraft lignin, charge density was analyzed by particle charge detector (Mütek PCD-03, BTG Inc., Switzerland). The 40 mg of SKL was dissolved into 40 ml of distilled water and stirred for 1 h at 150 rpm. And then, separation of liquid and solid part was conducted by centrifugation with 10,000 rpm for 10 min. The 10 g of liquid fraction was added to the PCD titrator cell. The titration were performed by using a polydiallyldimethylammonium (PolyDADMAC) as standard solution whose concentration is 0.001 mol/L. Charge density could be calculated by the following equation (Eq. 3-1).

$$\text{Specific charge density (q)} = vc/w \text{ (meq/g)} \quad (\text{Eq. 3-1})$$

c: the concentration of titrant (mol/L)

v: the volume of titrant used for titrating samples (ml)

w: the dried weight of sample added to the titrator

3.4.2. Solubility of sulfomethylated kraft lignin in water

After measurement of charge density of sulfomethylated kraft lignin, both of obtained liquid and solid fractions were gathered in 1G4 glass filter, and it was dried in 105 °C oven for 24 h. Solubility could be calculated by the following equation (Eq. 3-2).

$$\text{Solubility} = (w-f)/w \quad (\text{Eq. 3-2})$$

w: the dried weight of sulfomethylated kraft lignin

f: the dried weight of insoluble sulfomethylated kraft lignin

3.4.3. FT-IR spectrometer

SKL was analyzed by FT-IR spectrometer (Nicolet 6700, Thermoscientific, USA) equipped with attenuated total reflectance (ATR) (window ZnSe/diamond) to determine functional groups and bond types of solid polymer (No. of scan: 32; resolution: 8; wavenumber range: 4000-650 cm^{-1}).

3.4.4. Gel permeation chromatography (GPC)

To compare molecular weight distribution between unreacted and sulfomethylated kraft lignin, GPC was used. The 50 mg of each sample was

dissolved in 1 ml of pyridine / acetic anhydrous (1:1) solution and reacted in 105 °C for 2 h with mixing each 30 min. After the reaction, the acetylated lignin was poured into 20 ml of distilled water to be precipitated. After precipitation, centrifugation at 12,000 rpm for 15 min was carried out to separate acetylated lignin and liquid part. Freeze-drying process was conducted and the 2-3 mg of the sample was dissolved into tetrahydrofuran. After filtering by using hydrophobic filter (13jP050AN, ADVANTEC, Japan), the molecular weight was analyzed by GPC (Viscotek, England) with the flow rate (0.7 ml/min).

3.4.5. ³¹P-NMR analysis

³¹P-NMR data was acquired to compare the amount of each hydroxyl group type in kraft lignin. ³¹P-NMR spectra of lignin samples were obtained using a Bruker Avance II 400 MHz spectrometer. 40-45 mg of a dried lignin sample was dissolved in 500 µl of anhydrous pyridine/CDCl₃ mixture (1.6:1 v/v). A total of 200 µl of an endo-N-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/ml) as the internal standard and 50 µl of a chromium (III) acetylacetonate solution (5.6 mg/ml) in the above pyridine/CDCl₃ solution as the relaxation reagent were added. Finally, 100 µl of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and loaded into a 5-mm NMR tube for subsequent NMR acquisition.

3.4.6. Elementary analysis

Elementary analysis was conducted to investigate C, H, N and S in chemical structure by using elementary analyzer (Flask EA 1112, Thermo

Electron Corporation, USA). The oxygen content was calculated by subtracting the sum of C, H, N and S content from 100%.

4. Results & discussion

4.1. Analysis of salts produced by side reaction

4.1.2. Comparison between Sulfomethylated hardwood kraft lignin (SHKL) with and without dialysis

To find out the effect of salts remained with sulfomethylated lignin, elements, FT-IR spectra, charge density and fluidity of cement of SHKL with and without dialysis were compared.

Figure 2 showed the different FT-IR spectra of products obtained by reaction using only formaldehyde and sodium sulfite (Figure 2A), sulfomethylated lignin without dialysis (Figure 2B) and unreacted reagents obtained after dialysis (Figure 2C). In case of products obtained by reaction using only reagents and unreacted reagents obtained after dialysis, FT-IR spectra were analogous each other regardless of existence of kraft lignin during reaction. It seems that the reaction between formaldehyde and sodium sulfite was occurred separately from sulfomethylation of kraft lignin. Furthermore, product which was reacted without lignin and unreacted reagents obtained after dialysis did not show the bands for hydroxyl group between 3100 and 3600 cm^{-1} (Figure 2A and C). In addition, sulfomethylated lignin without dialysis showed the bands for aromatic ring between 1400 and 1600 cm^{-1} due to lignin (Derkacheva & Sukhov, 2008). Except for these two regions of band, the trend of three FT-IR spectra was similar.

Table 2 indicated the element content of product reacted without lignin, HKL, SHKL with and without dialysis. The content of sulfur, which is come from thiol group in HKL and from sulfonate in SHKL, increased after

sulfomethylation in case of SHKL with dialysis. It seemed that sulfomethylation of HKL caused to increase sulfur content. Moreover, the sulfur content increased with higher portion of unreacted reagents in samples.

Table 3 demonstrated the results of charge density and fluidity of cement for product reacted without lignin, SHKL with and without dialysis. In case of charge density, the results of the product with dialysis were higher than without dialysis. The result was 0.91 meq/g for the sample obtained without dialysis and 0.96 meq/g for the sample reacted with dialysis. The different charge density between the SHKL with and without dialysis was caused by the existence of unreacted salts. When the precipitated salts took over some portion of products, it brought about less charge on the products. In case of fluidity of cement, the SHKL without dialysis made cement paste increase diameter by 19.3 cm. On the other hand, the diameter of cement paste was 20.1 cm when the SHKL with dialysis was used as a superplasticizer. In the same view of charge density, the salt which had no charge disturbed for cement paste to spread out. Because charge of the SHKL without dialysis was lower than with dialysis, they could not adsorb to cement particles effectively (He & Fatehi, 2015).

Figure 3 showed FT-IR spectra of SHKL with and without dialysis after finishing sulfomethylation of HKL. The peaks between 1300 and 1100 cm^{-1} can be attributed to the S=O stretch and the band at 995 cm^{-1} is a characteristic of S-O stretch (Lou et al., 2013). The absorption peak at 617 cm^{-1} is assigned for C-S stretch. For the three peaks, tendency of FT-IR spectra was analogous regardless of dialysis. However, intensity was stronger for SHKL without dialysis than with dialysis.

Thus, unreacted salts had more sulfonate on their structure than SHKL (Figure 2), but they had the structure which charge was almost 0. For these reasons, the higher amounts of precipitated reagents in sample, the lower charge density and fluidity of cement were shown.

