## Polymer-grafted Lignin: Molecular Design and Interfacial Activities

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Chetali Gupta

B.S., Chemical Engineering, University of Maryland, College Park M.S., Materials Science and Engineering, Carnegie Mellon University

> Carnegie Mellon University Pittsburgh, PA

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Committee members: Dr. Kimberly Kurtis Dr. Greg Rohrer Dr. Jay Whitacre Dr. Newell Washburn

#### Abstract

The broader technical objective of this work is to develop a strategy for using the biopolymer lignin in a wide variety of surfactant applications through polymer grafting. These applications include emulsion stabilizers, dispersants and foaming agents. The scientific objective of the research performed within this thesis is to understand the effect of molecular architecture and polymer grafting on the interfacial activity at the air-liquid, liquid-liquid and solid-liquid interface. Research has focused on designing of these lignopolymers with controlled architecture using polyethylene glycol, poly(acrylic acid) and polyacrylamide grafts. The interfacial activity for all polymer grafts has been tested at all three interfaces using a broad range of techniques specific to the interface. Results have shown that the hydrophobicity of the lignin core is responsible for enhanced interfacial activity at the air-liquid and liquid-liquid interface. Conversely, improved hydrophilicity and "electrosteric" interactions are required for higher interfacial activity of the lignin at the liquid-solid interface. The high interfacial activity of the polymer-grafted lignin observed in the air-liquid and liquid-liquid interfaces not only resulted in viscosity reduction but also strength enhancement at the liquid-solid interface. The broader implication of this study is to be able to predict what chemical functionalities need to be adjusted to get the desired viscosity reduction.

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## **List of Acronyms**

- 1. AA Acrylic acid
- 2. AFm Alumina, ferric oxide, monosulfate phase
- 3. AFt- Hydrous calcium aluminate sulfate material, ettringite
- 4. AIBN Azobisisobutyronitrile
- 5. Am Acrylamide
- 6. ASCMs Alternative supplementary cementitious materials
- 7. ATRP Atom-transfer radical-polymerization
- 8.  $A_2 2^{nd}$  virial coefficient provides a measure of the strength of solute-solvent interactions
- 9. BET Brunauer Emmett- Teller technique
- 10. C<sub>3</sub>A Tricalcium aluminate
- 11. CAC/CMC Critical aggregation/micelle concentration
- 12. C<sub>4</sub>AF Tetracalcium aluminoferrite
- 13. CRP Controlled radical polymerization
- 14. C<sub>2</sub>S Dicalcium silicate
- 15. C<sub>3</sub>S Tricalcium silicate
- 16. C-S-H gel Calcium silicate hydrate gel
- 17. CT- Computed tomography
- 18. DI Deionized water
- 19. DLS Dynamic light scattering
- 20. DLVO Derjaguin, Landau, Verwey and Overbeek
- 21. DMF Dimethyl formamide
- 22. DP Degree of polymerization
- 23. E Ettringite
- 24. EDS Energy-dispersive X-ray spectroscopy
- 25. EIP- Emulsion inversion point
- 26. FRP Free radical polymerization
- 27. GM Glycidyl methacrylate
- 28. GPC Gel permeation chromatography
- 29. HLB Hydrophilic Lipophilic balance
- 30. HNMR Proton nuclear magnetic resonance
- 31. KL Kraft lignin
- 32. KLPEG PEGylated kraft lignin
- 33. LPAA- Lignin grafted polyacrylic acid
- 34. LPAM- Lignin grafted polyacrylamide
- 35. LS Lignosulfonate
- 36. LSPEG PEGylated lignosulfonate
- 37. MK Metakaolin
- 38. Mn Number average molecular weight
- 39. Mw Weight average molecular weight
- 40. Nano-CT- Nanoscale computed tomography
- 41. NMP Nitroxide mediated radical polymerization
- 42. NSF I-Corps National Science Foundation Innovation Corps
- 43. OPC- Ordinary portland cement

- 44. O/W Oil in water emulsion, where water is the continuous phase
- 45. P Portlandite
- 46. PAA Polyacrylic acid
- 47. PAm Polyacrylamide
- 48. PCE- Polycarboxylate ether
- 49. PDI Polydispersity index
- 50. PDMAEMA Poly(2-(dimethylamino) ethyl methacrylate)
- 51. PEG Polyethylene glycol
- 52. PFB Pentaflurobenzaldehyde
- 53. PGLN's Polymer-grafted lignin nanoparticles
- 54. PMAA Polymethacrylic acid
- 55. RAFT Reversible addition-fragmentation chain-transfer polymerization
- 56. RPM Rotations per minute
- 57. SCMs Supplementary cementitious materials
- 58. SEM Scanning electron microscopy
- 59. THF Tetrahydrofuran
- 60. TOC- Total organic carbon analysis
- 61. UV Vis Ultraviolet-visible spectroscopy
- 62. W/O Water in oil emulsion, where oil is the continuous phase
- 63. XRD- X-ray diffraction

#### 1. Introduction

#### 1.1 Motivation

Lignin is the third most abundant biomaterial. It is an aromatic biopolymer that is an important component of plants, comprising 18% of corn stover and 20-30% of wood. Aliphatic hydroxyl and phenolic hydroxyl groups are the native functional groups on lignin, but oxidation during processing can generate carboxylic acid moieties [1], [2]. One challenge facing the establishment of a robust biobased chemical industry is developing large-scale technological applications for lignin. While decomposition to aromatic chemical building blocks and incorporation into commodity plastics has been explored extensively, surfactant applications are currently the most widely used [3], [4]. This seems as an obvious application for lignin, as in its native form, it is present at the interface of two different phases cellulose and hemicellulose in the plant. It would be ideal if these functionalities could be exploited to produce lignin-based surfactants that can be used as dispersants and emulsion stabilizers.

Some lignin derivatives are currently used as low-cost and low-performance dispersants and emulsion stabilizers. Lignosulfonate, a lignin derivative from the sulfite pulping process, has a net negative charge and is used as a low-cost/low-performance dispersant in paints, dyes and concrete. With recent advances in grafting chemistries, there have been attempts to manipulate the various functionalities and augment the surfactant properties of lignin-based derivatives. For example Ji et al investigated sulphanilic acid-phenol-formaldehyde condensation polymers that incorporated lignosulfonates to improve dispersion properties [5]. Formulations based on methacrylated lignin derivative copolymerized with water-soluble acrylates have also been explored and patented [6]. However, both of these approaches have resulted in the formation of nanoscale aggregates with modest increases in dispersant properties when placed in high ionic strength systems such as cement. In attempts, to improve the interfacial properties, Kraft lignin has been functionalized with poly(ethylene glycol) (PEG) using a PEG epoxide [7]. Similarly, polypropylene oxide was reacted with kraft lignin to produce a species that lowered interfacial tension [8]. There have been some improvements in surfactant properties but still lowperformance compared to the petroleum-derived counterparts. Furthermore there has been no study in correlating how these lignin-based surfactants would do in a high ionic strength

dispersant application or how lignin-based dispersants synthesized for concrete applications behave at two interfaces. There is need for a systematic study to explore different architectures/grafting chemistries and hydrophilic polymers to understand how the same material can be used for many different applications, hence maximizing the potential of lignin based surfactants. Lignin has native interfacial properties, and the goal is to understand the interfacial activity of lignin-derived polymers at the air-liquid, liquid-liquid and solid-liquid interface.

## 1.2 Research objectives

The objective of this study is to understand how to improve the surfactant properties of lignin by different polymerization techniques, and to test them in relevant systems where good dispersion is necessary. To evaluate the improved surfactant properties of lignin a variety of different techniques were used which included tensiometry, emulsion stability and adsorption. To evaluate the performance of these lignin grafted polymer dispersants, they were tested in a cementitious system. This system included a model magnesium oxide suspension and portland cement with various geo-polymer additions. This research provides novel insights into the parameters that are needed to improve dispersion in high ionic strength systems where coagulation cannot be prevented solely by electrostatic interactions.

## 1.3 Hypothesis

This study will test the following hypotheses:

- 1. Polymer grafting can leverage the native interfacial activities of lignin at different interfaces.
- 2. Control over architecture results in higher interfacial activity at the air-liquid, liquidliquid and solid-liquid interface.
- Depending on the type of interface, different aspects of the lignin chemistry are required for enhanced interfacial activity. For an air-liquid and liquid-liquid interface, non-polar components of lignin are required and for solid-liquid interface, polar components of lignin are required.

4. The grafting chemistry of the polymer onto the lignin core will impart its native surfactant properties to the system. For the particular case of PEG, there will be improved steric interactions.

#### 1.4 Background

#### 1.4.1 Lignin

Lignin is the second most abundant terrestrial biopolymer after cellulose. It is the main byproduct of pulp and paper production as well as cellulosic ethanol production [1]. Lignin has a complex structure, comprising of aromatic alcohols as shown in Figure 1.4.1.1. There are three primary types of alcohols; coumaryl, coniferyl and syringyl alcohol, which undergo polymerization via an oxidative radical mechanism at the phenol groups [1]. Based on the source of the lignin the ratio of three alcohols changes, which impacts the properties of the molecule vastly. Due to the various functionalities present in lignin, it is quite difficult to characterize. Some of the basic characterization techniques include using dynamic light scattering (DLS) to measure size and gel permeation chromatography (GPC) to estimate molecular mass.



Figure 1.4.1.1. Representative chemical structure of lignin

There are two major types of processes used to manufacture lignin; kraft and sulfite pulping. The chemical structures of both are shown in Figure 1.4.1.2. Kraft pulping produces the largest

amount of lignin as a byproduct of the paper industry. During this process the phenolic groups are converted to a quinonemethide group by sodium hydroxide and subsequently the hydrogen sulfide attacks the ether linkage cleaving it off. This process continues on to produce low-molecular-weight fragments [9], [10]. Lignin carbon-carbon bonds are formed at the last stage of the process and forms a chemically robust lignin complex. Kraft lignin is used to describe a range of polydispersed and branched phenolic polymers. Kraft lignin contains aliphatic thiol and carboxylic acid groups and is hydrophobic. It is only soluble in solvents such as dimethylformamide (DMF) and pyridine with the solubility parameter estimated to be 20-24 MPa<sup>1/2</sup> [11].

The other major process to produce lignin is sulfite pulping. In this process wood or biomass is reacted with calcium/magnesium sulfite at 120-150 °C for 3-7 h. The process is acidcatalyzed to cleave the  $\alpha$  and  $\beta$  ether linkages. The lignin produced is soluble in aqueous solution due to the sulfonic acids present at the  $\alpha$  -carbon of the ether linkage. The resulting lignin is a mix of sulfonated lignins/lignosulfonates and other wood derivatives, which are soluble in water. The weight averaged molecular weight of the lignosulfonates is above kraft lignin in the range of 5-400 kDa and the polydispersity is generally quite high [10], [12].



Figure 1.4.1.2. Representative chemical structures of (a) kraft lignin and (b) lignosulfonates

Due to the heterogeneity of lignin, it finds relatively limited use as a raw material to produce vanillin and as polyol in the production of polyurethane. Kraft lignin is primarily burned as a fuel to produce power in the pulp mill [10], [13], [14]. Lignosulfonates are the far most extensively used technical lignin polymer and is used as a binder in ceramics, in animal feed or as a dispersant for clays, dyes and pigments [2]. The most common use of lignosulfonates however is as a plasticizer for cement. Lignosulfonates were one of the first superplasticizers developed for portland cement [15], [16] and continue to be used extensively because of their

low cost, consistent performance, enhanced ettringite formation and basis on renewable resources [17], [18]. In 2011, 400 000 tons alone were used as additives in concrete, making them the second most-used admixture [4]. The sulfonate groups present on the lignin help reduce the water-to-cement (w/c) ratio and ensure good dispersion by electrostatically stabilizing the cement particles. As mentioned previously, lignosulfonates are quite polydisperse and it is quite difficult to characterize them. It must be noted that from an industrial standpoint it is not critical to know the properties of the lignosulfonate, generally semi-quantitative characterization is often sufficient to provide information.

#### 1.4.2 Cement

Cement is a binder that has adhesive and cohesive properties that allow it to bond mineral fragments together. Cement is produced by adding limestone and aluminosilicates clay that are calcined in a kiln up to 1500 °C. The final product is known as clinker and is comprised of calcium silicates and calcium aluminates in varying ratios and is dependent on the type of cement. The calcination of limestone, accounts for 5% of all human-generated greenhouse-gas emissions of the carbon dioxide emissions [19]. Two major types of cements are formed based on the raw ingredients placed in the kiln: hydraulic and non-hydraulic. Hydraulic cement reacts with water to form insoluble products that are resistant to water. Non-hydraulic cement does not react with water, and instead reacts with atmospheric carbon dioxide. The research presented here strictly focuses on hydraulic also known as portland cement. Portland cement clinker consists of four major components namely tricalcium silicate (3CaO•SiO<sub>2</sub>, C<sub>3</sub>S, alite), dicalcium silicate (2CaO•SiO<sub>2</sub>, C<sub>2</sub>S, belite), tricalcium aluminate (3CaO•Al<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>A) and calcium aluminoferrites (4CaO•Al<sub>2</sub>O<sub>3</sub>•Fe<sub>2</sub>O<sub>3</sub>, C<sub>4</sub>AF). Depending on the ratio of the above components there are five different types of portland cements as shown in Table 1.4.2.1 [16].

	Classification	Characteristics	Applications
Type I	General purpose	Fairly high C <sub>3</sub> S content	General
			construction
Type II	Moderate sulfate	Low $C_3A$ content (< 8%)	Structures exposed
	resistance; moderate		to soil or water;
	heat of hydration		general use
Type III	High early strength	Ground finely	Rapid construction,
			cold weather
			construction
Type IV	Low heat of	Low content of $C_3S$ (< 50 %)	Massive structures
	hydration	and C <sub>3</sub> A	such as dams
Type V	High sulfate	Very low $C_3A$ content (< 5%)	Structures exposed
	resistance		to high levels of
			sulfate ions

Table 1.4.2.1. Different types of ASTM C150 portland cement and their characteristics and applications

The addition of water to hydraulic cement results in the setting of the cement and is responsible for its strength. The hydration of cement is a series of complex chemical reactions as shown in equations [1-5]. These reactions start immediately as the water is added and may continue for up to a year or longer. One of the first reactions to occur during hydration is the formation of stiff ettringite needles. The formation of these needles is based on the ratio of aluminates to sulfates present at any given moment in the system. The formation of these needles is favored at a high sulfate/aluminate ratio. This process is highly exothermic and leads the cement hydration into a dormant stage. In the dormant stage the C<sub>4</sub>AF forms an iron hydroxide gel coating on some particles and the calcium silicates start to hydrate and form calcium hydroxide. The major product of the hydration reaction is the C-S-H gel. This is a calcium silicate hydrate gel, which has a tobermorite/jennite like structure and is responsible for strength gain. Once the sulfate is consumed, the ettringite component decomposes to form hexagonal monosulfate crystals (AFm). A schematic showing the hydration curve is shown in Figure 1.4.2.1. The majority of the process is complete in 14-28 days [16].

$$3CaO \cdot Al_2O_3 + 3CaSO_4 + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{1}$$

 $\begin{array}{l} 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 3CaSO_4 + 3H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + Al_2O_3 \cdot Fe_2O_3 \cdot 3H_2O + Ca(OH)_2 \end{array}$ 

$$2Ca_3SiO_5 + 6H_2O \to Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2$$
(3)

$$2Ca_2SiO_4 + 4H_2O \to Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2$$
(4)

 $6CaO \cdot 2Al_2O_3 + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightarrow 9CaO \cdot 3Al_2O_3 \cdot 3CaSO_4 \cdot 54H_2O$ (5)



Figure 1.4.2.1. Hydration curve for cement over the course of 50 h

During the hydration process the early hydration products consume water and their interlocking crystals decrease the workability of the cement paste. To prolong the workability of the paste, additional water may be added to the system. However, the addition of excess water negatively impacts the compressive strength, by increasing porosity. To reduce the need for excess water to be added to the concrete to increase workability, plasticizers are used as an alternative. Plasticizers are generally polymeric materials that reduce the water added to the mix by increasing dispersion. They generally reduce the water demand between 4 to 8 %. There are also superplasticizers, which have enhanced dispersion properties and reduce the water demand upwards of 10%. Good dispersion of the cement paste can be achieved either via electrostatic or steric mechanisms or a combination of both. Most traditional plasticizers used electrostatics to achieve dispersion. However due to the ionic strength (250 mM) of the cement system it is next to impossible to achieve dispersion by electrostatics alone [20]. As shown in Figure 1.4.2.2 the cement paste is in the coagulated regime in the absence of a plasticizer. By the addition of a plasticizer the energy potential can be brought up to a flocculated regime but never to a well-

dispersed stable regime. Alite ( $C_3S$ ) and belite ( $C_2S$ ) have negative zeta potentials whereas calcium aluminates and aluminoferrites have positive zeta potentials [21]. This inherently results in an electrostatically aggregated system.

The first plasticizers were developed in the 1930s and are shown in Figure 1.4.2.3(a-c) primarily relied on electrostatics. These polymers were negatively charged and hence would attract to the positively charged species and electrostatically repel the rest. Additional sulfonate groups were soon added to the polymers, to ensure multiple attraction points on the cement particle. However, as shown from the curve in Figure 1.4.2.2, this did not seem to have a big effect, steric repulsion was needed. In addition, the sulfonate groups tend to interfere with the hydration chemistry, which results in improper curing, affecting the mechanical properties of the system [15]. Polycarboxylate ethers shown in Figure 1.4.2.3(d) were developed fifteen years ago and have since then been used to produce several million cubic meters of concrete. Polycarboxylate ethers have both combined steric and electrostatic repulsion. They have a poly(acrylic acid) (PAA) backbone with either poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMAA) grafted side-chains. When added to cement the PAA backbone becomes negatively charged and electrostatically adsorbs to the cement particles with side chains extending into the water. These are more commonly known as comb polymers [22], [23]. However, very high concentration of these comb polymers is needed to achieve good dispersion. There is need for polymers that use "electrosteric" interactions to improve the dispersion of cement particles at low concentrations.



Figure 1.4.2.2. State of cement dispersion based on potential [20]



Figure 1.4.2.3. Chemical structure of (a) sulfonated melamine polymer, (b) lignosulfonate, (c) sulfonated naphthalene formaldehyde polymer and (d) polycarboxylate ether

1.4.3 Supplementary cementitious materials and fillers

Due to the vast quantity of cement produced, cement production is responsible for 5-7% of the global CO<sub>2</sub> emission (0.95 tons of CO<sub>2</sub> per ton of portland cement). The most effective way to reduce CO<sub>2</sub> emission is by reducing the clinker content by blending supplementary cementitious materials (SCMs) and fillers. These SCMs typically include blast furnace slag, fly ash, silica fume, limestone and metakaolin (calcined kaolin). Fillers include limestone, binders, kaolin and other minerals, which are relatively inert, compared to SCMs. A fundamental understanding of the chemistry of cement is still lacking and the addition of SCMs further complicates it. The addition of SCMs can impact the strength, durability and workability of the cement paste. Minerals such as metakaolin, zeolite and limestones are known to improve the durability of the cement and early age strength as a result of filler effect [24]–[26]. However, due to the high surface area of these SCMs in comparison to portland cement, as soon as SCMs are added to cement paste the workability significantly decreases. The significant decrease in workability limits the use of SCMs in industrial scale construction applications.

In practice, several different types of superplasticizers can be used to improve concrete mixture workability. However the compatibility of dosing various types of plasticizers with SCMs and fillers has not been examined. The dosing of various superplasticizers can prove to be detrimental for the strength or workability when blended with SCMs without a thorough investigation. There is a need to find plasticizers that improve the workability of SCMs while not jeopardizing short or long-term performance. Examining the phases formed during the hydration period is a step toward ensuring this.

#### 2. Synthesis

#### 2.1 RAFT – Reversible addition-fragmentation chain-transfer

Reversible addition-fragmentation chain transfer (RAFT) is a type of controlled/living freeradical polymerization. Living polymerization allows the ability to control molecular weight and polydispersity. It allows to synthesize much more complex architectures that cannot by easily synthesized with other types of polymerization [27]. In order to extend the lifetime of the propagating chains, living polymerization relies on establishing a dynamic equilibrium between a low concentration of active propagating chains and a predominant amount of dormant chains that are unable to terminate. The dormant species are capable of reactivation, functionalization to form block copolymers that allows the system to behave as a "living" system. There are many different types of controlled/living polymerization processes such as atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP) [28].

RAFT polymerization is different than the other processes mentioned, as it is applicable for anionic monomers. A suitable chain transfer agent is required to control the polymerization process. Some of the commonly used RAFT agents include dithioesters, dithiocarbamates and xanthates. A typical RAFT chain transfer agent has a thiocarbonylthio group (S=C-S) with substituents R and Z. The R and Z impact the reaction kinetics and structure of the resulting polymer. The RAFT polymerization process is summarized in Figure 2.1.1 [27], [28].

Due to the versatility of the RAFT polymerization process, it was used to graft polyacrylamide and polyacrylic acid off of the lignin core. By using the lignin core as a macroinitiator a star like architecture was synthesized with polyacrylamide or polyacrylic acid arms.



Figure 2.1.1. Schematic of reversible addition-fragmentation chain-transfer (RAFT) polymerization

#### 2.1.1 Synthesis of lignin macroinitiator

The lignin macrointiator was prepared using potassium xanthanate (14.1 g, 88 mmol) and 2bromopropionic acid (5.36 mL, 59.5 mmol) in a dry tetrahydrofuran (THF) solvent at room temperature. The reaction was allowed to run for 24 h to yield xanthate carboxylic acid. This was reacted with 1 mol equivalent of thionyl chloride to acetylate the xanthate. Subsequently, the acyl chloride xanthate was reacted with lignin at room temperature for 12 h. The reaction is shown in Figure 2.1.1.1. Based on the amount of lignin added to the reaction two different grafting densities were prepared: 2 (100  $\mu$  mol) and 17 (700  $\mu$  mol) active sites per lignin particle. The density of the active sites on the lignin macroinitiator was verified using <sup>1</sup>H nuclear magnetic resonance (NMR) as shown in Figure 2.1.1.2.



Figure 2.1.1.1. Synthesis of lignin macroinitiator



Figure 2.1.1.2. NMR spectra of lignin macroinitiator prepared using RAFT with PFB internal standard.

## 2.1.2 Synthesis of polymer-grafted lignin

The RAFT lignin macroinitiator (0.1 g) along with azobisisobutyronitrile, AIBN (0.005 g, 0.03 mmol) was added to the monomer (0.3 g, 4 mmol) in dimethylformamide, DMF (4 mL). The solution was degassed under nitrogen for 30 min and then placed in an oil bath at 70 °C for 24 h. Scheme of the reaction is shown in Figure 2.1.2.1. A target conversion of 98% was reached over the course of the reaction for both monomers and was verified using <sup>1</sup>H NMR. The final solution was precipitated into hexanes, filtered washed with dichloromethane and placed under vacuum at 45 °C overnight.



Figure 2.1.2.1. Synthesis of polymer-grafted lignin using acrylamide

In order to analyze the molecular weight of the polymer-grafted lignin, the polymer was cleaved from the lignin. The polymer-grafted lignin was dissolved in a potassium hydroxide solution at 70 °C for 12 h. During this process the ester linkage between the kraft lignin and the polymer is cleaved. Following neutralization, the polymer was extracted in dichloromethane. Characterization was performed via NMR and GPC with an Alliance 265 separations module having a mobile phase composed of water, with 0.1 M sodium phosphate buffer and 0.01% sodium nitrate at room temperature with a flow rate of 1mL/min. The NMR and GPC trace used to characterize the polymer is shown in Figure 2.1.2.2 and 2.1.2.3.

A variety of samples were produced with varying graft densities and degree of polymerization. The list of the samples tested is shown in Table 2.1.2.1. The 2 or 17 refers to the grafts per lignin particle, Am or AA refers to acrylamide or acrylic acid and 50 or 100 refers to the degree of polymerization. In the case of LPAM-2-100, the cleaved polymer had an Mn of 11 300 g/mol, which corresponded to a degree of polymerization of 159 rather than 100. The samples also showed a polydispersity of 1.83, which was higher than expected from a controlled radical polymerization technique. This is possibly due to inaccessibility of some of the initiator sites despite using a good solvent.



Figure 2.1.2.2. <sup>1</sup>H NMR data of extract from base-treated lignin-g-PAM



Figure 2.1.2.3. GPC trace of extract from base-treated lignin-g-PAM (M<sub>W</sub>: 24355, PDI:1.829)

Sample	Monomer	Grafting sites	DP
LPAM-2-50	Acrylamide	2	50
LPAM-2-100	Acrylamide	2	100
LPAM-17-50	Acrylamide	17	50
LPAM-17-100	Acrylamide	17	100
LPAA-2-50	Acrylic acid	2	50
LPAA-2-100	Acrylic acid	2	100
LPAA-17-50	Acrylic acid	17	50
LPAA-17-100	Acrylic acid	17	100

Table 2.1.2.1. List of samples synthesized using RAFT

#### 2.2 Free radical polymerization

Free radical polymerization is one of the most commonly used methods of polymerization in industry. Nearly 50% of all commercial synthetic polymers are prepared using radical chemistry [28]. The polymer is formed by the successive addition of free radical building blocks [27]–[29]. The free radicals can be generated by a variety of mechanisms, these radicals then add to the monomer units and continue to do so growing the polymer chain until they are terminated. Conventional free radical polymerization has many advantages over other polymerization processes. It does not require stringent process conditions and can be used for a wide range of vinyl monomers.

#### 2.2.1 Synthesis of lignin-acrylamide copolymer

For preparing the lignin-acrylamide copolymer via free radical polymerization (FRP), kraft lignin was functionalized by reacting with glycidyl methacrylate (GM) through the epoxide ring. The lignin-GM macromonomer along with AIBN (0.03 mmol) was added to acrylamide (4 mmol) in DMF (4 mL). The flask was sealed and degassed for 30 min and then immersed in an oil bath at 70 °C for 24 h, as shown in Figure 2.2.1.1. The solution was then filtered with hexanes and washed with dichloromethane.



Figure 2.2.1.1. Synthesis of lignin-acrylamide copolymer using free radical polymerization

#### 2.3 PEGylation

PEGylation refers to the covalent attachment of a polyethylene glycol (PEG) chain to a molecule. The PEG chain is functionalized on either one or both of the terminals, which makes it chemically active and allows it to react with the desired molecule. PEG is primarily used as a dispersant due to its water solubility and high mobility in solution. Depending on the molecular weight, it can be used for different applications. For example, low molecular weight PEGs are used as a lubricant in inkjet printers [30]. The most commonly used application for PEGylation is to enhance the delivery of therapeutic molecules [31].

## 2.3.1 Synthesis of PEGylated kraft lignin

A simple PEG grafting reaction, shown in Figure 2.3.1.1, was used to prepare the final product. The starting product was a commercial kraft lignin ( $M_n$  25,000 g/mol) from Domtar. One molar equivalent of the kraft lignin was dissolved in water and then the pH was adjusted to 11. The basic kraft lignin solution was heated to 70 °C and subsequently six molar equivalents of poly(ethylene oxide) methyl ether tosylate ( $M_n$  900,  $M_n$  200 or  $M_n$  5000) were dissolved in water and subsequently added. The solution was allowed to stir overnight and was filtered before use. Composition of the product was measured by first removing unreacted PEG through dialysis then using <sup>1</sup>H NMR using a dimethylsulfone internal standard.



Figure 2.3.1.1. Synthesis of PEGylated kraft lignin



Figure 2.3.1.2. H NMR spectra of (a) kraft lignin and (b) PEGylated kraft lignin

## 2.3.2 Synthesis of PEGylated lignosulfonate

A simple PEG grafting reaction, shown in Figure 2.3.2.1, was used to prepare the final product. The starting product was a commercial sodium lignosulfonate (Ref. Code 720263,  $M_n$  20,000 g/mol) from Borregaard LignoTech. One molar equivalent of the lignosulfonates was dissolved in water and then the pH was adjusted to 11. The basic lignosulfonate solution was heated to 70 °C and subsequently six molar equivalents of poly(ethylene oxide) methyl ether tosylate ( $M_n$  900,  $M_n$  200 or  $M_n$  5000) were dissolved in water and subsequently added. The solution was allowed to stir overnight and was filtered before use. Composition of the product was measured by first removing unreacted PEG through dialysis then using <sup>1</sup>H NMR using a dimethylsulfone internal standard shown in Figure 2.3.2.2.



Figure 2.3.2.1. Synthesis of PEGylated lignosulfonates



Figure 2.3.2.2. H NMR spectra of (a) lignosulfonates and (b) PEGylated lignosulfonates

#### 3. Techniques

The techniques described below were used to evaluate the solution and surfactant properties of polymer solutions

#### 3.1 Dynamic Light Scattering (DLS)

Size distributions of particles and surface charge were measured in aqueous solution at a range of concentrations. The solutions were ultrasonicated for 2-3 min prior to being placed in a glass cuvette. The particle diameter and zeta potential was measured using a Zeta-Sizer DLS (Malvern Instruments)

#### 3.2 Surface tension

Static surface tension of aqueous solutions at a variety of concentrations was measured using a Du Noüy ring-type tensiometer from Krüss at 25 °C. In order to aid with dissolution, the solutions were ultrasonically agitated for 10 min. The solutions were then mixed with proper amounts of NaCl if need be (only for surface tension dependence on ionic strength). The solutions were then poured into glassware previously cleaned in a base bath to avoid contamination. For interfacial tension of cyclohexane and water, cyclohexane was then poured on top of the aqueous solution. All samples were allowed to stabilize for at least 48 h prior to measurement. The Du Noüy was first calibrated against a known mass and then deionized (DI) water prior to use. A minimum of six measurements per sample was recorded.

Dynamic surface tension was measured using the microtensiometer at 25 °C. The samples prepared for the Du Noüy ring were used as is in the microtensiometer. A schematic of the microtensiometer is shown below in Figure 3.2.1. The microtensiometer operates with the help of a constant pressure head to the end of the glass capillary that is submerged in the desired solution. The pressure is measured using a pressure transducer and the radius is measured using a camera that is connected to a microscope. Due to the size of the drop, the interface forms a spherical cap and gravitational effects can be ignored. The surface tension is calculated using the

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Laplace equation as shown in equation 6. It uses a continuous measurement of radius r and the pressure jump  $\Delta P$  [32]. The samples were generally measured over the course of 10,000 sec.



$$\gamma(t) = \frac{\Delta P(t)r(t)}{2} \tag{6}$$

Figure 3.2.1. Schematic of how the microtensiometer functions

## 3.3 Viscosity of polymer solutions

Viscosity of aqueous solutions was measured using a Brookfield cone-and-plate viscometer. The steady shear measurements were taken at a rotational rate of 100 rpm.

#### 3.4 Emulsification

Polymer-grafted lignin was dissolved into deionized water and mixed with hexanes/cyclohexanes using an ultrasonicator (Misonix S-4000) at a pulsing amplitude of 70% and power of 85 W. Each sample was ultrasonicated for 3-5 min and then allowed to equilibrate.

To determine which phases were the continuous and dispersed, simple dilution and dye solubility tests with water-soluble methyl blue dye were performed. The concentration of lignin

nanoparticles in the aqueous phase was measured with a Cary 5000 UV-Vis-NIR spectrophotometer. The absorbance was measured at 290 nm. Optical microscopy (Leica DM IL LED optical microscope) was used to view emulsion samples. Several pictures of each emulsion sample were taken and image-processing algorithms (circular Hough transform as implemented by the function imfind-circles in MathWorks MATLAB software) were used to obtain associated droplet size distrbutions.

#### 3.5 Ellipsometry

Adsorption of the lignin was measured at the air-water interface using phase modulation ellipsometry (Beaglehole Instruments picometer). Adsorption measurements at the air-water interface were conducted in a glass Petri dish at a range of incident angles from 50 - 56°. The ellipsometer and sample stage were mounted on vibration damping mats to minimize disturbances of the surface. The ellipticity ( $\rho$ ) measured for clean water surface was measured against the theoretical predictions at the start of the experiments. Ellipticity is defined as the ratio of the complex Fresnel reflection coefficient of the parallel-polarized r<sub>p</sub>, and perpendicularpolarized r<sub>s</sub> components of the beam. The ellipticity can further be divided into real and imaginary parts. The ellipsometer signal is represented by x and y parameters as shown below:

$$x = Re(\rho) \frac{2}{1 + Re(\rho)^2 + Im(\rho)^2}$$
(7)

$$y = Im(\rho) \frac{2}{1 + Re(\rho)^2 + Im(\rho)^2}$$
(8)

Concentrated lignin solution was slowly added to the previously measured clean air-water interface and allowed to stir for 24 h to allow homogenous mixing. The glass Petri dish with the lignin solution was then allowed to sit undisturbed for 2 h before the interface was measured again. The average change in y for each one of the angles was recorded, averaged and used to calculate the thickness of the film and surface excess concentration. Each measurement at a single angle was recorded for 300 sec and repeated in three independent experiments.

Changes in ellipticity were modeled using a single film of thickness  $d_1$  and refractive index  $n_1$ . The value of  $n_1$  and dn/dc was measured using a digital refractometer. The
corresponding apparent thickness  $d_1$  was calculated to match the change in y. The surface excess concentration  $\Gamma$  was then calculated as shown below:

$$\Gamma = \frac{d_1(n_1 - n_0)}{dn/dc} \tag{9}$$

The techniques described below were used to predict dispersant behavior of polymer solutions in cement or model systems.