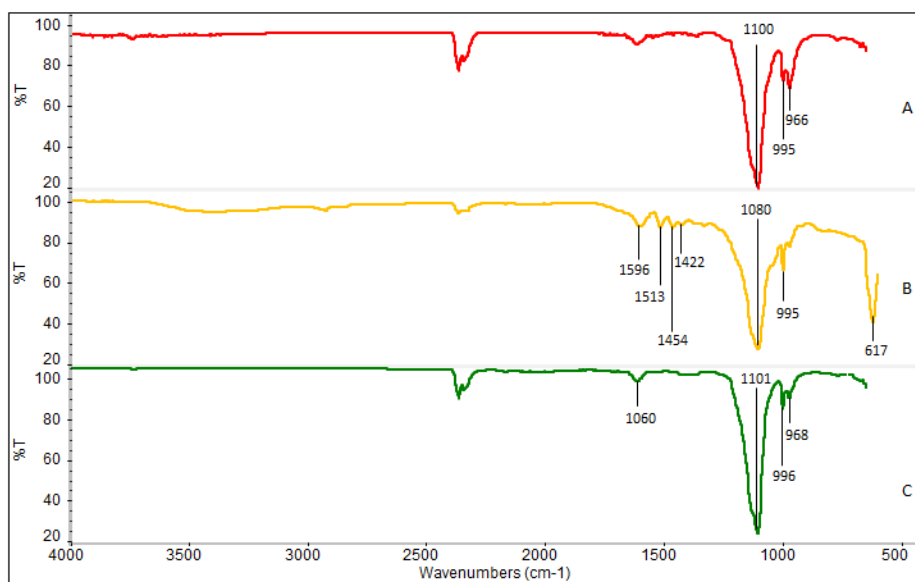


Figure 2. FT-IR spectra of the salts reacted without lignin, SHKL without dialysis and unreacted reagents obtained after dialysis.

A: Without lignin / 100 °C / 3 h / final pH 5

B: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)
/ without dialysis

C: Unreacted reagents obtained after dialysis

Table 2. Elementary analysis results of product reacted without lignin, HKL, SHKL with and without dialysis

Type of sample	C (%)	H (%)	O (%)	N (%)	S (%)
Product reacted without lignin*	1.82	0.16	91.93	0.00	6.09
SHKL without dialysis*	47.38	4.01	44.75	0.24	3.62
SHKL with dialysis*	57.64	5.17	34.92	0.32	1.95
HKL	58.85	5.52	34.90	0.29	0.45

*Reaction condition: 100 °C / final pH 5 / 3 h / 0.9 molar ratio of reagents to lignin

Table 3. Charge density and fluidity of cement for product reacted without lignin, SHKL with and without dialysis

Type of sample	Dialysis	Charge density (meq/g)	Fluidity of cement (cm)
Product reacted without lignin*	X	0.00	18.8
SHKL at final pH 5**	O	0.96	20.1
	X	0.91	19.3
SHKL at final pH 2**	O	0.69	19.8
	X	0.54	19.3

*Reaction condition: 100 °C / final pH 5 / 3 h / 0.9 molar ratio of reagents to lignin

**Reaction condition: 100 °C / 3 h / 0.9 molar ratio of reagents to lignin

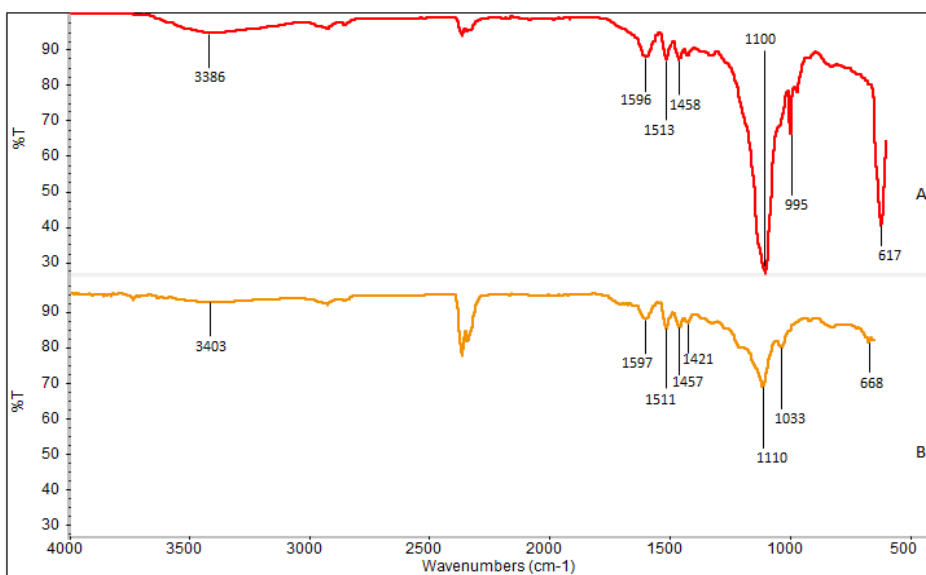


Figure 3. FT-IR spectra of SHKL with and without dialysis.

A: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)

/ without dialysis

B: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)

/ with dialysis

4.1.2. The analysis of unreacted salts

To reveal the characteristics of unreacted reagents obtained after dialysis were compared to various standard materials, which were sodium sulfate, sodium sulfite and sodium thiosulfate.

There were some researches to predict the unreacted reagents. The previous research assumed that sodium thiosulfate reduced charge density of products and fluidity of cement without dialysis. It was produced when formaldehyde and sodium sulfite were reacted (Konduri & Fatehi, 2015). Moreover, according to the patent about reaction of formaldehyde and sodium sulfite, the product was sodium formaldehyde bisulfite which had sulfonate group (Carrico, 2002). However, the different result was obtained in FT-IR spectrum against previous research. The comparison of FT-IR spectra of SHKL without dialysis to sodium sulfate, sodium sulfite and sodium thiosulfate was examined (Figure 4). All of these standard materials may have had S=O or S-O bond in their structure, but the shape of FT-IR spectra was not same each other due to different chemical structure. Moreover, the FT-IR spectrum for sodium sulfate was most similar to the spectrum of SHKL without dialysis.

In partial conclusion, the salt was more similar to sodium sulfate than sodium sulfite and sodium thiosulfate that were mentioned in other study.

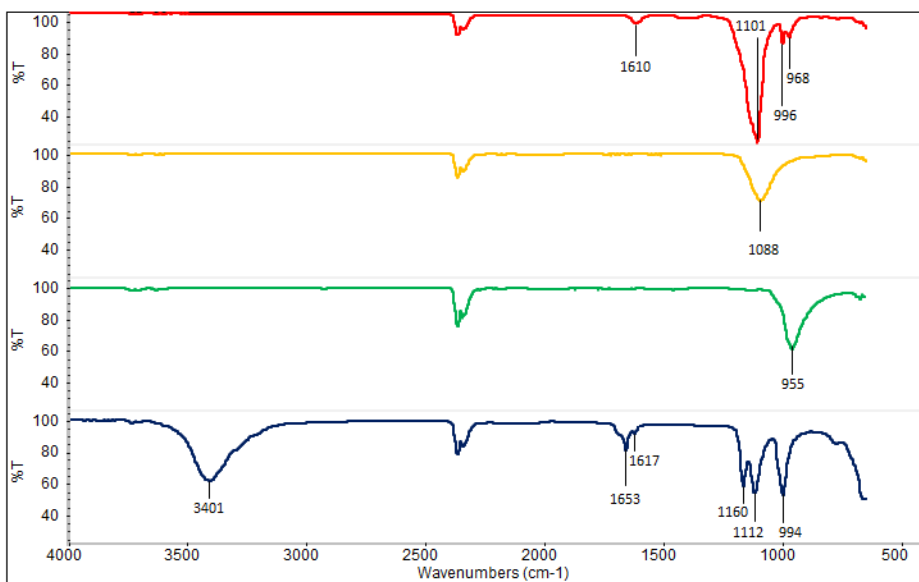


Figure 4. FT-IR spectra of unreacted reagents obtained after dialysis, sodium sulfate, sodium sulfite and sodium thiosulfate.

- A: Unreacted reagents obtained after dialysis
- B: Sodium sulfate
- C: Sodium sulfite
- D: Sodium thiosulfate

4.2. Effect of each factor to charge density

4.2.1. Final precipitating pH

Table 4 showed solubility and charge density in case of final pH 7, 5 and 2. Charge density at final pH 7 was lower than reaction condition with final pH 5 and 2. The maximum charge density was 0.96 meq/g at pH 5.

According to the previous study, surface potential is proportional to charge density, and the surface potential increased with decreasing of pH (GIBRAT & GRIGNON, 1982). However, the results of this study, the trend was opposite. It was assumed that more protons attached to sulfonate on the reacted kraft lignin when the pH was lower. However, as the pH of the surrounding of the SHKL became high, the proton may have been dissociated from the sulfomethylated kraft lignin. As a result, it was anticipated that the higher pH of solution was, the higher charge the sulfomethylated lignin had. According to similar study, carboxymethylcellulose contained free carboxyl group on their structure with increasing pH even though the tendency was different (Barbucci et al., 2000). It might indicate that lowering pH made the anionic chemicals have less negative charge.

Solubility was 0.22, 0.25 and 0.31 for final pH 7, 5 and 2, separately. The solubility increased with lowering final pH, but charge density did not show any tendency with solubility. However, Konduri et al. carried out sulfomehtylation to lignin and obtained results that the trend of charge density and solubility was almost identical. The product with higher solubility showed higher charge density (Konduri & Fatehi, 2015).

Figure 5 was FT-IR spectra of SHKL at different final pH. Dialysis was not carried out for the product with final pH 7, but it showed changed spectrum from HKL without interaction of salt. It may have considered that unreacted reagents started to precipitate between final pH 7 and 5. Moreover,

the band at 2915 and 2848 cm^{-1} was assigned to aldehyde C-H stretch (Stuart, 2004). It may have been regarded as formaldehyde did not react with HKL but condensed one another. At lower pH than 7, it was anticipated that the aldehyde group disappeared after pH 7 because the peaks at 2915 and 2848 cm^{-1} was vanished at pH 5 and 2 (Stuart, 2004).

Table 4. Charge density and solubility for SHKL at different final pH

Final pH	Charge density (meq/g)	Solubility
7*	0.65	0.22
5*	0.96	0.25
2*	0.69	0.32

*Reaction condition: 100 °C / 3 h / 0.9 molar ratio of reagents to lignin

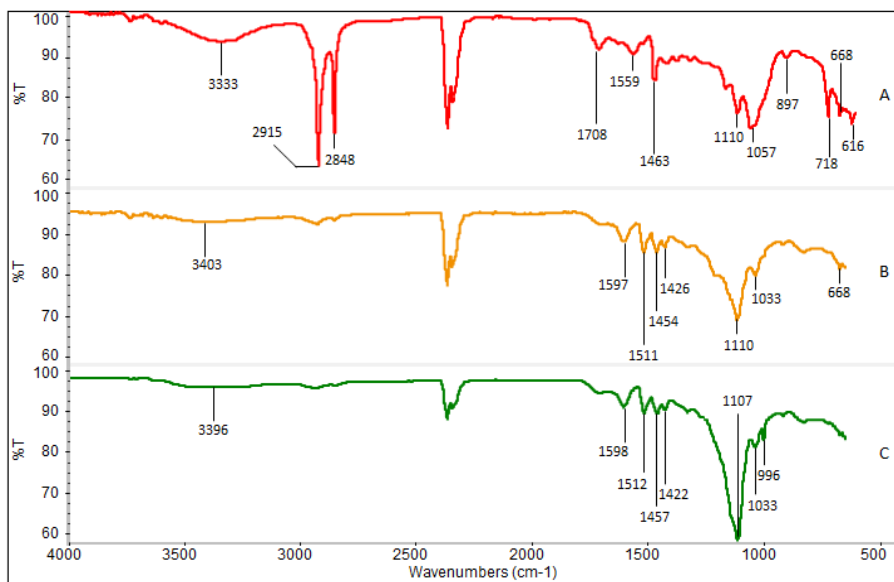


Figure 5. FT-IR spectra of SHKL at different final pH.

- A: SHKL / 100 °C / 3 h / final pH 7 / 0.9:1 (reagent ratio to lignin)
/ without dialysis
- B: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)
/ with dialysis
- C: SHKL / 100 °C / 3 h / final pH 2 / 0.9:1 (reagent ratio to lignin)
/ with dialysis

4.2.2. Reaction temperature

Table 5 demonstrated charge density and solubility for SHKL at different reaction temperature (80, 100 and 120°C). The highest charge density was 0.96 meq/g when the reaction temperature was 100°C. The tendency of solubility was not matched with charge density.

Gan et al. conducted carboxymethylation of alkali lignin from wheat straw, and they mentioned why the reaction was not carried out efficiently at lower temperature than the temperature for the highest charge density. Before the maximum point of charge density, the viscosity of lignin solution decreased before the utmost temperature point and the chemicals in solution moved slower and collided each other less frequently (Gan et al., 2012). For these reasons, the sulfomethylation was not conducted efficiently at lower temperature before 100°C. At higher temperature than the maximum point, side reaction to produce salts was faster than sulfomethylation of lignin (Yu et al., 2013b). Moreover, according to the similar study, Konduri and Fatehi obtained the result of the optimum charge density as 1.55 meq/g at 100°C for HKL (Konduri & Fatehi, 2015). It assumed that sodium thiosulfate which is an undesired chemical compound by side reaction was produced over 100°C instead of reaction with lignin, so the chemicals for sulfomethylation of HKL decreased. Finally, the degree of sulfomethylation of HKL decreased owing to the shortage of the reagents.

Table 5. Charge density and solubility for SHKL at different reaction temperature

Reaction temperature (°C)	Charge density (meq/g)	solubility
80*	0.89	0.58
100*	0.96	0.25
120*	0.64	0.43

*Reaction condition: final pH 5 / 3 h / 0.9 molar ratio of reagents to lignin

4.2.3. Reaction time

Table 6 demonstrated charge density and solubility for SHKL at different reaction time (1, 3, 5, 8 and 11 h). Charge density was the maximum as 1.31 meq/g when reaction time was 5 h. Solubility was not proportional to charge density

According to the previous experiment about sulfomethylation of HKL, the highest charge density was obtained as 1.54 meq/g when the reaction time was 3 h. They assumed that the reaction over 3 h caused to produce sodium thiosulfate (Konduri & Fatehi, 2015). With going along the reaction, the increase of charge density meant that sulfonate and hydroxymethylsulfonate were attached with going along the reaction on the aliphatic and aromatic ring, respectively. Moreover, it might be considered due to enough time to diffuse and collide for reagents to kraft lignin. On the other hand, the decline of charge density above 5 h was caused by the side reaction of reagents (Gan et al., 2012; Konduri & Fatehi, 2015). Moreover, Gan et al. revealed that the pH was dwindled with processing the reaction (Gan et al., 2012). In view of this result, sulfonate may have been substituted by hydroxyl group for prolonged time, so it caused decrease of charge density.