# 3.6 Rheometry

For MgO systems an Anton Paar MCR 302 rheometer was used to perform shear rate ramps and creep tests of the suspensions. A four-vane fixture in a roughened Couette cup was used to prevent wall slip. Preshear was applied before all tests by shearing the suspension at 500 s<sup>-1</sup> for 30 s, followed by a 10 s pause in the rotation before starting the test to ensure no residual stresses. All tests were conducted with fresh sample. Shear rate was increased from 0.01 to 100 s<sup>-1</sup> to simulate the behavior during concrete mixing. Creep tests were performed with an applied shear stress of 5 Pa for the 0.25 mg/mL concentration suspensions and 10 Pa for the 2.7 mg/mL suspensions as a general indicator of rheology during pipe flow and pouring.

For cementitious systems a DHR Rheometer (TI Instruments) was used. Vane fixture and Couette geometry were used to prevent sedimentation and wall slip and to assess changes in the viscoelastic properties of cement. [34,35]. An oscillatory strain sweep was performed on the samples at a constant frequency of 1 Hz. Tests were performed on pastes within 1 min of mixing at room temperature [21]. All samples were loaded into the rheometer and subjected to pre-shear of 100 s<sup>-1</sup> for 30 sec to ensure that they had the same mixing history. The experiments measured changes in complex viscosity ( $\eta$ ') under a strain magnitude sweep at a constant shear rate of 0.01 rad/s. The experiments were designed to probe the viscous response of the cement pastes as the colloidal gel network ruptured under oscillatory strains

To gauge changes in workability and yield stress of the cement pastes, mini-slump tests were performed on pastes of varying superplasticizer concentration and w/c ratios [33], [34]. Samples were prepared at room temperature using a planetary (Hobart) mixer with a paddle fixture at a speed of 62 rpm using tap water in accordance with ASTM C305.

The effectiveness of these samples in improving workability of mortar was also assessed using slump tests. The pastes were made with 75% sand and 25% cement, with a 0.50 w/c ratio. Samples were prepared at room temperature using a planetary (Hobart) mixer, also in accordance with ASTM C305.

Immediately after mixing, the samples were compacted into a 3-cm inner diameter and 5cm high mini-slump cylinder, and the cylinder was slowly raised (5-11 sec). The diameters along two orthogonal directions and the height difference between the cylinder and slump were immediately recorded.

# 3.7 Sedimentation studies

Suspensions were allowed to sit in graduated cylinders for one week to observe the volume of sedimented particles and the supernatant. Water-volumes were recorded at multiple time points and represented as a ratio of supernatant volume to the entire suspension volume. The ratio of supernatant to suspension volume was used to assess the sedimented particle packing and rate of sedimentation. To evaluate the viscosity of the supernatant that resulted from setline particles, separate suspensions were centrifuged at 1000 rpm for 2 min to extract the supernatant. Viscosity measurements of the supernatant at 1 s<sup>-1</sup> were made to correlate the adsorption of chains to the rate of particle sedimentation.

# 3.8 Solution-properties

Surface area for all samples was measured using the Brunauer-Emmett-Teller (BET) method using a Gemini VII Micrometrics surface area analyzer. Each sample was degassed for 24 h at 60 °C prior to being analyzed. Adsorption of the different samples onto the active phase was measured by analyzing the total amount of carbon left in the sample before and after adsorption. Each polymer solution was mixed with 5 wt. % active phase at a minimum of 5 different concentrations (0.25, 0.5, 1, 2 and 4 mg/mL) for 1 h and then centrifuged at 4400 rpm for 12 min to obtain the top layer. The top layer was subsequently diluted and the total organic carbon content was measured using a GE InnovOX TOC analyzer.

# 3.9 Isothermal calorimetry

Isothermal calorimetric measurements of cement hydration were performed using a 8-channel TAM Air (TA Instruments). Each sample was mixed in accordance with ASTM C305 at the desired plasticizer concentration and w/c ratio and was repeated three times. The heat flow measurement started 45 min after the preparation of cement paste, representing the typical equilibration time required. The heat flow was then measured over the course of 120 h, and the data were collected and analyzed using the TAM Air Assistant software.

# 3.10 Compressive strength

The compressive strength of each sample was tested at 1,3,7 and 28 days according to ASTM C109. Ten samples for each superplasticizer were tested and compared to portland cement. The paste for each sample was prepared in accordance with ASTM C305. The paste was then poured into a 2" x 2" plastic mold and cured at room temperature and 100% humidity. The cured samples were tested on a Testmark CM-2500 at a load rate of 20 psi/sec.

# 3.11 Nano-CT

The microstructural analysis of the samples was done using a Nano-CT (UltraXRM L-200, Xradia, Inc, Pleasanton, CA) that used a copper-rotating anode and lab-scale X-ray generator. The setup also included high precision X–ray optics that included a single-capillary condenser tube, pin hole and zoneplate to achieve nano-scale resolution. The X-ray computed tomography used radiographs obtained from different angles of the sample and computationally reconstructed the 3D structure by filtered back projection of the radiographs. The imaging was done at room temperature for all samples. The hydration for all cement samples was stopped using isopropanol. The maximum resolution achieved was 50 nm with a maximum pixel resolution of 16 nm. The radiographs were then reconstructed with the help of Avizo 3D reconstruction software. The samples were divided into the respective phases using the intensity thresholding function. The label function was subsequently used to quantify the phases of interest.

# **4.** Surfactant properties of polymer-grafted lignin prepared via RAFT polymerization *Published in Langmuir, vol. 30, no. 31, pp. 9303-9312, 2014.*

# 4.1 Introduction

Surfactants from renewable resources have become increasingly important compared to synthetic ones due to their similar performance and lower environmental impact. Surfactants from renewable resources have a similar structure with a polar head group and non-polar tail. They offer high levels of interfacial activity. Surfactants based on fatty acids, arginine lipopepetides and alkyl polyglycosides are currently being used in a broad range of applications [35]–[37]. The structure of surfactants from renewable resources tends to be more diverse in functionalities compared to their synthetic counterparts, but their properties are still understood in terms of hydrophilic-lipophilic balance (HLB). The HLB ratio for a surfactant predicts the affinity for different phase and subsequently this affects the solubility and interfacial activity [38].

Dispersants and emulsifiers derived from lignin tend to have a very strong hydrophobic lignin core due to its native properties. Many chemical strategies have been used to strengthen its amphiphilic interactions. For instance, kraft lignin has been successfully functionalized with PEG to improve its interfacial activity and results in a surface tension of 46 dynes/cm at critical micelle concentration [7]. Similarly, polypropylene oxide has been reacted with kraft lignin under basic conditions to result in a decrease from 3 to 1 dynes/cm of the water-octane interfacial tension [8]. Numerous studies in literature have shown that chemical modifications to lignin can be used as an effective strategy to increase its interfacial activity.

Controlled radical polymerization (CRP) techniques such as reversible additionfragmentation chain-transfer (RAFT) and atom transfer radical polymerization (ATRP) have been extensively used to modify proteins, cellulose and inorganic particles [39]–[44]. ATRP has been previously used to functionalize lignin with polystyrene and poly(methyl methacrylate) [45]. In this study RAFT was used to modify lignin with polyacrylamide (PAm) and poly(acrylic acid) (PAA) to increase the interfacial activity. RAFT was chosen as it allows a broader range of monomer chemistries.

# 4.2 Experimental

The synthesis of lignin grafted polyacrylamide and polyacrylic acid along with their characterization is presented in Section 2.1. A list of compositions prepared with grafting density and degree of polymerization is shown in Table 4.2.1. The polymers were characterized using dynamic light scattering. The interfacial activity was measured using a Du Noüy ring and by the stability of hexane and water emulsions when lignin grafted polymers were added.

Sample	Monomer	Grafting	Degree of	Mass fraction
		density ( $\mu$	polymerization	of polymer
		mol/g of lignin)	(DP)	
LPAM-17-50	Acrylamide	676	50	0.706
LPAM-17-100	Acrylamide	676	100	0.828
LPAM-2-50	Acrylamide	17	50	0.262
LPAM-2-100	Acrylamide	17	100	0.415
LPAA-17-50	Acrylic acid	676	50	0.708
LPAA-17-100	Acrylic acid	676	100	0.830
LPAA-2-50	Acrylic acid	17	50	0.265
LPAA-2-100	Acrylic acid	17	100	0.419

Table 4.2.1. List of compositions prepared with grafting density and DP

# 4.3 Results

All polymer-grafted lignin compositions were soluble in water at 1 mg/mL, where as kraft lignin itself is not soluble in water and any concentration. Dynamic light scattering was used to characterize the particle size of these aqueous solutions and the results are summarized in Table 4.3.1. For most of the DLS data two main peaks were observed. For 100 DP the smaller particles ranged between 15-20 nm whereas the larger particles ranged from 60-100 nm. For 50 DP the smaller particle sizes ranged from 50-80 nm, which suggests that aggregates were the primary species present. The driving force for aggregation was assumed to be water-lignin interactions, which likely promoted a collapsed lignin conformation at pH 7. Due to this conformation, polymer-grafted lignin can be considered as a polymer-grafted nanoparticle. By considering polymer-grafted lignin as a polymer-grafted nanoparticle, it is easier to understand the behavior of the system and compare it to other similar systems reported in the literature. DLS experiments

were also performed below the critical concentration at 0.1 mg/mL and showed that isolated polymer-grafted lignin was the primary species in solution. The DLS data hence suggest that aggregation is strongly correlated to degree of polymerization rather than graft density.

Sample	Low particle	Low particle	High particle	High particle
	diameter (nm)	volume (%)	diameter (nm)	volume (%)
LPAM-17-50	34.93	74	194.2	26
LPAM-17-100	46.32	89	164.7	9
LPAM-2-50	53.66	100	-	-
LPAM-2-100	16.25	96	143.6	4
LPAA-17-50	88.15	100	-	-
LPAA-17-100	16.5	74	121.8	26
LPAA-2-50	26.27	94	128	6
LPAA-2-100	15.19	98	367.4	2

Table 4.3.1. Particle size of aqueous solutions for LPAM and LPAA

The static surface tension values of aqueous solutions of lignin grafted with poly(acrylic acid) and poly(acrylamide) as a function of concentration are shown in Figure 4.3.1 and compared with acidified lignin used in the preparation of the polymer conjugates. The list of surface tensions values for all the samples listed at higher concentrations along with viscosity data can be found in Appendix A. The viscosity data suggests that there was no significant entangling of the polymers. In Figure 4.3.1, only surface tension values for LPAM-2-100 and LPAA-2-100 are shown. Non-grafted lignin has only weak effects on the surface tension, with an inflection point appearing near 1 mg/mL, the concentration at which particle aggregates become visible in solution. In contrast, a sharp decrease in surface tension at concentrations slightly less than 0.1 mg/mL was observed for both polymer-grafted compositions, consistent with a critical aggregation concentration (CMC/CAC), although the aggregation was likely distinct from true micellization. The PAA compositions tended to lower the water surface tension to a greater extent than those based on PAm, and this effect was found to be dependent on grafting density and degree of polymerization, although the CAC appeared to be independent of these variables, indicating the CAC may be associated with the transition to larger (but still nanoscale) aggregates.



Figure 4.3.1. Surface tension versus concentration LPAM-2-100 and LPAA-2-100

The samples grafted with poly(acrylic acid) had significant changes compared to the samples grafted with polyacrylamide. Samples grafted with poly(acrylic acid) had the lowest surface tension value of 42 dynes/cm for the highest grafting density and lower graft molecular weight. This value is significantly lower than the surface tension of the homopolymers; PAA (73 dynes/cm) and PAm (69 dynes/cm), providing confirmation of the importance of grafted architecture and lignin core. Previous work done on lignin has shown significant improvements in surface tension. For instance, sodium lignosulfonate can reduce the surface tension to 50 dynes/cm at concentrations of 1 mg/mL and PEGylated kraft lignin can reduce the surface tension to 44 dynes/cm at 0.25 mg/mL [7], [46]. This suggests that the chemistry of the hydrophilic groups attached to the lignin core sensitively affect the interfacial activity.

Microtensiometry was used to understand the how the grafted polymer and degree of polymerization affect the interfacial activity in depth. The dynamic surface tension for samples with constant grafting density at a concentration of 1 mg/mL over the course of 10,000 sec is shown in Figure 4.3.2. Dynamic surface tension provides insight into how the polymer-grafted lignin is adsorbing to the interface. For instance, each of the samples seem to have two different regions, the first one is diffusion controlled where the surfactant is moving from the bulk solution to the interface and the second one is rearrangement of the surfactant at the interface.

From the data shown in Figure 4.3.2, LPAA samples are much more interfacially active compared to LPAM. LPAA-2-100 had slightly faster dynamics overall compared to LPAA-2-50, which can be explained due to the collapsing of the anionic polyacrylic acid onto the lignin core to screen the surface charges. The slope for both the diffusion controlled and rearrangements at the interface regime are shown in Table 4.3.2. The slope for the LPAA samples in the diffusioncontrolled regime is an order of magnitude higher than the LPAM samples. LPAA samples have a lower static surface tension as seen in Figure 4.3.1 compared to the LPAM samples due to the screening of the surface charges, which results in them preferentially populating the air-water interface and hence a higher slope. For the rearrangement regime, the opposite is observed as the LPAM samples have a higher slope than LPAA. The difference between the magnitudes of the slopes of both samples is not as drastic as observed for the diffusion-controlled regime. Both the LPAM and LPAA samples shield the lignin core to some extent, which helps reduce the effect of surface charge on the rearrangement, hence resulting in similar magnitudes. Despite shielding the core, both LPAM and LPAA work through different mechanisms. As previously mentioned, the LPAA sample the anionic polyacrylic acid collapses onto the lignin core to shield the surface charge and provides some steric effects due to the collapsed polymer, whereas for LPAM the grafts possibly extend out onto the aqueous phase more, resulting in enhanced steric effects. It can be hypothesized that the steric effects of LPAM are more significant for rate of rearrangement compared to completely shielding the core effects in LPAA. It is important to note that despite the affects on the rearrangement slope, LPAM samples had a lower surface tension than LPAA samples. This suggests that a combination of both charge and steric effects is required for an interfacially active sample. This also suggests that the attraction between the lignin cores is the main reason for the lack of interfacial activity and cannot be prevented alone by a grafting a non-ionic polymer. All the polymer-grafted lignin samples tested were surface active for prolonged periods of time, which is not observed for traditional surfactants [32].



Figure 4.3.2 Dynamic surface tension measured using a microtensiometer for lignin samples at a concentration of 1 mg/mL.

Table 4.3.2. Slope for the bulk diffusion and rearrangement regime for dynamic surface tension data

Sample	Bulk diffusion regime	Rearrangement regime
	slope (dynes/cm-s)	slope (dynes/cm-s)
LPAA-2-50	-0.032	-0.0005
LPAA-2-100	-0.061	-0.0004
LPAM-2-50	-0.009	-0.0007
LPAM-2-100	-0.004	-0.0006

Ellipsometry was used to see how effectively the samples are packing the interface. The thickness and surface excess concentration for all four samples is shown in Table 4.3.3. All the samples have similar interface thickness however the LPAA samples had a much higher surface excess concentration compared to LPAM. This confirms that the polyacrylic acid is collapsing onto the lignin core to screen the surface charge which allows it to pack the interface much more effectively compared to LPAM samples which strictly rely on steric stabilization. Also all the samples had a similar final surface tension value, which shows that the lignin core is primarily responsible for the interfacial activity. The samples were then rinsed off the interface using water, and a majority of the surfactant came off the interface showing good reversibility.

The surface tension measurements shown in Figure 4.3.1 and 4.3.2 show the partitioning of different lignin species to the air-water interface and hence their effects on surface tension.

Non-ionic surfactants such as polyoxoethylene-alkanols can reduce the surface tension to 35 dynes/cm at 10<sup>-4</sup> M, by presenting the akyl groups normal to the water surface and hence reducing the cohesive energy of the interface and the resultant surface tension [47]. It is not clear what drives the polymer-grafted lignin to the air-water interface at lower concentrations than non-grafted lignin. At the CAC, the partitioning to the surface competes with the formation of aggregates in bulk solution. It is possible that the hydrophilic polymers inhibit lignin-lignin interactions resulting in a saturated air-water interface where the hydrophilic polymers are extending into the bulk water.

Sample	Thickness (nm)	Surface Excess (mg/m <sup>2</sup> )
LPAM-2-100	$3.60 \pm 0.715$	$3.12 \pm 0.235$
LPAM-2-50	$3.20 \pm 0.340$	$2.40 \pm 0.10$
LPAA-2-50	$3.80 \pm 0.140$	$6.69 \pm 0.120$
LPAA-2-100	$3.60 \pm 0.340$	$4.75 \pm 0.050$

Table 4.3.3. Ellipsometry data for polymer-grafted lignin samples at 1 mg/mL

To test emulsion formation, all the samples were dissolved in water at 1 mg/mL and pH 7, and then emulsions were formed by adding an equal volume of hexanes followed by ultrasonication. For all the samples only two phases were observed; the aqueous phase and the emulsion phase. The hexane phase appeared to be completely incorporated into the emulsion irrespective of graft density, polymer chemistry or degree of polymerization. Non-grafted lignin, in contrast had three phases and a very low tendency to stabilize emulsions. The volume fractions were 40% aqueous, 20% emulsion and 40% hexanes. This concluded that the ability to form stable emulsions using kraft lignin is due to the polymer grafting.