Table 6. Charge density and solubility for SHKL at different reaction time

Reaction time (h)	Charge density (meq/g)	Solubility
1*	0.77	0.42
3*	0.96	0.25
5*	1.31	0.28
8*	0.93	0.43
11*	0.97	0.42

*Reaction condition: 100 °C / final pH 5 / 0.9 molar ratio of reagents to lignin

4.2.4. The dosage molar ratio of reagents to lignin

Table 7 showed charge density and solubility at different dosage molar ratio of reagents to lignin (0.225, 0.45, 0.9 and 1.2:1 molar ratio to lignin). Solubility had no tendency with charge density, which tended to increase with higher dosage of reagents by 0.9:1 molar ratio to lignin. And then, it was constant tendency after the amount of reagents for the maximum charge density.

These results indicated that the lower dosage of formaldehyde and sodium sulfite under 0.9:1 molar ratio to lignin was not enough to react with HKL, so sulfomethylation could not be carried out completely. The higher dosage of reagents above 0.9:1 molar ratio to lignin was reacted via side reaction that produced sodium thiosulfate prior to react with kraft lignin (Konduri & Fatehi, 2015). Moreover, the charge density did not increase after using over 0.9:1 dosage to lignin. This result showed that the 0.9:1 molar ratio to lignin the suitable dosage of reagents for tipping point of charge density.

Table 7. Charge density and solubility at different dosage molar ratio of reagents to lignin

The dosage of reagents to lignin	Charge density (meq/g)	Solubility
0.225:1*	0.60	0.3
0.45:1*	0.90	0.38
0.9:1*	0.96	0.25
1.2:1*	0.96	0.41

*Reaction condition: 100 °C / final pH 5 / 3 h

4.3. The reaction condition for the highest fluidity of cement

According to previous studies, it was anticipated that the trend of charge density and fluidity of cement was same because anionic charge made cement particle more spread out. It was suggested that charge density and fluidity of cement were in proportional relation each other (He & Fatehi, 2015). However, there was not proportional tendency between charge density and cement fluidity.

In view of reaction temperature, the maximum cement fluidity was obtained as 20.1 cm when the reaction temperature was 100°C (Table 8). Li et al. carried out sulfonation after hydroxymethylation of lignin under various temperatures from 65 to 100 °C. The best reaction for the highest of cement fluidity as 20 cm was performed at 95 °C. Moreover, fluidity of cement was soared over 75 °C. They reported the sulfonation was conducted efficiently at higher temperature, and the degree of sulfonation was almost unchanged over 95 °C (Li et al., 2011).

Measurement of cement fluidity was carried out by adding the SHKL with different reaction time. The fluidity of cement was 20.1 cm as the highest diameter of cement paste with SHKL reacted for 3 h (Table 9). Previous study revealed that the fluidity of cement increased with prolonging reaction time for wheat straw lignin. However, the increasing rate of cement fluidity dwindled steadily along the time, and it was almost flat especially over 3 h. They concluded that it was caused by finishing sulfonation at the hydroxymethyl lignin after 3 h (Li et al., 2011).

When the dosage of reagents was 0.45:1 for molar ratio to lignin, fluidity of cement was the tipping point as 20.4 cm (Table 10). Similar study was reported about sulfomethylated wheat straw lignin precipitated by ethanol. Li et al. showed that the fluidity of cement was the maximum as 20.5 cm when the ratio of sodium sulfite to hydroxymethyl lignin was 1:3. It was

assumed that all of the possible sites to react were sulfonated after the dosage for the best fluidity of cement (Li et al., 2011). Another study revealed the reason for decrease of both charge density and fluidity of cement. After the dosage for the maximum fluidity of cement and charge density, too much formaldehyde brought about the aldol condensation between lignin molecules. It meant that the number of hydroxymethyl group for sulfonation was decreased. As a result, fluidity of cement was dwindled with the decrease of charge density (Yu et al., 2013a).

According to similar study, comparison of apparent viscosity for coal water slurry was conducted with different molecular weight. The result was that the viscosity of coal water slurry tended to be higher when using low molecular weight (Zhou et al., 2006). However, the result in this study did not follow the tendency of previous study. Even though the molecular weight was analogous among all SHKL samples, the fluidity of cement was dissimilar one another.

Hence, the highest fluidity of cement was obtained when the reaction condition was final pH (5), reaction temperature (100°C), reaction time (3 h), the molar ratio of reagents to lignin (0.45:1).

Table 8. Charge density, fluidity of cement and molecular weight at different reaction temperature

Reaction temperature (°C)	Charge density (meq/g)	Fluidity of cement (cm)	Molecular weight (Mw, Da)
80*	0.89	19.2 (±0.21)	3055
100*	0.96	20.1 (±0.10)	3940
120*	0.64	19.5 (±0.06)	3511

*Reaction condition: final pH 5 / 3 h / 0.9 molar ratio of reagents to lignin

Table 9. Charge density, fluidity of cement and molecular weight at different reaction time

Reaction time (h)	Charge density (meq/g)	Fluidity of cement (cm)	Molecular weight (Mw, Da)
1*	0.77	19.0 (± 0.36)	3202
3*	0.96	20.1 (± 0.10)	3940
5*	1.31	19.8 (± 0.10)	3654
8*	0.93	19.5 (± 0.00)	3419
11*	0.97	19.4 (± 0.53)	-

*Reaction condition: 100 °C / final pH 5 / 0.9 molar ratio of reagents to lignin

Table 10. Charge density, fluidity of cement and molecular weight at different dosage molar ratio of reagents to lignin

The dosage molar ration of reagents to lignin	Charge density (meq/g)	Fluidity of cement (cm)	Molecular weight (Mw, Da)
0.225:1*	0.60	20.3 (± 0.21)	3177
0.45:1*	0.90	20.4 (± 0.31)	3360
0.9:1*	0.96	20.1 (± 0.21)	3940
1.2:1*	0.96	19.7 (± 0.15)	3102

*Reaction condition: 100 °C / final pH 5 / 3 h

4.4 The relation among sulfur content, charge density and fluidity of cement

In comparison of the relation among sulfur content, charge density and fluidity of cement, it was not the proportionally increasing tendency in case of both charge density and fluidity of cement.

Figure 6 and 7 illustrated the relation to the content of sulfur content about charge density and fluidity of cement, separately. Also, Figure 8 illustrated the relation between charge density and fluidity of cement. There was no linearly proportional tendency in each relation, and these were the different result compared with previous studies. One of the past researches insisted that charge density was induced by sulfonate group on the lignin because the functional group let lignin retain negative charge. It was one of the reasons why fluidity of cement was developed. Cement particles had cationic charge on their structure and sulfomethylated lignin could be adsorbed on the surface of cement particles (Ran et al., 2010). According to similar study, it was assumed that the fluidity of cement going up by increasing charge density. They published that the reason was increase of anionic charges surrounded cement particle which increase electrostatic repulsion (He & Fatehi, 2015). Moreover, another study mentioned that cement fluidity had a relation with its hydration about fineness and composition. During this process, the cement particles obtained cationic charge on their surface, and they tended to make flocculation. However, anionically charged chemicals could neutralize this particle, so fluidity of cement might be increased (Chandra & Björnström, 2002).

According to another research, the researchers carried out the comparison of cement fluidity with different molecular weight of lignosulfonate. They separated molecular weight of lignosulfonate in five parts (less than 5000, 5000-10000, 10000-30000, 30000-50000 and more than

50000 g/mol). The result was that the amount of sulfonate and carboxyl group decreased with increasing of molecular weight, and the viscosity of coal water slurry did not have opposite tendency with molecular weight (Yang et al., 2007). It may have meant that the molecular weight was not a key factor to affect the fluidity of cement.

Previous research published that comparison between SNFC whose molecular weight was 15000 g/mol and polycarboxylate whose molecular weight was 70000 g/mol. Dispersing agents generated stern layer which is electrostatic double layer with adsorption to cement surface. Negative charge which was adsorbed for SNFC was higher than polycarboxylate, but zeta potential which is electrostatic area for repulsion of cement particle was larger in case of polycarboxylate. When molecular weight was low, the shape of polymer was 'train-formation', 'loop-formation' was for polymers with high molecular weight (Andersen & Roy, 1987). The model of adsorption to cement was described in Figure 9. Moreover, there was more linear chained structure in polycarboxylate than in SNFC. This structure caused steric hindrance of cement particle. However, this research also showed the tendency between zeta potential and dispersion was not fitted linearly. As a conclusion, in this study, the charge on dispersing agents lead to adsorb to cement particle, but the steric hindrance from linear hydrophilic chain was more influenced in fluidity of cement. (Björnström & Chandra, 2003).

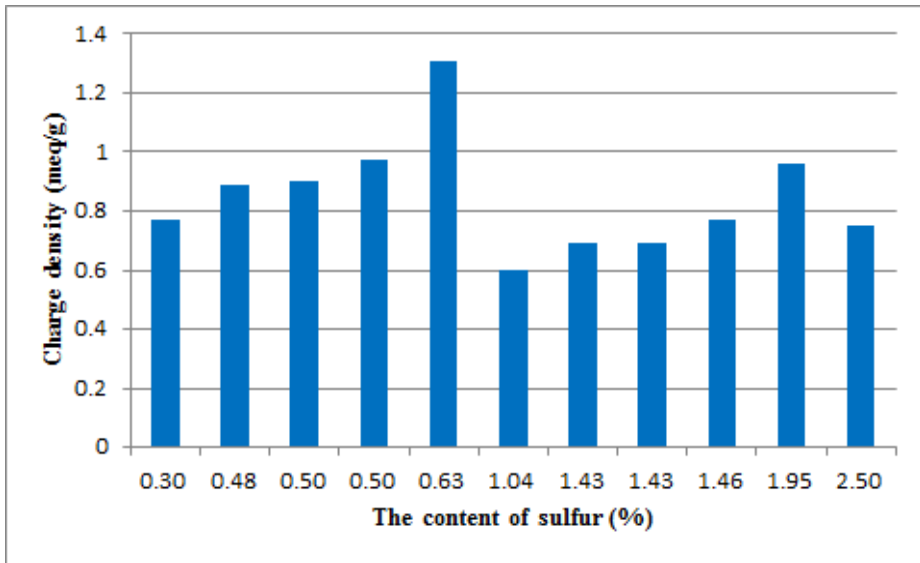


Figure 6. The relation between the content of sulfur and charge density.

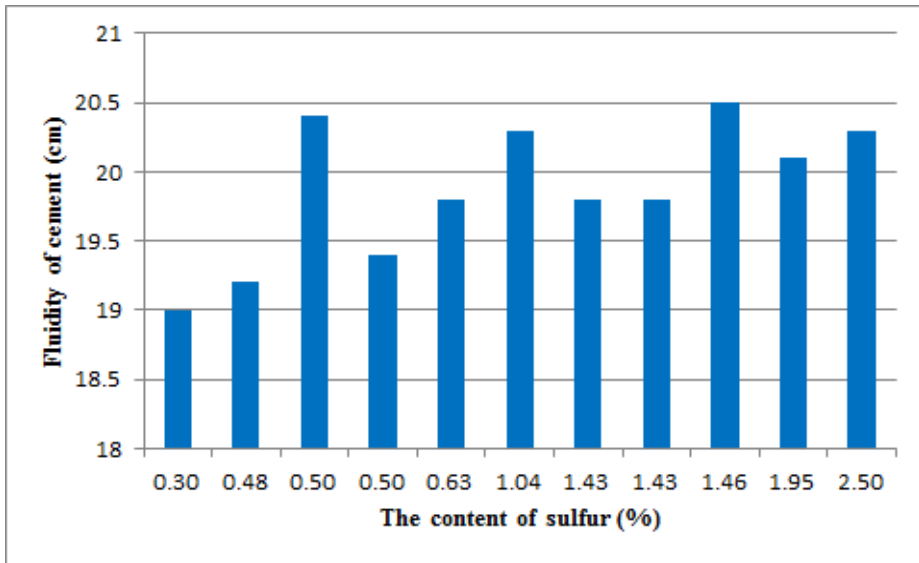


Figure 7. The relation between the content of sulfur and fluidity of cement.

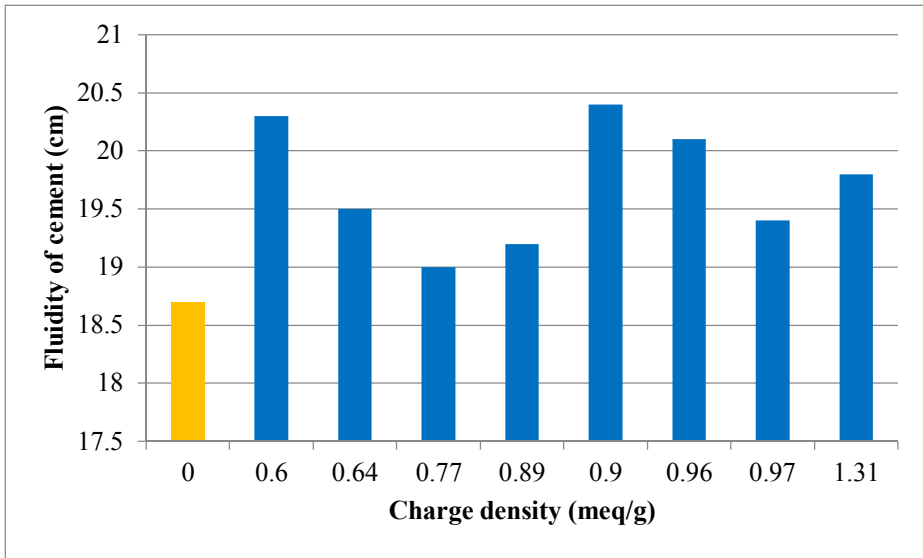


Figure 8. The relation between charge density and fluidity of cement.