Droplet sizes of 5-40  $\mu$  m were observed in the emulsion phase as shown in Figure 4.3.3. PAA-grafted lignin emulsions had a droplet size on average of about 10  $\mu$  m, whereas PAmgrafted lignin emulsions had a droplet size on average of about 20  $\mu$  m. These emulsions were stable for weeks at room temperature, which is consistent with other studies on polymer-grafted nanoparticles [48]. The continuous phase for all of the emulsion phases was hexanes and was verified using conductivity measurements. This was unexpected as polymer-grafted lignin is insoluble in hexanes. Also, this did not agree with the theory of Pickering emulsions. Pickering emulsions are modeled as reducing the interfacial energy according to

$$\Delta E = \pi r^2 \gamma_{OW} (1 - |\cos\theta_{OW}|)^2 \tag{10}$$

where r is the particle radius,  $\gamma_{OW}$  is the interfacial tension and  $\theta_{OW}$  is the contact angle [49]. The  $\theta_{OW}$  for the polymer-grafted lignin samples < 90°, this would predict that water would form the continuous phase in these emulsions. When a samplebehaves according to equation 10, it satisfies the Bancroft rule [50], [51]. Polymer-graft lignin samples do not obey the Bancroft rule, which is consistent with patchy particles [52]–[54]. However, this is still interesting as the exposed lignin core is not soluble in hexanes and there is no obvious driving force for the formation of water-in-oil emulsions.



Figure 4.3.3. Water in oil emulsions using LPAM-2-100 (left) and LPAA-2-100 (right)

To further investigate the behavior of polymer-grafted lignin emulsions, LPAM-2-100 and LPAA-2-100 were tested at the same concentration and pH in a series of emulsions ranging from 10 to 90% water. The volume fraction of emulsions was determined by the height of the emulsions and the fraction of lignin in the emulsion phase was determined by measuring the residual concentration of lignin in the aqueous phase using UV-vis spectroscopy at a wavelength of 290 nm. The results are plotted in Figure 4.3.4. For all the compositions tested, hexanes were found to be the continuous phase with the absence of an emulsion inversion point (EIP). The emulsion % decreases linearly for both samples as the amount of water increases, which suggests that for a given surfactant, the emulsion has a constant structure in terms of droplet size and volume fraction. The LPAA-2-100 sample partitioned much more strongly into the emulsion phase for all samples compared to LPAM-2-100. The difference in partitioning of the LPAM and

LPAA, correlated with the difference in droplet size shown in Figure 4.3.3. By mass balance, this shows that the molecular density of both the samples at the interface is the same, and the difference in droplet size is driven by the lower surface tension of the LPAA sample.



Figure 4.3.4. Volume fraction of emulsion and percent polymer-grafted lignin in emulsion phase for water-hexanes mixtures containing (A) LPAM-2-100 and (b) LPAA-2-100

Lignosulfonates only stabilize oil in water emulsions (O/W) [55]. Lignosulfonates as mentioned previously have a disorganized structure, that results in some interfacial activity, but generally very high concentrations are needed to achieve reductions in surface tension. The significant reduction in surface tension and CAC suggest that these hybrid biopolymers have high levels of surface activity. The lack of an EIP and preference of hexanes can be explained due to the low grafting density and random placement of grafts and as a result the formation of a collapsed conformation. The collapsed conformation allows for high coverage at the interface and shielding between hexane-water interactions. The proposed conformations for the air-water and oil-water are shown in Figure 4.3.5. The polymer-grafted lignin samples have extended conformations at the air-water interface but a collapsed conformation in hexane-water. Ellipsometry measurements performed in hexane-water could provide further insight into these conformations.



Figure 4.3.5. Schematic representation of polymer-grafted lignin at air-water interface (left) and hexanes-water interface (right)

# 4.4 Conclusion

Grafting water-soluble polymers onto kraft lignin results in increased interfacial activity. While the solution viscosities did not increase significantly, surface tensions were found to decrease as a function of concentration, graft density, graft molecular weight and polymer chemistry. Despite the aqueous solubility of polymer-grafted lignin, stable water-in-oil emulsions were formed with the hexanes. The partitioning of LPAA was much higher than LPAM. The data suggests that the architecture of polymer-grafted lignin is critical in determining interfacial properties and the native-hydrophobic lignin core plays a very important role in interfacial activity.

# **5. Tunable Pickering emulsions with polymer-grafted lignin nanoparticles (PGLN's)** *Published in Journal of Colloid & Interface Science, vol. 466, pp. 91-100, 2016.*

# 5.1 Introduction

In previous experiments it was demonstrated that by grafting polyacrylamide onto kraft lignin by using RAFT, polymer-grafted lignin nanoparticles (PGLN's) could be synthesized that can tune aggregation strength while retaining interfacial activities and form Pickering emulsions. Pickering emulsions are of particular interest because they are inherently stable against coalescence than their surfactant counterparts due to the large energetic barrier associated with particle desorption from the surface. The desorption energy of these nanoparticles can reach up to  $10^7 k_{\rm B}T$  [49]. The stability in emulsions that were seen in the previous experiments can be in part attributed to the steric repulsion between grafts, preventing droplet flocculation and subsequent coalescence. The stability of those emulsions over the course of weeks suggests a high-energy barrier for desorption. It is possible that PGLN's could provide an even higher energy barrier to desorption because a single particle interface, now is associated with many polymer chains that could be surface active.

To understand what variables can affect these stable emulsions; graft density, ionic strength, initial water and cyclohexane volume fractions were systematically varied and the effects on droplet size and aggregation were observed. LPAM samples were used for this indepth analysis and acrylamide is one of the most commonly used polymers prepared via radical polymerization and is water-soluble. However, it needs to be noted than even 1% conversion of the monomer to acrylic acid via hydrolysis is sensitive to monovalent salt concentrations as low as 1 mM [56]. This study aims to test the ability of PGLN to form stable emulsions at neutral pH with tunable properties as a function of volume fraction of cyclohexane and ionic strength.

# 5.2 Experimental

Two different types of LPAM were used in this set of experiment LPAM-2-100 and LPAM-17-100. Since the degree of polymerization is the same for both samples, they will be referred to as LPAM100 and LPAM700 respectively, as 2 grafting sites corresponds to approximately 100  $\mu$  mol of grafts and 17 graft sites corresponds to 700  $\mu$  mol of grafts per gram of lignin. Particle behavior, interfacial tension and emulsion stability was measured for LPAM100 and LPAM700 at three different ionic strengths 0 mM, 1 mM and 10 mM NaCl.

# 5.3 Results

#### 5.3.1 Particle behavior

PGLN's were studied at a concentration of 1mg/mL, which is above its CAC that was previously measured to be 0.1 mg/mL [3]. This value is consistent with literature values of kraft lignin [57]–[59]. DLS was used to characterize the solutions and the results are shown in Figure 5.3.1.1. The PGLN's were ultrasonicated and then size was measured after two weeks to mimic stable conditions. At 0 mM NaCl, PGLN's aggregated to form clusters of roughly 100 nm in radius for both graft densities. The broad peaks of LPAM100 suggested there was some degree of polysdispersity. At 1 mM and 10 mM NaCl, LPAM100 exhibited peaks at 14 and 10 nm respectively. There were some larger aggregates still present. At 1 mM and 10 mM NaCl, LPAM700 exhibited peaks at 7 and 12 nm respectively. This data shows that the addition of salt, inhibited aggregate formation to a significant extent. The non-grafted lignin particles have a radius of about 5.0 nm [60]. Polyacrylamide grafts of 100 DP add a radius of gyration of about 2.8 nm based on molecular weight relation for polyacrylamide in water [61]. This shows that the peaks associated with the smaller hydrodynamic radii at increased ionic strength represent single PGLN's in solution.

The lack of aggregation in the presence of salt was unexpected. In previous studies it has been reported that monovalent salts drive the precipitation of kraft lignin under alkaline conditions [62]. Hence, it was expected that the addition of NaCl would further increase the hydrophobicity of the lignin core. This is true for other biosurfactants such as rhamnolipids that have similar disorganized structure and tend to aggregate with the addition of salt [63]. The increase in solubility of the PGLN's on the addition of salt, suggests that the interactions of the hydrophobic lignin core and grafts are responsible, not necessarily through complete chain collapse onto the core but possibly through greater associations that partially shield the waterlignin interaction.

Kraft lignin particles are known to have a negative surface charge due to the presence of carboxylate and sulfonate on its surface [64]. To elucidate the effects of the polymer grafting on the surface potential, the zeta potential of LPAM100 and LPAM700 was measured at different ionic strengths. The data is shown in Figure 5.3.1.2. At neutral pH the zeta potential was similar to that of kraft lignin. LPAM100 and LPAM700 had a surface charge within error of the measured value of kraft lignin. This suggests that the lignin core dominates the surface charge of PGLN's. This is very atypical of biosurfactants, as the hydrophobic nature is strongly responsible for aggregation and minimal reduction is seen with salt effects. The magnitude of the zeta potential decreased as the ionic strength was increased, indicating that salt ions were screening some of the surface charge. Generally, when the surface charge decreases in magnitude the system is more prone to aggregation, which was not observed in this case. This suggests that PGLN's behave like typical colloidal particle with electrical double layers that obey DLVO theory [65], [66]. A much more complex interaction is taking place which could possibly explain the anomalous behavior. As the ionic strength is increased, the surface charge of the lignin core is screened, reducing inter-particle repulsive forces and increasing the hydrophobicity of the core. This increase in hydrophobicity may cause the hydrophilic polyacrylamide grafts to collapse onto the lignin core to shield it from the aqueous environment. This shielding mechanism probably interferes with some of the complex hydrophobic interactions that promote aggregation of the lignin particles despite their intrinsic high surface charges [57]. This indicates that the presence of salt decreases effective surface charge and the extent of aggregation, which is shown in Figure 5.3.1.1. This also suggests that the aggregated clusters are only week aggregated, and such behavior has not been reported for any other biosurfactant. This shows that the hydrophobicity is responsible for reduction in aggregation even in PGLN's.



Figure 5.3.1.1. Dynamic light scattering for (a) LPAM100 and (b) LPAM700 at salt concentrations of 0 mM, 1 mM and 10 mM NaCl



Figure 5.3.1.2. Zeta potential for LPAM100 and LPAM700 as a function of NaCl concentration

# 5.3.2 Interfacial tension lowering

Previously, it was demonstrated that PGLNs were capable of reducing the surface tension of water [3]. In this study, the interfacial tension between cyclohexane and water was measured, to understand how grafting density affects interfacial adsorption. The clean interfacial tension between water and cyclohexane has been measured to be between 48.5 and 50.0 dynes/cm. A Du Noüy ring apparatus was used and measurements were corrected for meniscus geometry using the parameters of the ring. All the samples were allowed to stabilize for three days to account for the slow dynamics of particle transport and adsorption [59], [67].

The interfacial data for both LPAM100 and LPAM700 and varying ionic strength is shown in Figure 5.3.2.1. LPAM100 lowered the surface tension more strongly than LPAM700, 24.5 versus 26.8 dynes/cm. Increase in ionic strength further decreased the interfacial tension to 19.2 dynes/cm for LPAM100 and 23.3 dynes/cm for LPAM700. These numbers are not as low as those observed for other grafted nanoparticles such as 10.8 dynes/cm for PDMAEMA-grafted silica nanoparticles. This can be attributed to the grafted polymer and grafting density. Polyacrylamide homopolymer is not very surface active, which results in a minimal decrease in interfacial tension [68]. However, the lignin core is interfacially active and based on how exposed the core is (grafting density) it can help lower the interfacial tension. Nonetheless, there was a significant degree of adsorption at the interface. LPAM700 consistently had a higher interfacial tension than LPAM100. Increased graft density results in an overall more hydrophilic particle, which is less wettable by the oil phase. This, in turn, would lessen the extent to which it penetrates the oil-water interface and hence reduce the decrease in interfacial tension compared to LPAM100. Increased graft density in LPAM700 also leads to increased steric repulsive forces between particles, which reduces packing at the interface and hence a higher interfacial tension as predicted by the Gibbs adsorption equation

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln c}\right)_{P,T} \tag{11}$$

where  $\Gamma$  is the surface concentration, R is the ideal gas constant, P is the pressure, T is the temperature,  $\gamma$  is the interfacial tension and c is the bulk concentration. Increasing ionic strength would have the opposite effect to grafting density. By increasing the ionic strength, the electric double layer repulsion forces would decrease allowing greater packing at the interface and lower interfacial tensions. Also, based on the DLS data, increasing salinity reduces aggregation through graft collapse, which may allow more individual particles that would normally be trapped in aggregates to adsorb at the interface. The difference in magnitude of interfacial tension between 0 mM and 1 mM is much greater than that between 1 mM and 10 mM. This is thought to be due to graft collapse by 1 mM and there is no further change in graft conformation after that. It is important to note that the rheological changes of the interfacial film may also play a significant role in interfacial tension lowering. In fact, while operating the Du Noüy ring apparatus, the cyclohexane-water interface appeared to behave like a semi-solid

viscoelastic skin, which has been documented elsewhere for lignin particles [69], [70]. These effects warrant further investigation.



Figure 5.3.2.1. Interfacial tension between cyclohexane and water in the presence of 1mg/mL of LPAM100 and LPAM700 as a function of NaCl concentration

# 5.3.3 Emulsion production and efficiency

Emulsions were prepared with cyclohexane and aqueous solutions of LPAM100 and LPAM700 at 1 mg/mL concentrations. Ultrasonication was used to prepare the emulsions in pules of 1 sec duration for a total of 5 min. Although steady state droplet size can depend on the time used to homogenize the samples, further ultrasonication after 5 min did not seem to have any effect on the structure of the emulsion [71], [72]. Representative images of LPAM100 and LPAM700 emulsions are shown in Figure 5.3.3.1. All emulsions prepared were oil-in-water (o/w) emulsions as confirmed by dilution ad dye solubility tests. This was opposite to what was noticed for lignopolymers emulsions when hexanes were used (Section 4.3). This can be attributed to the variability of lower molecular weight chains present in the hexanes. The dilution test consisted of placing a small amount of the emulsion in water and cyclohexane. All emulsions readily dispersed in water, indicating they were o/w. Furthermore, when added to the emulsion, methyl blue (water-soluble dye) was found in the continuous phase of all samples when viewed under an optical microscope. This behavior follows the Bancroft rule as stated previously in equation 10. All the emulsions tested were o/w despite a large range of initial volume fractions indicates that

PGLNs do not undergo a catastrophic phase inversion in the range of conditions studied [49], [73], [74].



Figure 5.3.3.1. Images of emulsions formed with 1 mg/mL of (a) LPAM100 and (b) LPAM700. From left to right, the initial volume fraction of cyclohexane was 0.1 to 0.9 v/v.

Emulsions were remarkably stable for a period of months and did not exhibit any droplet coalescence or Ostwald ripening [75]. Emulsion stability at low particle concentrations has been observed before for polymer-grafted nanoparticles [32], [68], [76]. This stability is due to the steric repulsive forces between grafts, which would prevent droplet coalescence. There are also other factors that attribute to the stability of emulsions. First, it is well known that particles of intermediate hydrophobicity are better emulsion stabilizers than those with strong hydrophobic/hydrophilic interactions [73], [77]. PGLNs fit the criteria of intermediate hydrophobicity due to their disorganized structure. Second, it has been shown that Pickering emulsions are most strongly stabilized when particles weakly flocculate, which is the case of PGLNs [49], [77], [78]. Finally, as noted with interfacial tension measurements, a dense viscoelastic film formed by the aggregated lignin could provide the interface with rheological properties that deter coalescence [70], [77].

Despite great stability, all emulsions exhibited relatively fast creaming over a period ranging from 1 h to 24 h. In fact, emulsions stabilized by lignosulfonates also exhibit creaming [69]. The final volume of emulsion produced after creaming was found to be dependent on graft density, ionic strength and initial volume fraction as shown in Figure 5.3.3.2. In general, LPAM100 samples were able to produce more emulsion compared to LPAM700 samples. The presence of salt increased the volume of emulsion formed at all initial conditions for both PGLNs. The maximum value of emulsion was measured at 0.5 volume fraction of cyclohexane. This suggests, that a balance exists between the amount of PGLNs and the amount of cyclohexane available to form emulsions. At 0.8 v/v cyclohexane, the initial aqueous volume fraction evidently did not contain enough PGLNs to stabilize a large volume of emulsion under all conditions tested.