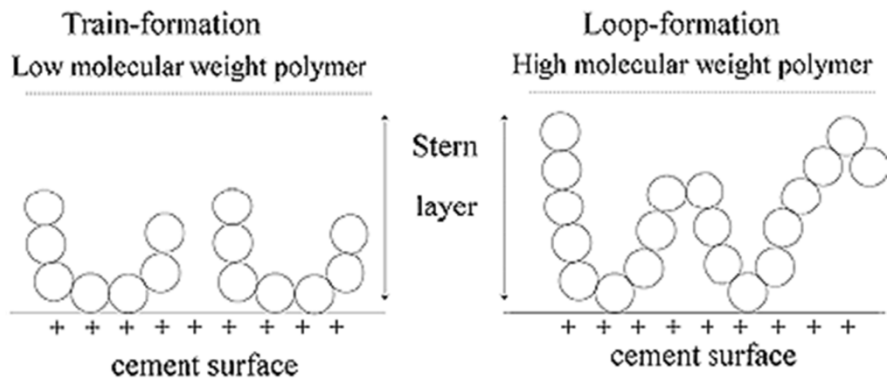


Figure 9. Model of train- and loop-formation for low and high molecular weight polymer (Björnström & Chandra, 2003).

4.5. Comparison between SKL & HKL

4.5.1. Analysis of unreacted SKL & HKL

Figure 10 illustrated the FT-IR spectra of unreacted HKL and SKL without sulfomethylation. In case of HKL, the bands at 1597, 1513 and 1423 cm^{-1} were attributed to vibrations of aromatic ring in phenyl propane structure. The absorption peak at 1454 cm^{-1} was assigned to C-H asymmetric deformation for methyl and methoxyl group. C-O stretching in syringyl group contributed to the bands at 1326 cm^{-1} and 1112 cm^{-1} . The peaks at 1214 cm^{-1} indicated C-O stretching in syringyl and guaiacyl ring. The aromatic C-H in plane deformation for guaiacyl structure attributed the bands at 1032 cm^{-1} . The bands at 913 and 825 cm^{-1} were assigned to C-H out of plane for both aromatic and aliphatic structure, separately (Anglès et al., 2003). However, the FT-IR spectrum of SKL was different from HKL at 3374, 1265, 1112 and 1080 cm^{-1} . SKL indicated the bands at 3374 cm^{-1} attributed to O-H stretching. Sulfonation substituted hydroxyl group to sulfonate, so SKL had the potential to have more anionic properties after sulfomethylation than HKL. The characteristics of guaiacyl ring breathe with C-O stretching and the aromatic C-H syringyl type were assigned to 1265 and 1112 cm^{-1} , respectively. Moreover, 1080 cm^{-1} was assigned to C-O stretching in lignin (Traore et al., 2016).

Table 11 showed solubility, charge density and fluidity of cement for SKL and HKL. Charge density of both SKL and HKL was too low to measure. Moreover, fluidity of cement was almost same after adding both types of the kraft lignin into cement. It may be assumed that original lignin without any reaction has no anionic functional group on the chemical structure to develop

adsorption to cement particles.

Table 12 indicated the result of ^{31}P -NMR of SKL and HKL. In case of SKL, the amount of aliphatic, syringyl and guaiacyl hydroxyl group was 2.10, 1.91 and 4.89 mmol/g, respectively. Meanwhile, HKL had 0.54, 3.10 and 1.44 mmol/g for aliphatic, syringyl and guaiacyl hydroxyl group, separately. Guaiacyl type of lignin could be hydroxymethylated by formaldehyde before sulfonation because hydroxymethylation occurred at *ortho* position of phenolic hydroxyl group (Kamoun et al., 2003). It could be potential to be carried out for more sulfomethylation in SKL.

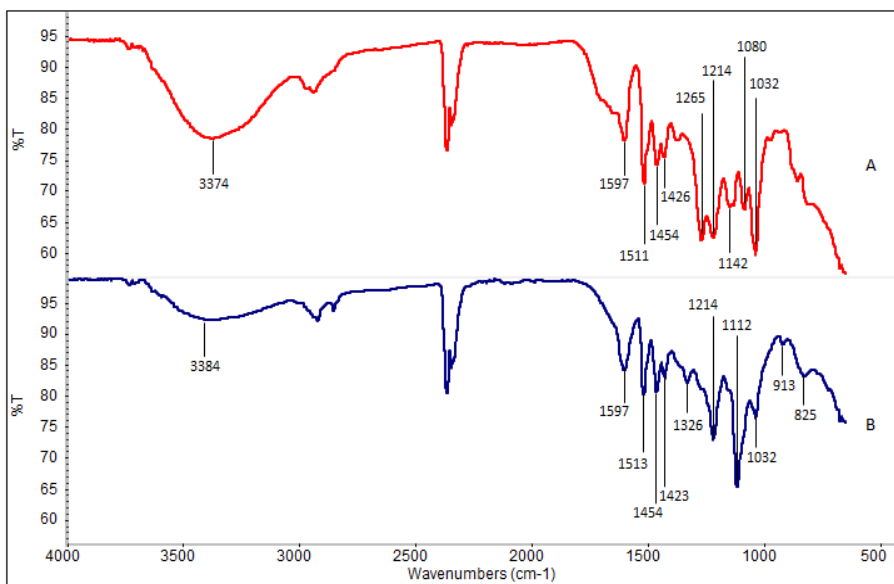


Figure 10. FT-IR spectra of SKL and HKL without sulfomethylation.

A: SKL

B: HKL

Table 11. Solubility, charge density and fluidity of cement for SKL and HKL

Type of sample	Solubility	Charge density (meq/g)	Fluidity of cement (cm)
SKL	0.30	0.00	18.8 (± 0.00)
HKL	0.12	0.00	18.7 (± 0.00)
Cement only	-	-	18.7(± 0.00)

Table 12. Comparison of the amount of each type of hydroxyl group for SKL and HKL by using ^{31}P -NMR

Type of sample	Aliphatic OH (mmol/g)	Syringyl OH (mmol/g)	Guaiacyl OH (mmol/g)	Carboxyl OH (mmol/g)
SKL	2.10	1.91	4.89	0.00
HKL	0.54	3.10	1.44	0.35

4.5.2. Comparison of unreacted and sulfomethylated SKL & HKL

Table 13 indicated solubility, charge density and fluidity of cement for sulfomethylated softwood kraft lignin (SSKL) and SHKL. Charge density was obtained 1.07 and 0.96 meq/g and fluidity of cement was 20.5 and 20.1 cm for SSKL and SHKL, separately. Moreover, solubility was 0.42 and 0.25 for SSKL and SHKL, respectively. Solubility and charge density for SSKL were higher than SHKL. Following the result of ^{31}P -NMR (Table 12) which was comparing unreacted SKL and HKL as previously mention in chapter 4.5.1., it was anticipated that more anionic functional groups were attached to the SSKL than SHKL due to the higher content of guaiacyl units in SSKL. It might be evidence that *ortho* position of phenolic hydroxyl group is one of the important factors that affect sulfomethylation.

It demonstrated that sulfomathylation changed both kinds of kraft lignin to have anionic charge. Because of sulfonate on aliphatic and hydroxymethylsulfonate on aromatic ring, it could be adsorbed to cement particle. Ran et al. performed to make copolymer of methylpolyethyleneglycol-acrylate and acrylic acid to reveal the mechanism of a dispersant. They mentioned cement particles had positive charge on the structure, so the particles interacted with anionic chemicals electrostatically (Ran et al., 2010). As a result, the fluidity of cement was developed because the particles, which are surrounded by SHKL that had anionic charge, had electrostatic repulsion each other. Moreover, it was regarded that negative charge on the structure made these hydrophobic compounds more soluble to water. According to similar study, Güzel et al. tried to give anionic property on phthalocyanine to increase solubility into water via sulfonation. (Güzel et al., 2017). It may have been considered that the more water-soluble meant that fluidity of cement was better because sulfomethylation occurred more on unreacted kraft lignin.