Figure 5.3.3.2. Volume fraction of emulsion produced after creaming for (a) LPAM100 and (b) LPAM700 as a function of initial cyclohexane volume fraction and salinity.

In order to determine the amount of PGLN incorporation into the emulsion partition, UV-vis spectroscopy was used to measure the concentration of lignin in the aqueous phase and calculate the concentration in the emulsion partition via the following equation that assumes volume and mas conservation:

$$c_{emul} = \frac{c_0 \phi_{0,aq} - c \phi_{aq}}{\phi_{emul}} \tag{12}$$

where  $c_{emul}$  is the PGLN concentration in the emulsion partition,  $c_0$  is the initial PGLN concentration (1 mg/mL), c is the measured concentration and  $\phi$  represents the volume fractions of the aqueous (aq) or emulsion (emul) partitions after emulsification or initially (0). The results are presented in Figure 5.3.3.3. There are two major trends in the data, one for samples without any salt and one with salt. The samples without salt showed an increase in emulsion PGLN concentration as the volume fraction of cyclohexane increased. The samples with salt showed the opposite. As seen from the previous data, increasing the ionic strength results in an increase in the emulsion phase due to interfacial packing. Also, due to the presence of salt, there are possibly more non-aggregated particles that are free to line the interface and are consistent with Figure 5.3.1.1.



Figure 5.3.3.3. Concentration of PGLNs in the emulsion partition as a function of initial cyclohexane volume fraction, graft density, and salinity.

The droplet size distributions for each emulsion were determined for all samples using optical microscopy. Several pictures of each emulsion were taken and the droplets were identified through image processing. As shown in Figure 5.3.3.4, droplet size was a complex function of graft density, ionic strength and volume fraction. First, a lower grafting density corresponded to lower droplet sizes. LPAM100 had maximum droplet radii of 19  $\mu$  m, 20  $\mu$  m and 49  $\mu$  m, whereas LPAM700 had maximum droplet radii of 24  $\mu$  m, 89  $\mu$  m and 189  $\mu$  m for 0 mM, 1 mM and 10 mM NaCl respectively. Second, droplet sizes increased for both grafting densities with increasing salt concentration. Third, intermediate cyclohexane volume fractions (0.5-0.8) produced the largest droplet sizes, especially in the presence of salt, under which the distributions transformed from relatively uniform to perhaps bimodal [Figure 5.3.3.4 a to b]. The droplet size trends were rather complicated and can be explained by noting that a higher hydrophile-lipophile balance (HLB) value for non-ionic surfactants corresponds with larger droplet sizes and wide droplet distributions [72]. LPAM700 is more hydrophilic than LPAM100

due to more polyacrylamide and leads to larger droplet sizes. At 1 mg/mL, LPAM100 might exhibit smaller droplet sizes as there are more particles in solution compared to the emulsions containing higher molecular weight LPAM700, as an inverse correlation between particle concentration and droplet size for Pickering emulsions has been established [77]. It has also been reported in the literature, that some emulsions have shown increasing droplet size with increasing dispersed phase volume fraction [70], [75], [79]. For PGLN systems, as the volume fraction of cyclohexane increases, there are not enough PGLNs to stabilize an increase in the interfacial area. Hence, droplet size increased to compensate for the relative lack of PGLNs available to adsorb to the interface.



Figure 5.3.3.4. Emulsion droplet size distributions as a function of intial cyclohexane volume fraction for LPAM100 (a) without salt, (b) with 1 mM NaCl, and (c) with 10 mM NaCl and LPAM700 (d) without salt, (e) with 1 mM NaCl and (f) with 10 mM NaCl



Figure 5.3.3.5. Emulsion droplets for (a) LPAM100 with 0.4 v/v initial cyclohexane and (b) LPAM700 with 0.5 v/v initial cyclohexane and 10 mM NaCl

The salt effects are somewhat anomalous considering the interfacial tension data. As seen from Figure 5.3.2.1, increasing the ionic strength results in a decrease in interfacial tension, allows more packing at the interface and hence with increased ionic strength the droplet size should decrease, which is not the case. Some studies have shown an increase in droplet size as the ionic strength increase, this suggests that the effects are system dependent [78], [79]. For PGLNs, it is possible that there is increased packing at the interface at higher ionic strength, but due to the increase in charge the electrical repulsion is screened which allows for coalescence. This effect may be particularly significant for LPAM700 with 10 mM salt. Also due to the increased hydrophilicity of LPAM700 relative to LPAM100, the lower energetic barrier to desorption may also contribute to increase droplet size in that a decrease in interfacial area may occur to compensate for the lack of flocs available in solution for droplet stabilization since it is a general rule that larger particles stabilize larger droplets [80]. However, more data is needed to confirm these hypotheses.

Interfacial surface concentration of PGLNs for each emulsion samples was calculated using equation 13 [72], [81].

$$\Gamma_{drop} = \frac{(c_0 - c)\phi_{0,aq}}{(\phi_{0,cyc} - \phi_{cyc}) \left(\frac{3\Sigma r_i^2}{\Sigma r_i^3}\right)}$$

(13)

where  $\Gamma_{drop}$  is the PGLN surface concentration on emulsion droplets,  $\Phi_{0,cyc}$  is the initial volume fraction of cyclohexane,  $\Phi_{cyc}$  is the volume of cyclohexane after emulsification, and the summation terms are over the radii,  $r_i$ , in the droplet size distribution. As shown in Figure 5.3.3.6, surface concentration increased with increasing ionic strength, which was expected. Also, the surface concentration between LPAM100 and LPAM700 was comparable, except for at 10 mM where the value of LPAM700 jumped significantly. This behavior supports the hypothesis of droplet coalescence. Using  $\Gamma_{drop}$ , the average area occupied per particle at the interface was calculated using equation 14.

$$A_{particle} = \frac{M}{\Gamma_{drop}N_A}$$

(14)

where M is the molecular weight of the PGLN and  $N_A$  is Avogadro's constant. LPAM100 and LPAM700 were estimated to have molecular weights of 39,216 g/mol and 145,836 g/mol respectively. Figure 5.3.3.7 displays the calculated areas and does not account for the error in estimating molecular weight. The area occupied per particle decreased with increasing ionic strength, which was expected based on electric double layer repulsion and graft collapse, and also further validates the interfacial tension lowering phenomena. LPAM700 had consistently greater areas, which is expected due to steric repulsive forces. A cross sectional area of 190 nm<sup>2</sup> was found for aggregates using the Langmuir-Blodgett film technique [58] and is similar to the calculated areas for 0 mM in Figure 5.3.3.7. In the presence of salt, the calculated areas are as small as 10 nm<sup>2</sup>, which suggests that PGLNs do not exist as aggregates on the interface.



Figure 5.3.3.6. Concentration of PGLNs on the surface of emulsion droplets for (a) LPAM100 and (b) LPAM700



Figure 5.3.3.7. Estimated area occupied per PGLN particle for (a) LPAM100 and (b) LPAM700

# 5.4 Conclusion

The extent of aggregation, interfacial tension lowering, volume fraction of emulsion formed, and emulsion droplet sizes have been shown to be strong functions of ionic strength and graft density. All the interactions can be ultimately explained in terms of the hydrophobic and hydrophilic interactions among lignin cores and polyacrylamide grafts.

Polymer-grafted lignin nanoparticles (PGLNs) represent a new class of bio surfactants with tunable amphiphilicity and hydrophobicity. PGLNs at only 0.1 wt.% were capable of producing Pickering emulsions composed of cyclohexane and water that were stable against coalescence for a period of months.

# 6. Importance of architecture for polymer-grafted lignin

# 6.1 Introduction

From previous work it has been demonstrated that LPAM and LPAA can act as surfactants and emulsifiers with tunable properties. The observed enhanced interfacial activity compared to kraft lignin itself is in part due to the native functions and the architecture. Both these samples have a well-grafted star like architecture, which was achieved using controlled radical polymerization. However, techniques like controlled radical polymerization are expensive and require stringent processing conditions. Hence, it is essential to understand how important a well-grafted architecture really is. It has been well documented in the literature that architecture plays an important role in the improvement of surfactant properties [28], [32]. Many studies have been done on surfactants synthesized using ATRP such as silica grafted with poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA), to show improvement in not only interfacial activity but also emulsifying capability compared to the polymer or bare particle itself [32]. However, for a disorganized and heterogeneous structure such as lignin, it is important to understand how precise grafting off a functional group using RAFT compares to no control over architecture at all and if the same surfactant properties can be achieved. This is important because native lignin has high interfacial activity and it is possible that control over architecture would have no added benefit compared to a nano-cross linked aggregate synthesized with free radical polymerization (FRP). In order to examine how this change in architecture would affect the surfactant properties a head to head comparison of a polymer-grafted lignin synthesized using RAFT and FRP was performed.

# 6.2 Experimental

Two different types of polymer-grafted lignin were synthesized, one using RAFT and the other using FRP. The synthesis scheme and conditions for both products is shown in Section 2.1 and 2.2 respectively. The particle size for each sample was measured using DLS to understand the nature of the species in solution. The static and dynamic surface tension along with ellipsometry was measured for each sample at the air-water interface at a range of concentrations.

# 6.3 Results

The RAFT product was expected to exist as a single species in solution, due to the polyacrylamide grafts on the lignin core. These grafts were hypothesized to provide steric repulsion and subsequently prevent aggregation. This was confirmed through experiments discussed in Section 4.3. Conversely, the FRP product was expected to exist as a nano-crosslinked aggregate comprised of a cluster of lignin particles with the polyacrylamide attached to all the particles. A schematic of both of the products is shown in Figure 6.3.1. The presence of these particles as a single species or aggregate was confirmed using dynamic light scattering and is shown in Figure 6.3.2. The RAFT product had an average diameter of about 20 nm, with a larger peak past 100 nm, suggesting a slightly flocculated structure for some of the species. The FRP product had an average diameter of 100 nm, which shows that there is no single species in solution unlike the RAFT product. The diameter of lignin particle in DMF has been recorded to be around 10 nm, this suggests that the FRP product has a cluster of lignin particles [60]. The FRP product had polyacrylamide randomly woven through clusters of lignin clusters, as it was fairly water-soluble. If the polyacrylamide were grafted on every individual particle the sample would have been completely water-soluble like the LPAM-2-100 synthesized using RAFT. This confirms that a polymer corona, or control over architecture is needed to maximize repulsion between particles to promote good dispersion in solution.



Figure 6.3.1. Schematic of (a) LPAM-2-100 (RAFT) and (b) LPAM100 (FRP)



Figure 6.3.2. Hydrodynamic diameter of the RAFT and FRP product

The surfactant properties of both FRP and RAFT were measured to understand how architecture affected the orientation and activity at an interface. Static and dynamic surface tension was measured for both samples at the air-water interface shown in Figure 6.3.3 and 6.3.4 respectively. The static surface tension of RAFT and GM was compared to that of kraft lignin in solution. Kraft lignin has minimal surface activity, as the surface tension drops by 4 dynes/cm over two orders of concentration with the lack of a well-defined critical micelle/aggregation concentration. RAFT product had a well-defined critical aggregation concentration close to 0.05 mg/mL. The evidence of a clearly defined CAC is important because it suggests the formation of aggregates and display of amphiphilic behavior. In the case of polymer-grafted lignin this suggests shielding of the hydrophobic core by the polymer corona. CAC/CMC is commonly used to characterize different surfactants, as past this concentration there is no significant change in surface tension. There was a surface tension drop by 8 dynes/cm over the two orders of magnitude. For the FRP sample, there is an evidence of CAC at 0.05 mg/mL, however the surface activity is much lower than the RAFT sample. The drop at CAC is close to 1 dynes/cm, which is marginal. This suggests there is some form of aggregation happening to shield the lignin core, but not as effectively.

A similar trend was noticed from the dynamic surface tension data, as the FRP sample stabilizes quicker than the RAFT product. The slopes for both the diffusion from bulk solution and steric rearrangement regime are shown below in Table 6.3.1. The FRP sample has a higher

slope for the diffusion from the bulk solution, which can possibly be attributed to the larger hydrodynamic diameter of the particles as this would lead to repulsion between the particles floating in solution and forcing them to the interface. As mentioned previously the kraft lignin core without any grafting is interfacially active. However, this does not explain why the FRP sample has double the slope of the RAFT sample. The difference in slope can possibly be attributed to the coverage of the lignin core. By grafting polymers using FRP, the lignin core is intermittently covered which would result in a lower coverage of the lignin core. In comparison, by grafting polymers using RAFT, which has a well-defined architecture, it would result in a higher coverage leading to lower interfacial activity during the bulk diffusion regime compared to the FRP sample. For the rearrangement slope regime, the opposite trend was observed. There was a six times increase in the rearrangement slope for the RAFT sample compared to the FRP. This was expected, as the RAFT samples are more interfacially active as seen from the dynamic surface tension and has a smaller particle size that helps it pack the interface more effectively. It is important to note that the surface tension for the RAFT sample continues to decrease up to 10000 sec whereas the FRP sample stabilizes comparatively early on at 1000 sec. The complete dynamic surface tension curve for the RAFT sample is shown in Figure 4.3.2 by the LPAM-2-100 sample. The continuous decrease in surface tension suggests that the RAFT sample continues to rearrange and pack the interface and confirms the significant drop observed in the static surface tension data. As shown in Figure 6.3.4, the surface tension dependence over time for the FRP product was not as clean as the RAFT one, this was due to the large amount of aggregated species attaching to the interface resulting in varying calculated surface tension values throughout the measurement. During the RAFT measurements, there were no such aggregated species. Also the drop in static surface tension noted for both samples was confirmed by dynamic surface tension measurements when allowed to run for longer periods of time.



Figure 6.3.3. Static surface tension of the RAFT and FRP product at the air-water interface



Figure 6.3.4. Dynamic surface tension measured using a microtensiometer for lignin samples at a concentration of 1 mg/mL.

Table 6.3.1. Slope for the bulk diffusion and steric rearrangement regime for dynamic surface tension data

Sample	Bulk diffusion regime	Rearrangement regime slope
	slope (dynes/cm-s)	(dynes/cm-s)
RAFT	-0.0048	-0.0012
FRP	-0.0079	-0.0002

In order to understand more about how the architecture is affecting interface packing, ellipsometry was performed on both samples and the results are shown in Table 6.3.2. FRP had interface thickness of 5.34 nm compared to RAFT which has a value of 3.60 nm. The FRP product is a cross-linked aggregate structure that has a diameter five times larger than the RAFT product. As a result of the significant larger diameter the FRP product is expected to have a larger interface thickness, however this does not suggest that it packs the interface more effectively. The surface excess concentration highlights the interfacial packing of both samples. The RAFT sample  $(3.12 \text{ mg/m}^2)$  has a higher surface excess concentration compared to the FRP sample (2.99  $mg/m^2$ ), which suggests that it is packing the air-water interface more effectively. It is possible that for the RAFT product the polymer corona shields the lignin core, and hence the surface charge and also results in enhanced steric interaction, which allows the particle to pack the interface more effectively. Whereas, for the FRP product, the lignin core is not as effective in shielding and may result in further aggregation between particles and hence the particles cannot effectively pack the interface. A schematic for the proposed mechanism of how both the RAFT and FRP samples pack the interface is shown below in Figure 6.3.5. Previous literature studies have shown that the efficient and dense packing of the interface is responsible for increased surface activity in many other systems [32].

Table 6.3.2. Ellipsometry data for lignin samples at 1 mg/	mL
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Sample	Thickness (nm)	Surface Excess (mg/m <sup>2</sup> )
RAFT	$3.60 \pm 0.715$	$3.12 \pm 0.235$
FRP	$5.34 \pm 0.670$	$2.99 \pm 0.058$



Figure 6.3.5. Schematic of (a) FRP and (b) RAFT at air-water interface

# 6.4 Conclusion

Previous experiments have confirmed that the lignin core is interfacially active. The grafting of a polymer from the lignin core results in typical "surfactant-like" properties such as the presence of a CAC or CMC. A specific architecture is needed to enhance the surface activity, as the nano-cross-linked aggregates provided minimal improvement over kraft lignin itself compared to the sample synthesized using RAFT. This can be explained due to the steric repulsion provided by the polymer corona around the lignin core for the RAFT sample. Other types of polymers and lignin should also be explored to improve the surfactant activity while maintaining the "grafting-from" architecture.

# 7. Surfactant properties of PEGylated lignin

# 7.1 Introduction

From the previous experiments it is clear that a well-defined "grafting-from" architecture is needed for good surface activity. Polyacrylamide and poly(acrylic acid) were used as the grafts due to their hydrophilic nature. Both these polymers are also used in numerous surfactant applications such as enhanced oil recovery, and as a dispersant for proteins and nucleic acids. There are many other hydrophilic polymers that can be used instead of polyacrylamide or poly(acrylic acid) such as polyethylene glycol. Polyethylene glycol (PEG) is a flexible, water-soluble polymer with low toxicity. It is commonly used in dispersive applications for personal hygiene. PEG however is known to have limited surfactant application but increased hydrophilicity [35]. Also PEG can be attached to the lignin core without the used of any type of control radical polymerization technique while maintaining the star-like architecture. It would be interesting to see how much of an effect the grafted polymer has on the surfactant properties.

For all the above experiments only kraft lignin has been, but there is also another type of lignin known as lignosulfonates (Section 1.4.1). Lignosulfonates have a higher hydrophilic character than kraft lignin due to the added sulfonate groups. They are commonly used for dispersive application due to the added electrostatic repulsion provided by the sulfonate groups. Both kraft lignin and lignosulfonate will be grafted from PEG while maintaining the architecture and the surfactant and emulsifying properties will be measured.

# 7.2 Experimental

Polymer grafted kraft lignin and lignosulfonate were prepared using the PEGylation method, which is described in Section 2.3. The size of both products was verified using DLS. Surfactant properties were measured using static surface tension at the air-water interface and cyclohexane-water interface and ellipsometry. Emulsifying properties were examined by making cyclohexane and water emulsions with PEGylated lignin. The droplet size and height of the emulsions were measured as an indication of stability.

# 7.3 Results

In order to determine the effect of PEGylation on lignin behavior at air-water interfaces, the static surface tension was measured with the results shown in Figure 7.3.1. Due to kraft lignin's hydrophobic nature, larger surface excess was expected from the PEGylated kraft lignins (KLPEG) than the PEGylated lignosulfonates (LSPEG). It was hypothesized that the kraft lignin core would drive the species to the surface while the lignosulfonates, being hydrophilic, should partition more into the bulk aqueous phase and therefore be less surface active. Previous studies have shown that between lignins with comparable numbers of carboxylate or sulfonate groups that those with sulfonate groups have less surface activity, which supports this hypothesis [82]. This led to the expectation that the PEGylated kraft lignins would have a stronger effect on surface tension than the lignosulfonates, which is what is observed.



Figure 7.3.1. Static surface tension data for (a) KLPEG and (b) LSPEG

PEGylated kraft lignin had a lowest surface tension of 51-57 dynes/cm at 10 mg/mL compared to 54-63 dynes/cm of PEGylated lignosulfonates. It is also interesting to note that there was no clear CAC/CMC observed for the PEGylated lignosulfonates. However, the PEGylated kraft lignin had a CAC around 0.1 mg/mL. The surface tension values for both KLPEG and LSPEG were comparable or lower than that of LPAM. Similar to the results presented here previous studies have shown that lignosulfonates reduce surface tension but do not exhibit a critical micelle concentration (CMC) inherent to traditional surfactants [83]. For the PEGylated lignin samples, based on trends in anionic and non-ionic surfactant trends, a decrease in surface activity upon the addition of longer PEG chains was expected, yet the data show that while these samples

reduce surface tension, surprisingly the two sets of PEGylated lignins exhibited only modest reductions in surface tension and performed similarly with no strong differences between the different lignin cores or the varying PEG chain lengths.

The surface tension data presented above suggest that the PEGylated samples irrespective of graft length or lignin core show interfacial activity. To further understand how each of these species are organized at the air-water interface, ellipsometry was performed and the results are shown in Table 7.3.1. These results provided insight into the surfactant monolayer thickness and the surface excess concentration at the air-water interface. The adsorption behavior of the samples onto the interface can also be correlated to the measured surface tension using the Gibbs adsorption equation for an electrolyte surfactant described above in equation 11.

Sample	Thickness (nm)	Surface Excess (mg/m <sup>2</sup> )
KLPEG 900	$3.84 \pm 0.725$	$3.33 \pm 0.125$
KLPEG 2000	$4.86 \pm 0.645$	$4.21 \pm 0.056$
KLPEG 5000	$2.51 \pm 1.33$	$2.61 \pm 0.135$
LS	$1.88 \pm 0.678$	$1.22 \pm 0.055$
LSPEG 900	$2.4 \pm 0.1$	$2.09 \pm 0.01$
LSPEG 2000	$1.45 \pm 0.07$	$1.26 \pm 0.01$
LSPEG 5000	$1.50 \pm 0.08$	$1.22 \pm 0.08$

Table 7.3.1. Ellipsometry data for PEGylated lignin samples at 1 mg/mL

The PEGylated kraft lignin samples all exhibited a larger surface excess concentration than the lignosulfonate samples, aligning with the initial hypothesis that the hydrophobic nature of the kraft lignin core drives the particle to the surface more so than the hydrophilic lignosulfonate core. The PEG chain length also appears to affect the packing of the PEGylated lignins at the surface, with the lignosulfonate samples showing a significant decrease in the surface excess concentration between the shorter PEG 900 chain and the longer PEG 2000 and PEG 5000 chains. This may be attributed to the addition of the longer PEG chains increasing the hydrophilicity of the surfactant thereby weakening the effect of the aromatic groups in the lignosulfonate core that could drive the surfactant to the air-water interface. In the kraft lignin samples, the surface excess and thickness increases between the 900 and 2000 graft lengths but then decreased with the 5000 graft. It is hypothesized that this may be due to the PEG chain being fully extended into the solution with the short chain lengths and then collapsing in on the
core with the 5000 Mn chain length. Assuming the PEG chain exists as an expanded random coil, the radius of gyration in water, a good solvent for PEG, should measure to a PEG chain length of 1.9 nm, 3.2 nm, and 5.9 nm for the 900, 2000, 5000 Mn lengths respectively. From the NMR measurements it was found that we have about 2 grafts per lignin core and DLS measurements show that we have kraft lignin particles of roughly 3-15 nm and lignosulfonate particles of roughly 5-10 nm. Therefore, for the kraft lignin only the 5000 Mn graft length will be able to fold back and shield the core, which would result in a lower thickness as seen in Table 7.3.1. This shielding affect may also be at work with the lignosulfonates but due to the lignosulfonates smaller particle size the affect may be observed with shorter molecular weight PEG chains.



Figure 7.3.2. Interfacial tension at the cyclohexane-water interface for (a) KLPEG and (b) LSPEG

To understand further the effects that lignin core and PEGylation have at the oil-water interface, interfacial tension measurements at the cyclohexane-water interface were performed. The interfacial tension at the bare cyclohexane-water interface is 50 dynes/cm and the data shown in Figure 7.3.2 demonstrate that both the PEGylated kraft lignin and lignosulfonate exhibited significantly greater activity at the oil-water interface than at the air-water interface [84]. The interfacial tension values exhibit a distinct critical micelle concentration (CMC) in the PEGylated kraft lignins near 0.1 mg/mL while the lignosulfonate samples do not appear to reach a CMC but do show PEG chain-length dependence on interfacial tension below 5 dynes/cm exhibiting the ability to reduce cyclohexane-water interfacial tension to low values comparable

to commercial surfactants and significantly lower than LPAM. The lignosulfonate samples reduced the interfacial tension significantly as well with the least active LSPEG 5000 reducing the interfacial tension by more than half at 10 mg/mL. PEGylated kraft lignins displayed greater interfacial activity than PEGylated lignosulfonates, which is consistent with the initial hypothesis, that the chemical characteristics of the core are significant at these interfaces. Unlike the surface tension measurements, the interfacial tension measurements show that the number of ethylene oxide units of the PEG plays a significant role on the interfacial tension reduction ability of the polymer at the cyclohexane-water interface. From an HLB perspective this trend may arise due to larger length PEGs increasing the solubility of the PEGylated lignin, therefore drawing more of the PEGylated lignin into the bulk solution and away from the surface. While this explanation fits the interfacial tension data it does not account for the lack of this trend in the surface tension measurements. Another possible explanation is that both cores due to the aromatic groups have some favorable interactions with the oil phase and that there are stronger interactions with the aqueous phase for the larger PEG chains leading to fewer particles at the surface and thereby less interfacial activity. A noticeable difference between the kraft lignin core samples and lignosulfonate core samples at the cyclohexane-water interface led to the conclusion that the functional groups on the core can have significant impact at fluid-fluid interfaces. With the lignin cores containing both phenol and carboxylate/sulfonate moieties, it was anticipated that they would exhibit both nonionic and anionic character due to functional groups present.

In order to determine the emulsion-forming characteristics of PEGylated lignins, emulsions were tested by maintaining a constant 1 mg/mL aqueous concentration of PEGylated lignin while varying the initial cyclohexane-water volume fraction and the results are shown in Figure 7.3.3 and 7.3.4. The emulsions presented in this paper were all oil-in-water emulsions as expected by Bancroft's rule described in equation 10. Both the lignin core and the length of the PEG chain appeared to determine the amount of emulsion formed. Interestingly, the largest emulsion phase was observed at a 70/30 cyclohexane-water ratio. While the samples with the kraft lignin core exhibited on average larger maximum emulsion formation, at ratios with water composition above the optimal ratio lignosulfonates exhibited larger emulsion formation with the exception of KLPEG 900. The KLPEG 900 may form larger emulsions than the other samples due to the short PEG chain length adding sufficient aqueous solubility to the core without shielding the core from interacting with the hydrophobic phase. The lignosulfonate sample had similar emulsion-formation characteristics to PEGylated lignosulfonate having the two longer chain lengths while the lignosulfonate with the short PEG has the lowest emulsion formation. This runs counter to the lignosulfonate interfacial tension results and may indicate that another factor than HLB may need to be reconsidered for lignosulfonate-containing emulsion systems.



Figure 7.3.3. Cyclohexane-water emulsions with (a) KLPEG 900 and (b) LSPEG 900. Vials are aligned from initial volume fraction of 10% water (left) to 90% water (right)



Figure 7.3.4. Volume fraction of (a) KLPEG and (b) LSPEG emulsion in cyclohexane-water mixtures

The partition coefficient of lignin in the emulsion phases was determined by analyzing via UVvis spectroscopy the change in concentration of the lignin in the aqueous phase and is shown in Figure 7.3.5. The UV/vis results within each samples trend together with the amount of emulsion formed indicated that to form larger amounts of emulsions, not only is the cyclohexane-water ratio important but that the amount of lignin available is a factor as well. Among the kraft lignin samples, the KLPEG 900 required the least amount of lignin to form emulsions but formed the largest emulsions of the kraft lignin samples across most cyclohexane-water ratios studied. This supports the interfacial tension results where the KLPEG 900 was the most active at reducing interfacial tension.



Figure 7.3.5. Percent of (a) KLPEG and (b) LS and LSPEG in the emulsion phase for cyclohexane-water emulsions



Figure 7.3.6. Droplet size distribution at 1mg/mL for (a) KLPEG and (b) LSPEG emulsions

Droplet size in the emulsion phase is a strong indicator of emulsion stability with droplet radii less than 50  $\mu$ m indicating thermodynamically stable micro-emulsions and radii less than 100  $\mu$ m indicating kinetically stable nano-emulsions [85]. Figure 7.3.6 shows the droplet size distribution in each of the reported samples. Droplet size was found to be dependent on both lignin core and ethoxylate chain length. Kraft lignin samples exhibited average droplet radii ranging from 30-50  $\mu$  m and lignosulfonate samples between 35-55  $\mu$  m. However, due to the broad distribution it is difficult to suggest a significant difference between KLPEG and LSPEG samples. The bubble size does not seem to be correlated either to the amount of emulsion, interfacial tension or sample which is unlike the LPAM100 and LPAM700 sample described in Section 5.3.3. These radii suggest that stable emulsions were produced and no visible change in the emulsions were observed after storage for months. The stability of the emulsions primarily suggests that PEG is responsible for the uniform droplet size as this was also noticed for polyacrylamide or poly(acrylic acid). Kraft lignin samples exhibit narrower distributions and smaller droplet radii indicating that the emulsions were more stable than the lignosulfonate samples. This aligns with interfacial tension data that suggest that the kraft lignin samples had stronger interactions between both fluid phases in a cyclohexane-water system. In addition, larger ethoxylate chain lengths correspond to smaller droplet radii and narrower distributions, which may arise due to stronger steric interactions of the particle with the aqueous phase allowing the droplet to curve more and prevent creaming and coalescence of the bubble irrespective of graft length.

At the air-water interface it was found using ellipsometry that the PEGylated kraft lignin samples exhibited larger surface excess concentrations than the lignosulfonate samples but this did not correlate directly with the static surface tension, where no significant differences in surface tension between the PEGylated samples were observed. In this it is concluded that these lignin particles do not necessarily follow the expected results from the Gibbs adsorption equation, which predicts that the surface tension decreases as the surface excess concentration increases. To explain these observations, it is noted that lignins exhibit a strong tendency to aggregate and form associated complexes, and the anomalous concentration dependences may be due to the aggregation of lignin particles that change both the specific surface area and the partitioning to interfaces [86].

In the measurements at cyclohexane-water interfaces, the large decreases in interfacial tension are attributed to specific interactions with both fluid phases. Since lignin can be considered a disorganized nanoparticle, both hydrophilic and hydrophobic domains are presented to the cyclohexane and water phases. Assuming similar concentrations of hydrophobic aromatic groups in kraft lignin and lignosulfonates, sulfonates have a strong solubilizing effects in water but also a strong enthalpic penalty in their interactions with cyclohexane. In contrast, carboxylate groups in kraft lignin may not solubilize in water as effectively but also do not have such a

strong enthalpic penalty in their interactions with cyclohexane, and the impressive reductions in interfacial tension by KLPEG are attributed to this balance.

Building upon the kraft lignin interfacial results, it is seen that the kraft lignin with the shorter graph length was the most active in forming emulsions while the longer graft lengths showed diminished capacity for this. The kraft lignin emulsion heights along with the UV-vis data on lignin concentration in the emulsions correlate with the interfacial tension data that indicated that KLPEG 900 was the most active at the oil-water interface. The results on lignosulfonate emulsions run counter to both the interfacial tension results and what would be expected when approaching the data from an HLB perspective indicating once again that HLB may not be suitable for describing lignin surfactant activity. As emulsifiers, these PEGylated lignins show large emulsion fractions and the small droplet sizes consistent with stable emulsion that persist without visible differences for greater than 4 months.

#### 7.4 Conclusion

By preserving a similar architecture to the RAFT product, enhanced surfactant behavior was observed for both KLPEG and LSPEG samples. PEGylated lignins imparted modest reductions in aqueous surface tension but had significantly stronger activities at oil-water interfaces, suggesting these may have potential as an emulsifier. However, increasing the PEG molecular weight did not result in changes in activities expected based on traditional surfactant models, suggesting that in designing surfactants based on PEGylated lignin, both molecular architecture and its effects on aggregation must be considered. The KLPEG samples showed enhanced interfacial activity at the air-water and cyclohexane-water interface than the LSPEG samples. The LSPEG samples showed a lack of a critical concentration for most surface tension experiments. The data suggests that PEG graft irrespective of length provides steric interaction to stabilize the system and prevents coalescence.

#### 8. Model systems for cement suspensions – Magnesium oxide

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#### 8.1 Introduction

From the previous experiments performed, polymer-grafted lignin has shown to be interfacially active at the air-liquid and liquid-liquid interface. In order to assess the lignopolymer's interfacial activity at the solid-liquid interface, portland cement was chosen. For a solid-liquid system, interfacial activity can be measured by how well dispersed the system is. Portland cement is a complex system with non-uniform particle size distributions that continues reacting, hardening, and releasing ions, making it difficult to perform analysis on the composite. Magnesium oxide (MgO) suspensions have gained more popularity as a model system for portland cement due to their non-reactive and uniform nature. MgO based systems allow the particle and polymer (superplasticizer) interactions to be studied without the interference of the hydration reactions. It is essential to point out that MgO systems can only be used to look at the initial flow behavior. The hydration reactions that take place in portland cement drastically affect the superplasticizer efficiency. Such model cementitious systems can be used effectively to delineate the flow characteristics of cement pastes during pouring and placement.

To assess the polymer's efficiency in improving cement workability, empirical based tests such as slump cones are conducted on site [87], [88]. Roussel et al. have used slump cone results to model the rheology of the paste but a thorough understanding of the effects of the polymer on various stages of cement mixing, pouring, and placement cannot be deduced [34]. To understand the connections between macroscopic flow, polymer architecture, and polymer interactions a more detailed analysis is required. Rheometry analysis with shear ramp rates to assess the pouring and placement and creep tests for pumping provide insight into the polymer-particle flow properties, which are unavailable from slump tests.

#### 8.2 Experimental

Magnesium oxide was used with an average particle size 3.8  $\mu$  m, with 84.1% of the particles with size less than 10  $\mu$  m and 0.41% less than 1  $\mu$  m in diameter [89]. Representative XRD traces of MgO can be found in Appendix B. To broadly understand the effects of grafting density and degree of polymerization of hydrophilic polymers onto kraft lignin four different samples were tested as shown in Table 8.2.1 along with a commercial polycarboxylate polymer. Two different polymer concentrations were tested; 0.25 mg/mL and 2.7 mg/mL. The higher loading of polymer refers to the recommended concentration provided by the manufacturers of the commercial polycarboxylate. A 0.42 water:MgO weight ratio was used for the experiments to replicate a commonly used particle loading in portland cement. The magnesium oxide was slowly added to the polymer solution with constant agitation [90]. Two different rheology tests were performed to evaluate MgO suspensions performance. The viscosity was measured over ramped shear rate to simulate behavior during mixing of the cement paste. Creep tests were also performed, where the shear rate was measured as a function of time at a constant applied stress. These tests were used to simulate the behavior when cement paste is poured.