FT-IR spectra of SHKL and SSKL was illustrated in Figure 11. Comparing to Figure 10, the peak of 1265 cm^{-1} attributed to guaiacyl ring breathing with C-O stretching vanished. Furthermore, the peak of 1214 cm^{-1} concerning C-O stretching in syringyl and guaiacyl ring disappeared after sulfomethylation and the bands between 1300 and 1100 cm^{-1} assigned to S=O stretching of sulfonate appeared. Moreover, the bands between 3600 and 3100 cm^{-1} were assigned to hydroxyl group (Anglès et al., 2003), which decreased evidently after sulfomethylation. It meant the amount of hydroxyl group was dwindled after sulfomethylation in both type of kraft lignin. It was considered that hydroxyl groups at aliphatic part and at hydroxymethyl group at aromatic were changed to sulfonate by sulfomethylation. However, the peaks for syringyl, guaiacyl and sulfonate group were overlapped at near 1110 cm^{-1} , so it may be impossible to consider whether sulfomethylation was conducted by using FT-IR. Moreover, the peak at 1263 cm^{-1} was different between SSKL and SHKL. The trend of guaiacyl type lignin was not changed after sulfomethylation. This peak only showed in case of SSKL because of difference in the ratio of S/G type for hardwood and softwood. The band at 1208 cm^{-1} was contributed to the asymmetric stretching vibration of S=O, and the peaks at 1110 , 1033 and 1031 cm^{-1} were attributed to symmetric stretching vibration of S=O (Lou et al., 2013). However, the type of bond structure was quite different between SSKL and SHKL. It was probably assumed that the peak at 1110 cm^{-1} was indicated by C-O stretching in syringyl group. It may have considered that the peak intensity was strong in case of SHKL even though sulfomethylation was conducted more in SSKL.

Table 13. Solubility, charge density and fluidity of cement for SSKL and SHKL

Type of sample	Dialysis	Solubility	Charge Density (meq/g)	Fluidity of cement (cm)
SSKL*	O	0.42	1.07	20.5 (± 0.06)
SHKL*	O	0.25	0.96	20.1 (± 0.10)

*Reaction condition: 100 °C / final pH 5 / 3 h / 0.9 molar ratio of reagents to lignin

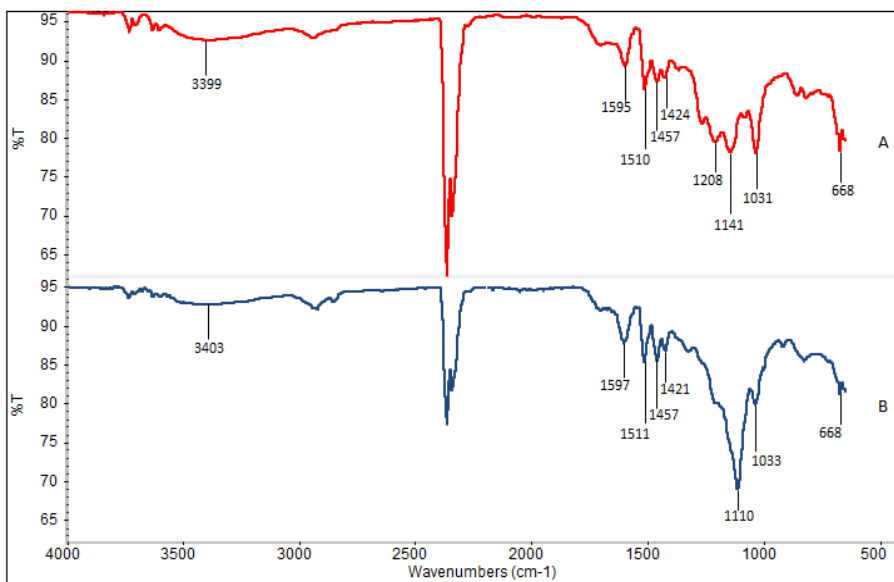


Figure 11. FT-IR spectra of SSKL and SHKL.

A: SSKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)
 / with dialysis

B: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)
 / with dialysis

4.6. Comparison between SHKL & commercial lignosulfonate

To evaluate the potential for sulfomethylated lignin to use as a superplasticizer, FT-IR, PCD analyses and mortar flow table test was conducted.

Figure 12 showed FT-IR spectra of SHKL and commercial lignosulfonate. Both SHKL and commercial lignosulfonate showed the peak for sulfonate near 1100, 1000 and 650 cm^{-1} (Derkacheva & Sukhov, 2008). Moreover, the peak for aromatic ring was indicated between 1400 and 1600 cm^{-1} . However, the intensity for commercial lignosulfonate, which showed higher content of sulfur and oxygen on their structure, was lower than SHKL (Table. 14). For these reasons, it may have assumed that lignosulfonate had less sulfonate than SHKL and different structure from SHKL, so it caused higher fluidity of cement.

Table 15 showed that the difference between SHKL and commercial lignosulfonate in charge density and fluidity of cement. In case of SHKL, charge density and fluidity of cement were obtained as 0.90 meq/g and 20.4 cm, separately. For commercial lignosulfonate, the results were 3.00 meq/g and 21.6 cm as charge density and fluidity of cement, respectively. It indicated that both charge density and fluidity of cement were higher for commercial lignosulfonate. It may have been brought out due to the higher amount of sulfonate resulted from the higher content of sulfur with different structure.

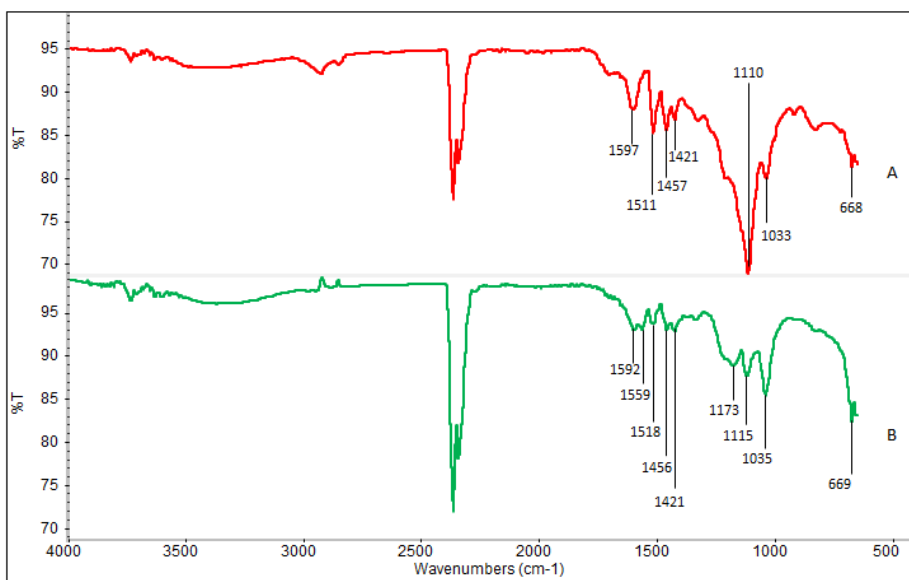


Figure 12. FT-IR spectra of SHKL and commercial liginosulfonate.

A: SHKL / 100 °C / 3 h / final pH 5 / 0.9:1 (reagent ratio to lignin)
/ with dialysis

B: Commercial liginosulfonate

Table 14. Elementary analysis results of SHKL and commercial lignosulfonate

Type of sample	C (%)	H (%)	O (%)	N (%)	S (%)
SHKL*	55.6	5.19	38.46	0.24	0.5
Commercial lignosulfonate	42.05	4.96	48.17	0.00	4.82

*Reaction condition: 100 °C / final pH 5 / 3 h / 0.45 molar ratio of reagents to lignin

Table 15. Charge density and fluidity of cement for SHKL and commercial lignosulfonate

Type of lignin	Charge Density (meq/g)	Fluidity of cement (cm)
SHKL*	0.90	20.4 (± 0.31)
Commercial lignosulfonate	3.00	21.6 (± 0.10)

*Reaction condition: 100 °C / final pH 5 / 3 h / 0.45 molar ratio of reagents to lignin

5. Conclusion

In this study, sulfomethylation was conducted to modify kraft lignin for use as a superplasticizer.

The comparison between SHKL with and without dialysis was conducted to reveal that the salts produced by side reaction did not influence positively in fluidity of cement. The unreacted reagents had no charge and did not change fluidity of cement after adding into cement paste. For these reasons, removing the salts generated by side reaction was recommended to increase the performance of a superplasticizer.

The reaction condition for the highest charge density was obtained at final pH (pH 5), reaction temperature (100°C), reaction time (5 h) and the dosage molar ratio to lignin (0.9:1), separately. However, in case of the highest fluidity of cement, final pH (pH 5), reaction temperature (100°C), reaction time (3 h), the dosage molar ratio to lignin (0.45:1) was investigated, respectively. Furthermore, it was conducted to figure out the trend between charge density and fluidity of cement, but there was not proportional tendency each other. Moreover, the sulfur content on SHKL also did not show proportional relation to charge density and fluidity of cement. Considering there was not proportional tendency among the content of sulfur, charge density and cement fluidity, there may have been the main factor to be related to fluidity of cement directly. According to previous study, polycarboxylate and SNFC were compared. Polycarboxylate had low charge density, high molecular weight and long chain structure. On the other hand, in case of SNFC, it showed high charge density, low molecular weight and shorter molecular structure. Consequently, polycarboxylate was performed better to increase fluidity of cement. Another study was published about comparing the fluidity of cement in different molecular weight of lignosulfonate. Fluidity of cement was dwindled with increasing molecular weight of lignosulfonate.

Regarding the two researches, charge density and molecular weight may not have been the most importantly considered factors for higher cement fluidity, but the linear chain structure may have been the key factor to increase the performance of a superplasticizer.

Softwood showed higher content of guaiacyl unit that could be more sulfomethylated. As a result, SKL indicated both of higher charge density and fluidity of cement. For applications to a superplasticizer for increase of cement fluidity, softwood may have had possibility to be better superplasticizer than hardwood.

In conclusion, the material based on biomass was utilized to apply for industry of cement. Sulfomethylation of kraft lignin increased fluidity of cement compared with HKL. However, the performance of SHKL was not better than commercial lignosulfonate. Consequently, further research for sulfomethylation of kraft lignin is needed to surpass lignosulfonate.

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초록

크라프트 리그닌의 시멘트 첨가제 사용을 위한 설포메틸레이션 조건 연구

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크라프트 펄핑 공정으로부터 생산되는 많은 양의 크라프트 리그닌은 연소과정을 통해 태워지고 있다. 그러나, 크라프트 리그닌의 고부가가치화의 가능성이 제시되고 있다. 설파이트 펄핑으로부터 생산되는 리그노설포네이트는 시멘트 첨가제로 사용되고 있지만, 설파이트 펄핑이 크라프트 펄핑으로 대체되고 있기 때문에 생산량이 한정적이다. 이러한 이유로 크라프트 리그닌의 화학적 개질을 통해 리그노설포네이트를 대체하려는 연구가 많이 진행되고 있다.

본 연구에서는 formaldehyde 와 sodium sulfite 를 사용하여 크라프트 리그닌의 sulfomethylation 을 다양한 조건 하에 진행하였다. 용매는 sodium hydroxide 를 사용하였다. 그 후에 최종 pH 를 1M 황산용액을 사용하여 조절하였고, 12000 rpm 으로 15 분동안 원심분리를 하여 고상과 액상을 분리하였다. Sulfomethylation 은 최종 pH (7, 5, 2), 반응온도(80, 100, 120°C), 반응시간(1, 3, 5, 8, 11 시간), 리그닌 대비 투입 시약 비율(0.225, 0.45, 0.9, 1.2:1)에 따라 다르게 진행이 되었다. Particle charge detector 와 적정제로 polydiallyldimethylammonium (PolyDADMAC)를 사용하여 sulfomethylation 된 크라프트 리그닌의 전하밀도를 측정하였다. 그 후, 동결건조를 통해 건조된 시료를 얻었다. FT-IR 분석법으로 리그닌의 작용기변화를 확인하였고, guaiacyl 과 syringyl 구조의 비율은 ^{31}P -NMR 로

측정하였다. 또한, 설폰네이트의 함량 비교를 위해 원소분석을 실시하였고, 이러한 분석을 통해 개질 조건에 따른 sulfomethylation 의 특성을 비교하였다.

최대 전하밀도를 나타내는 조건은 최종 pH 5, 반응온도 100℃, 반응시간 5 시간, 리그닌 대비 투입 시약 비율 0.9:1 이었다. 반면, 최종 pH 5, 반응온도 100℃, 반응시간 3 시간, 리그닌 대비 투입 시약 비율 0.45:1 일 때, 시멘트 유동성이 최대였다. 전하밀도가 증가할수록 시멘트 유동성이 증가할 것이라고 예상했지만, 전하밀도와 시멘트 유동성의 경향은 일치하지 않았다. 또한, 시료의 황 함량과 전하밀도, 시멘트 유동성과의 경향도 일치하지 않았다. 몇몇 연구에 따르면, 높은 분자량, 낮은 전하밀도, 비교적 긴 사슬구조를 가진 polycarboxylate 와 낮은 분자량과 높은 전하밀도를 가진 sulfonated naphthalene formaldehyde condensate (SNFC) 과 비교하였다. 그 결과, 시멘트 유동성은 polycarboxylate 를 사용하였을 때 더 좋았다. 더 나아가, 리그노설폰네이트를 분자량마다 나누어 시멘트 유동성을 분석한 결과, 분자량과 시멘트 유동성은 비례하지 않았다. 전하밀도와 분자량이 시멘트 유동성과 비례관계가 아닌 것을 고려해보았을 때, 긴 사슬구조가 시멘트 유동성의 핵심 인자라고 사료된다.

리그닌 구성단위의 반응에 대한 영향을 조사하기 위해, 침엽수 크라프트 리그닌을 활엽수 크라프트 리그닌과 같은 반응 조건으로 sulfomethylation 을 하였다. Sulfomethylation 이 된 침엽수 크라프트 리그닌이 활엽수 크라프트 리그닌보다 더 높은 전하밀도와 시멘트 유동성을 나타내었다.

주요어: 리그닌, sulfomethylation, 전하밀도, 시멘트 유동성, 리그닌

개질, 음전하

학번: 2016-21465