Sample	Grafted polymer	Number of graft	Degree of Polymerization
LPAA-2-100	PAA	2	100
LPAM-2-100	PAM	2	100
LPAM-17-50	PAM	17	50
LPAM-17-100	PAM	17	100

Table 8.2.1. Molecular characteristics of different kraft lignopolymers tested

# 8.3 Results

# 8.3.1 MgO suspensions containing 0.25 mg/mL plasticizer

The suspensions with 0.25 mg/mL polymer had peak viscosities that were an order of magnitude lower than the control MgO sample as seen in Figure 8.3.1.1. LPAM samples irrespective of grafting density or degree of polymerization had the lowest viscosity compared to LPAA, kraft lignin, or PCE. From Figure 8.3.1.1 (a), the LPAM samples had the lowest viscosity when the

shear rate was ramped. LPAM-17-100 had the lowest value out of all the LPAM samples. For creep measurements, PCE had the lowest shear rate at longer time points, followed by LPAM-17-100, then LPAM-2-100, and finally LPAM-17-50. LPAM-17-50 maintained the greatest observed shear rate over intermediate shear rates. The magnitude of shear rates demonstrates the ease of flow under applied shear stress. It must be noted that the rheology of these pastes is very dynamic. In both experiments, LPAA was comparable to the kraft lignin. This shows that the LPAM samples seemed to be a more effective dispersant at the 0.25 mg/mL concentration and short time scales.



Figure 8.3.1.1. (a) Viscosity curves for the suspensions and (b) creep tests at 5 Pa with 0.25 mg/mL lignopolymer suspensions for the control (black), LPAA-2-100 (blue), kraft lignin (green), PCE (grey), LPAM-17-50 (pink), LPAM-2-100 (red), and LPAM-17-100 (dark red)

The viscosity reduction in LPAM samples can be explained by the extension of the PAM chains into the water while the lignin core is electrostatically attracted to the MgO particle. The minimal improvement in dispersion of LPAA samples may be attributed to the deprotonation of the carboxylic acid groups under basic conditions. Kraft lignin and LPAA had a pH of 3.0 and 3.45 respectively, making them the most acidic samples. The remaining polymers were either neutral or slightly acidic. When the MgO suspension was added, all the polymer solutions turned basic. However, LPAA still maintained the lowest pH compared to the LPAM samples, suggesting the carboxylic acid groups were deprotonated and stick to the lignin core [91], [92]. The deprotonation of the carboxylic acid groups has been previously reported in literature and was further confirmed with zeta potential measurements as shown in Table 8.3.1.1. The magnitude of

the zeta potential for MgO and LPAM samples were less than 12 mV, whereas PCE, kraft lignin and LPAA had higher magnitudes. The greatest difference in zeta potential was observed with the LPAA sample with the addition of MgO, which can be attributed to the anionic charges along the deprotonated side chains as shown in Table 8.3.1.1. The lower zeta magnitude of the LPAM samples is due to the anionic charged lignin core with the uncharged PAM side chains, which effectively screen the core charge. This also corroborates that PAA chains stick to the MgO core, whereas the PAM chains extend into the aqueous environment. However, zeta potential alone cannot be used to predict aggregation due to the steric interactions in the system. The conformation of these PAA and PAM side chains leads to different levels of aggregation directly impacting their viscosity reducing abilities. Based on the zeta potential and pH values, the proposed LPAM and LPAA structures are shown in Figure 8.3.1.2.

Sample	pH without	pH with MgO	Zeta potential	Zeta potential
	MgO		without MgO	with MgO
			(mV)	(mV)
MgO	-	10.6	-	-10.8
PCE	6.85	11.1	-28.1	-17.8
Kraft Lignin	3.00	10.3	-24.2	-20.1
LPAA-2-100	3.45	10.4	-14.9	-26.1
LPAM-2-100	6.63	10.6	-7.6	-8.2
LPAM-17-50	7.19	10.4	-8.3	-11.0
LPAM-17-100	7.03	10.9	-6.0	-5.7

Table 8.3.1.1. pH and zeta potential of samples with and without MgO



Figure 8.3.1.2. Schematic of the proposed adsorption conformation of LPAM and LPAA on MgO particles

To further understand the viscosity reducing abilities of LPAM, sedimentation and adsorption studies were conducted. For the sedimentation studies, the suspensions were allowed to settle over time. The rate of sedimentation, sediment volume fraction, and viscosity of the centrifuged water were measured to provide insight into the particle-particle interaction. The data is shown for all the polymers tested in Table 8.3.1.2. At 0.25 mg/mL, the LPAM samples showed the fastest sedimentation followed by the remaining samples. LPAM-17-100 reached its final sedimented volume fraction after 3 h, whereas LPAM-17-50 and LPAM 2-100 took 33 h. PCE and LPAA-2-100 took the longest time to sediment out. The extremely swift sedimentation of the LPAM samples suggested minimal interference between particles. The viscosities of the centrifuged water from each sample suggested the same.

In order to relate the viscosity of the centrifuged water to the particles settling, Stoke's law was used because the samples were larger than 1  $\mu$  m [93], [94]. The lowest viscosity was 0.011 Pa.s for LPAM-17-100 sample, suggesting that there is a very low concentration of non-adsorbed chains in the system. There was limited stabilized particle-particle interaction, which is why the sample had a very high rate of sedimentation. Large volume of non-adsorbed polymers tends to increase the viscosity of the supernatant resulting in long sedimentation times. LPAM-2-100 and LPAM-17-100 had the lowest supernatant viscosity had the highest adsorption to the MgO surface shown from the TOC data. Similar trends have been reported in literature for settling studies of comb polymers, where higher adsorption resulted in faster settling time due to the lack on non-adsorbed polymers in solution [95].

The TOC data provided further insight into the differences in adsorption of different polymers. It needs to be noted that TOC is a dynamic process as polymers are constantly adsorbing and desorbing from the surface. The TOC data was reported at steady-state levels of adsorbed polymers during the constant adsorption-desorption process. Theoretically, the polymer with the lowest centrifuged viscosity of the supernatant should have the highest adsorption, but this was not the case. The TOC data showed the following trend LPAM-17-100 > LPAM-2-100 > PCE > LPAA-2-100 > LPAM-17-50 > kraft lignin. LPAM-17-50 and kraft lignin do not follow the trend.

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For the 0.25 mg/mL concentration, out of all the LPAM polymers, LPAM-17-100 had the most effective dispersing capabilities. It had the lowest viscosity out of all the suspensions (Figure 8.3.1.1) and had the lowest magnitude of zeta potential (-6.0 mV and -5.7 mV with MgO). LPAM-17-100 has the most chains extending into the slipping plane and screening the negative charge of the lignin core. When compared to PCE, LPAM-17-100 had higher MW grafts, which resulted in higher adsorption to the surface. Many studies on PCE graft architecture have shown that decreasing side chain length increases the anionic charge density, which results in lower adsorption onto the particle surface [96]. This is exactly what was observed with the LPAA sample. Lower concentration, higher graft density and high molecular weight help reduce the viscosity of the system.

Table 8.3.1.2. Maximum sedimentation rates, and particle volume fraction at end of sedimentation tests along with the viscosity of supernatant

Sample	Maximum	Sediment	Viscosity of	TOC	Conc. of non-
	rate of	volume	centrifuged	Adsorption	adsorbed
	sedimentation	fraction	water at 1s <sup>-1</sup>	(%)	chains
	(mL/min)		(Pa.s)		(mg/mL)
Control	0.125	0.64	0.157	-	-
PCE	0.125	0.67	0.117	75.3	0.062
Kraft Lignin	0.33	0.65	0.128	8.4	0.23
LPAA-2-100	0.125	0.73	0.186	32.6	0.17
LPAM-2-100	0.50	0.66	0.061	86.9	0.033
LPAM-17-50	0.25	0.64	0.086	27.3	0.182
LPAM-17-100	0.67	0.65	0.011	99.7	0.001

8.3.2 MgO suspensions containing 2.7 mg/mL plasticizer

The rheometry results were very different for the systems at a higher concentration dose. As seen in Figure 8.3.2.1 the PCE suspension had the lowest viscosity followed by LPAA-2-100 and LPAM-2-100. The remaining two samples had viscosities lower than the control. The trend is opposite to that observed at 0.25 mg/mL concentration, which indicates the importance of grafting density. The creep test data is shown in Figure 8.3.2.1. Lignopolymer suspensions in general had shear rates of 100-250 s<sup>-1</sup> greater than PCE, control and kraft lignin. This shows the ease of flow for LPAM solutions at 2.7 mg/mL.



Figure 8.3.2.1. (a) Viscosity curves for the suspensions and (b) creep tests at 5 Pa with 2.7 mg/mL lignopolymer suspensions for the control (black), LPAA-2-100 (blue), kraft lignin (green), PCE (grey), LPAM-17-50 (pink), LPAM-2-100 (red), and LPAM-17-100 (dark red)

Lignopolymers with two grafted chains are the second highest viscosity reducers after PCE. At lower concentrations (0.25 mg/mL) the PAM seemed to perform better than PAA grafts, however the opposite is seen at higher concentrations. This suggests that at higher concentrations the dynamics are different, and the graft density matters more than the grafted polymer itself. PCE which was the most effective at reducing viscosity at higher concentration has 15 grafts, which is an order of magnitude higher than 2. However, if more grafts meant more effective viscosity reduction LPAM-17-50 and LPAM-17-100 should have performed better. This suggests that at least for lignopolymers higher number of grafts does not result in effective viscosity reductions past a threshold concentration. Sedimentation experiments were performed to further understand the viscosity reduction mechanisms. Maximum rate of sedimentation data is shown in Table 8.3.2.1. LPAA-2-100 had the highest rate of sedimentation at 1.50 mL/min. LPAA-2-100 and LPAM-2-100 sedimented most rapidly out of all the other samples. This supports the finding that the most effective lignopolymer dispersants have quicker sedimentation rates. Such a low number of grafted side-chains has been previously associated with greater sedimentation and particle stability at higher concentrations [95]. Kraft lignin also supports this trend, as it had a very low level of sedimentation due to the increase in the viscosity of the supernatant probably due to aggregation of the non-adsorbed polymer.

Rheology and sedimentation data collected at 2.7 mg/mL shows that for lignopolymers lower grafts are superior viscosity modifiers. Viscosity reduction can also be explained based on adsorption strength of the lignopolymer to the MgO particle. LPAA-2-100 and LPAM-2-100 were the most effective at reducing viscosity out of all the lignopolymers, which is due to the low number of grafts. The two anionic side chains for LPAA-2-100 contribute to a higher charge density, resulting in higher adsorption and superior viscosity modification. LPAM-2-100 also has two chains, but PAM grafts are neutral and detract less from the charge of the anionic lignin. It has been previously reported in literature that higher charge density results in higher adsorption especially for polycarboxylates [97]–[99].

PCE had the lowest viscosity of all the suspensions, which is explained in part by the TOC data. PCE had a 17% increase in adsorption from the lower to higher concentration and improved particle dispersion [100], [101]. Also PCE adsorbs in layers or aggregates onto surfaces which is why greater viscosity reduction occurred at 2.7 mg/mL [102], [103]. TOC adsorption data resulted in the following trend kraft lignin > PCE > LPAM-17-100 > LPAM-2-100 > LPAA-2-100. Kraft lignin had the highest adsorption (96.8 %) at 2.7 mg/mL but had the lowest adsorption (8.38%) at 0.25 mg/mL. The kraft lignin has a disorganized molecular structure and low molecular weight (~25,000 g/mol) which causes it not to adsorb at low concentrations [101]. Strong aggregation of kraft lignin could also explain the increased adsorption at higher concentrations.

Sample	Maximum	Sediment	Viscosity of	TOC	Conc. of non-
	rate of	volume	centrifuged	Adsorption	adsorbed
	sedimentation	fraction	water at 1s <sup>-1</sup>	(%)	chains
	(mL/min)		(Pa.s)		(mg/mL)
Control	0.125	0.64	0.157	-	-
PCE	0.125	0.68	0.064	91.9	0.219
Kraft Lignin	0.375	0.80	0.016	96.8	0.086
LPAA-2-100	1.50	0.70	0.062	54.3	1.23
LPAM-2-100	0.50	0.69	0.0173	82.7	0.47
LPAM-17-50	0.25	0.74	0.001	73.6	0.713
LPAM-17-100	0.50	0.77	0.002	88.3	0.316

Table 8.3.2.1. Maximum sedimentation rates, and particle volume fraction at end of sedimentation tests along with the viscosity of supernatant

#### 8.3.3 Particle interaction summary

Rheometry, sedimentation and other experiments conducted in this study of model systems are influenced by inter-particle interactions. Particle-particle interactions are dependent on a number of factors as seen in the results such as electrostatics, type of polymer chain and architecture. For lignopolymers concentration is also a factor, as higher concentration results in aggregation, which influences the inter-particle interaction significantly. The most effective way to reduce inter-particle interaction is using steric repulsion achieved by adding side chains to the polymer. The adsorbed polymer has side chains that repel other particles and hence stabilizing the system [21], [93], [104], [105]. This explains why despite the high adsorption of kraft lignin at 2.7 mg/mL it was ineffective in viscosity reduction. However, by increasing the side chain length there is a risk of the chain adsorbing to the particle itself [97].

Another major factor is the concentration of non-adsorbed polymers floating around in solution. These non-adsorbed polymers can result in concentration and in turn osmotic pressure gradients within the solution, which results in the expulsion of free, non-adsorbed chains and brings the particles closer together this is known as depletion flocculation [66], [106], [107]. In some cases, depletion flocculation can compete with steric effects especially when there is low adsorption of the polymer to the particle surface, which might have been the case for some of the lignopolymers at higher concentrations.

#### 8.4 Conclusions

Rheometry experiments with magnesium oxide suspensions are an analog of the flow behavior of different polymers in cement pastes [91], [96], [100], [108]. This study showed that PCE is quite effective as a viscosity reducing agent but only at higher concentrations. Lignopolymers can be used effectively as a replacement for PCE to produce similar viscosity reduction at concentration. Lignopolymers are significantly influenced by graft density and type of graft polymer depending on the concentration.

# **9.** Molecular architecture requirements for polymer grafted lignin superplasticizers *Published in Soft Matter, vol. 11, pp. 1-9, 2015.*

#### 9.1 Introduction

Superplasticizers are a class of high-performance anionic polymers used to inhibit aggregation in cement, creating a well-dispersed system [109]–[111]. These polymers modify the rheological properties and lower the water requirements. The leading commercial superplasticizer is a copolymer of acrylic acid and poly(ethylene glycol) (PEG) acrylate, known as polycarboxylate ether (PCE) [112]. It has an anionic backbone that adsorbs to cement-particle surfaces and the PEG side chains reduce aggregation through steric interactions at concentrations of 5 mg/mL.

Lignosulfonates on the other hand are commonly used as low cost/low-performance dispersants for hydraulic cement. They can reduce water requirements by 5-10% and use electrostatic interactions to inhibit aggregation [15]. Lignosulfonates have weaker interfacial activities compared to kraft lignin [8], [55], [113]. Various hybrids of lignin and hydrophilic polymers have been investigated in the literature to improve the plasticization properties of lignosulfonates. Only minor improvements in plasticization have been reported in literature as a result of the modification of lignosulfonates. The minor improvement in properties is attributed to nano cross-linked aggregates that are formed when lignin is reacted with other polymers, which are not as effective at adsorbing to the surface. Controlled radical polymerization can be used to synthesize discrete grafted architectures composed of lignin cores and synthetic polymer coronas that will have enhanced adsorption to the surface and, hence, improve the plasticization properties [60], [114]. LPAM synthesized using RAFT has shown to be surface active and performed well in model cementitious systems. A head-to-head comparison of how molecular architecture impacts the rheological properties, adsorption, and strength of cementitious systems would provide insight into their effectiveness as a superplasticizer. LPAM was compared against a lignin-polyacrylamide cross-linked aggregate, which was synthesized using free radical polymerization and PCE.

#### 9.2 Experimental

LPAM-2-100 and lignin-acrylamide copolymers were synthesized using the procedure previously described in Section 2.1.2. Individual mineral components of OPC were prepared using solid-state or sol-gel synthesis. Dicalcium silicate ( $C_2S$ ) was prepared using CaCO<sub>3</sub> and SiO<sub>2</sub> in stoichiometric amounts. The powder was ball milled for 24 h and then calcined at 1500 °C for 24 h. Tricalcium silicate (C<sub>3</sub>S) were prepared using sol-gel synthesis, 0.5 mol of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> was mixed with 0.05 wt.% of nitric acid as a catalyst that was added to 200 mL of deionized water. Subsequently, 1.5 mol of Ca(NO<sub>3</sub>)<sub>2</sub>.4H2O was added while stirring. The solution was then maintained at 60 °C until gelation occurred and then was dried at 120 °C for 4 h. The final product was then calcined at 1450 °C for 8 h [115]. Tetracalcium aluminoferrite (C<sub>4</sub>AF) powders were synthesized by adding CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> in stoichiometric amounts. The powder was ball milled for 24 h and then calcined at 1350 °C for 24 h. Tricalcium aluminate  $(C_3A)$  powders were synthesized using the modified Pechini method using  $Ca(NO_3)_2.4H_2O$  and  $(Al(NO_3)_3.9H_2O)$ , which were dissolved in 45 mL of ethanol to obtain a CaO:Al<sub>2</sub>O<sub>3</sub> molar ratio of 3:1. Citric acid was added such that molar ratio of citric acid:total cations was 1:1. The mixture was stirred until a clear solution was obtained and then ethylene glycol was added to obtain a molar ratio of ethylene glycol:citric acid of 2:1. The solution was stirred at 80 °C for 24 h, until the formation of a viscous gel. The gel was then thermally treated at 150 °C for 24 h and formed a brown resin-type precursor. The precursor was calcined at 600 °C for 2 h,1300 °C for 4 h, and then 1350 °C for 1 h [116]. The final products for each phase were characterized using X-Ray diffraction (X'Pert Pro MPD) using a continuous scan from 5-65° at a scan speed of 0.75°/min. Representative XRD plots can be found in Appendix B. The portland cement used for slump tests was characterized using Rietveld analysis and can be found in Appendix B.

# 9.3 Results

# 9.3.1 Solution Properties

PCE, LPAM-2-100 (RAFT) and lignin-grafted polyacrylamide synthesized using free radical polymerization (FRP, GM) aqueous solutions were characterized using dynamic light scattering (DLS) and the representative traces are shown in Figure 9.3.1.1. The LPAM-2-100 (RAFT) had an average diameter of 35.9 nm and a zeta potential of -36.2 mV. The FRP-lignin-PAM had a diameter of 101.6 nm and a zeta potential of -39.2 mV. The diameter of the FRP-lignin-PAM suggests the formation of nano-cross linked aggregates. The PCE had a diameter of 4.1 nm and a zeta potential of -48.9 mV similar to previously reported values [89].



Figure 9.3.1.1. (a) Polymer size characterization using DLS at 0.25 mg/mL, (b) picture of RAFT, FRP and PCE solutions (left to right), (c) zeta potential and average diameter and (d) schematic of RAFT (left) and FRP (right) products.

# 9.3.2 Cement Paste Rheology

To investigate how the architecture of the polymer would impact rheology of the cement-paste, slump tests and rheometric experiments were conducted. The slump tests are the most common and economical way of measuring hydraulic cement rheology [117]. For the slump tests, the cement paste was mixed at a 0.42 w/c ratio and the two orthogonal diameters and height

difference were recorded. Even though only two variables were recorded, slump tests have very good reproducibility under controlled conditions. The slump spread was measured as a function of superplasticizer concentration and the data is shown in Figure 9.3.2.1. The RAFT product followed a gradual linear increase in slump as the superplasticizer concentration increased. Whereas the FRP product (GM) seemed to show minor differences in slump and did not strongly depend on concentration of superplasticizer, which is similar to what has previously been reported in literature with lignin-polymer hybrids. The PCE curve had steep increases in slump spread at 0.175 wt. %, close to the recommended dosage level by the supplier. At 0.025 wt. %, the RAFT product has a slump spread greater than neat portland cement by 20-30 mm. The RAFT products also consistently had higher viscosity reduction than the GM product, suggesting that nano cross-linked aggregates forming in the GM product inhibit it from interacting with the cement particles and improve plasticization.



Figure 9.3.2.1. Slump spread for OPC as a function of superplasticizer concentration at a 0.42 w/c ratio

In slump tests, the cement paste flows until the yield stress exceeds the shear stress. Roussel et al. developed an analytical function to calculate the shear stress ( $\tau_0$ ) using inputs from a slump test. This analytical relationship ignores surface tension effects and an oblong geometry is assumed and given in equation 15, where  $\rho$  is the paste density, g is the gravitational constant, and V is the volume. Using this, the yield stress of OPC was calculated to be 236.3 ± 15.3 Pa and

at 2.7 mg/mL concentration RAFT was  $31.8 \pm 6.2$  Pa compared to  $20.6 \pm 5.4$  Pa for PCE. These values show that even small difference in slump spread result in significant decreases in yield stress.

$$\tau_0 = \frac{225\rho g V^2}{128\pi^2 R^5} \tag{15}$$

To further understand the rheological properties of how superplasticizers affect cement pastes, oscillatory rheometry experiments were performed. The experiments were designed to probe the viscous response of the cement pastes as the colloidal gel network ruptured under oscillatory strains. The viscoelastic response measured from the cement pastes is a function of the state of dispersion. The response is Newtonian at higher w/c and superplasticizer loading, otherwise thixotropic [5], [118], [119]. Figure 9.3.2.2 shows  $\eta$  ' for cement pastes at superplasticizer concentrations of 0.05 wt. % and 0.1 wt. %. Shear thinning was observed for all the different formulations from oscillatory strains of 0.05 to 50%. As expected, at 0.05 wt. % neat OPC had the highest viscosity at 581 Pa.s, followed closely by the rest. In contrast, at 0.10 wt. %, PCE had a viscosity of 190 Pa.s, which was significantly lower than the rest of the samples. The RAFT product led to significant reductions in yield stress observed in slump tests and viscosity reductions in model systems, it only had modest effects on viscosity in cement paste.



Figure 9.3.2.2. Effect of superplasticizers on OPC viscosity ( $\eta'$ ) at (a) high concentration (0.1 wt. %) and (b) low concentration (0.05 wt. %)

The discrepancy observed in the viscosity and slump data can be attributed to subtle differences in the nature of each dispersion. Cement pastes containing PCE are thought to be highly dispersed at high superplasticizer concentration, which results in reduction of both the yield stress and viscosity. The GM product, as mentioned, forms nano cross-linked aggregates due to their disorganized structure. These aggregates can contain multiple lignin particles and possibly form strongly bonded flocs, possibly resulting in an increase in both yield stress and viscosity compared to neat cement pastes. The RAFT product on the other hand, results in the formation of weakly bonded flocs compared to the GM product and maintains viscosity close to neat cement pastes but has lower yield stress values and larger slump spreads.

In order to quantitatively understand and model how aggregation impacts the viscosity, the Krieger-Dougherty equation was used [120]. In equation 16, the dependence on particle volume fraction ( $\phi$ ) and maximum volume fraction ( $\phi_M$ ) relationship is shown, where  $\eta_c$  is the viscosity of the continuous fluid phase and [ $\eta$ ] is the intrinsic viscosity of the suspension. An intrinsic value of 2.5 is expected for suspensions of spherical particles, and a different value is an indication of flocculation. In previous studies done on portland cement at a w/c ratio of 0.32 and  $\phi_M$  of 0.64, the intrinsic viscosity was a sensitive function of dispersion. The intrinsic viscosity ranged from 5.1 for naphthalene based dispersed systems to 6.3 for flocculated systems without superplasticizer [5].

$$\frac{\eta}{\eta_c} = (1 - \frac{\phi}{\phi_M})^{-[\eta]\phi_M} \tag{16}$$

The Krieger-Dougherty equation was used to analyze the viscosity data shown in Figure 9.3.2.2. A constant  $\phi_M$  value of 0.54 was used for both shear magnitudes, and was optimized based on a  $\phi$  value of 0.51, which was calculated for a 0.42 w/c ratio. The intrinsic viscosity was the only free parameter. The low-strain data are more sensitive measure of aggregation, as all pastes were well dispersed at high oscillatory strains. The results of the Kreiger-Dougherty fit are shown in Table 9.3.2.1. The results obtained from the fit at higher strain are all similar, which was expected. The data at lower strains is consistent with the interpretation that the RAFT product formed weakly

bonded flocs (6.93), compared to the GM product, which formed strongly aggregated flocs (7.16). The intrinsic viscosity for the GM product was higher than that of neat cement paste at low strain, which is consistent with the earlier discussion.

	High Strain (50.0%)		Low Strain (0.05 %)	
Sample	0.10 wt.%	0.05 wt. %	0.10 wt. %	0.05 wt. %
OPC	4.49	4.49	7.13	7.13
RAFT	4.43	4.40	6.91	6.93
GM	4.51	4.39	7.32	7.16
PCE	4.28	4.40	6.50	6.87

Table 9.3.2.1. Intrinsic viscosity values for different superplasticizers

To gain a deeper understanding of the interactions of the superplasticizers, adsorption experiments were performed on every individual OPC component was measured. OPC clinker is composed of calcium silicates ( $C_2S$  and  $C_3S$ ) and calcium aluminates ( $C_3A$  and  $C_4AF$ ), where the silicates have a weak anionic charge while the aluminates are cationic. Total organic carbon analysis was used to measure the adsorption and 0.5 wt. % plasticizer solutions was mixed with 5 wt. % material for 1 h; the results are shown in Figure 9.3.2.3 along with the zeta potential. The adsorption results are reported in terms of adsorption percentage normalized by the BET surface area of each mineral component.



Figure 9.3.2.3. Adsorption data for superplasticizers at different concentrations for cement phases normalized to BET surface area of each mineral (a)  $C_2S$  (BET = 0.9845 ± 0.0099 m<sup>2</sup>/g;  $\zeta = -5.96 \pm 0.42$  mV) (b)  $C_3S$  (BET = 0.8252 \pm 0.0047 m<sup>2</sup>/g;  $\zeta = -7.77 \pm 0.22$  mV) (c)  $C_3A$ 

(BET =  $0.3492 \pm 0.0133 \text{ m}^2/\text{g}; \zeta = 3.23 \pm 0.44 \text{ mV})$  (d) C<sub>4</sub>AF (BET =  $0.5797 \pm 0.0017 \text{ m}^2/\text{g}; \zeta = 26.35 \pm 1.46 \text{ mV})$ 

From Figure 9.3.2.3, PCE had the strongest adsorption across all the phases, which is consistent with the high dispersing capabilities that were observed in effective viscosity reduction. The GM product had similar adsorption to PCE for the aluminates phase but was much lower for the silicates phases. The opposite trend was observed for the RAFT product, which had a significantly low adsorption percentage for the C<sub>4</sub>AF phase. It is important to note that commercial portland cement is comprised of up to 60% of C<sub>3</sub>S and the RAFT product adsorbed significantly to this phase. The PCE and GM plasticizers followed adsorption trends that followed with their zeta potential. PCE solution had a zeta potential of -48.9 mV and GM solution had a zeta potential of -39.2 mV, and both of them strongly adsorbed to the aluminate phases. The RAFT product had a zeta potential of -36.2 mV, which did not follow the trend. Ideally, the RAFT product should have had a stronger interaction with the C<sub>4</sub>AF phase, and a lower adsorption with the silicate phases than GM. However, the opposite was observed, suggesting lignin interactions are quite complicated and cannot be strictly determined by columbic forces between particles and particle surfaces.

From the above experiments, LPAM-2-100 seemed to be an effective superplasticizer in reducing the yield stress but had weak effects on the low strain viscosity, whereas PCE reduced both the yield stress and low strain viscosity. The yield stress for PCE and LPAM-2-100 calculated from the slump tests were  $31.89 \pm 2.5$  Pa and  $20.64 \pm 1.3$  Pa, respectively, at 0.1 wt. % concentration. This stress is significantly higher than the stress exerted by the rheometer. At low strains, the stress applied by the vane fixture was 1 Pa and at high strains it was 10 Pa. In both cases, this suggests that the initial shear stress in slump tests was enough to disrupt the aggregates and ensure that the solution is in the disaggregated state. Even though there have been some attempts to describe the rheological characteristics of cement paste and fresh concrete by the Herschel-Buckley model [121], it is difficult to use a general microscopic model to describe this macroscopic model. It is especially difficult due to the dynamic chemical evolution involving dissolution, gelation, and remineralization. These processes significantly impact the

microstructure making it very challenging to predict the behavior of superplasticizers in paste [122], [123].

The microscopic basis for the difference in the rheological properties between the different cement pastes containing PCE and LPAM-2-100 is thought to stem from the difference in molecular architecture. PCE is a linear polymer with a high number of grafted PEG side chains and the effect of design on rheological properties is well understood [98], [124]. LPAM-2-100 has a more disorganized structure with fewer pendant chains. The effect of design on rheological properties is much more complicated due to the presence of aromatic, aliphatic, ether hydroxyl, phenoxide, and carboxylate functionality in a cross-linked architecture. It is extremely difficult to predict which group will have what effect on the paste.

# 9.3.3 Compressive Strength

Viscosity reduction and low yield stress are very important parameters for a superplasticizer, however, one of the most important parameters is how it affects the mechanical strength of the cement. A preliminary assessment of the effects of LPAM-2-100, GM, and PCE on compressive strength was measured at 7 days as shown in Figure 9.3.3.1. The data showed that all three superplasticizers had compressive strengths higher than OPC. The LPAM-2-100 and GM product had higher strengths than PCE, which suggests that the lignin is enhancing the mechanical strength of the system. These data suggest that the effects of architecture are negligible on compressive strength, and native lignin itself is playing an important role. As seen from surface tension data, the lignin was quite surface active. It is possible that the lignin was preferentially accumulating at the air-water interface in the cement, which would be the pores. This would result in resistance of crack propagation, hence, resulting in a high compressive strength. In order, to understand if lignin was affecting the amount of air or pore size distribution, nano-computed tomography (nano-CT) was conducted on the samples.



Figure 9.3.3.1. Compressive strength of the different samples at 7 and 28 days

Nano-CT was conducted on neat portland cement and LPAM-2-100. The samples were allowed to cure for 28 days at 100% humidity before polishing. Three phases were identified based on the attenuated intensity: brightest phase, gel phase and porosity. The composition of each phase is shown in Table 9.3.3.1. Due to the low attenuation of carbon and the concentration it was difficult to find the polymer phase. However, the data show that there was a 5% increase in the gel phase in the LPAM-2-100 sample, which is thought to be the mechanism for compressive strength changes. Also, the porosity reduced by 4% from the neat portland cement to the LPAM-2-100 sample, resulting in the 25% increase in compressive strength compared to neat portland cement. However, it is still unclear whether the lignin was preferentially adsorbing to the pores. Further studies need to be conducted to understand how the lignin is improving the compressive strength of these samples.

Table 9.3.3.1. Composition of the different cement phases in portland cement and LPAM-2-100 (RAFT)

Phase	Portland cement	LPAM-2-100 (RAFT)
Brightest	36.8%	35.1%
Gel	54.1 %	59.9 %
Porosity	9.1 %	5.0 %



Figure 9.3.3.2. Original and segmented data for (a) portland cement and (b) LPAM-2-100 (RAFT) at 28 days

# 9.4 Conclusion

These experiments showed that the architecture of the lignin polymer affects the rheological properties of the cement paste, but has no effect on the compressive strength of the system. Since the design principles for PCE superplasticizers are well understood and documented, there is need to experiment with various polymers and architectures for lignin to improve both the yield stress and viscosity while maintaining high compressive strength.

# 10. Lignin grafted polyacrylamide superplasticizers for alternative supplementary cementitious materials

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\* Calorimetry experiments were performed by Kurtis group at Georgia Institute of Technology

#### 10.1 Introduction

Grafting hydrophilic polyacrylamide from a kraft lignin core results in a lignopolymer that effectively plasticizes portland cement paste [21]. Here, the potential of this lignopolymer is examined for improving the workability of portland cement blended with two naturally finely divided mineral materials; kaolin and clinoptilolite, which can be potentially used in combination with portland cement as a means to reduce the cement clinker content [125]. Both mineral materials are known to participate in hydration reactions but can significantly reduce workability when blended with portland cement, presenting a challenge for their practical large scale use [26].

In concrete, challenges with workability are typically overcome with the use of water reducing chemical admixtures, which are long chain polymers with anionic side groups. Water reducing admixtures can help solve this problem as they improve particle dispersion and ensure mix water is available for lubrication during early age mixing and placing. However, with finely divided materials such as zeolites or kaolin, even the addition of such water reducing chemical admixtures at recommended dosage rates does not produce a significant improvement in workability. This is due to the difference in the charge and the surface area associated with these materials compared to cement. The extremely high surface area of these materials in particular leads to a high rate of admixture adsorption and their low surface charge promotes aggregation [25], [26]. The goal of this study is to investigate lignin grafted polyacrylamide as superplasticizer to be used in blends of high surface area, reactive ASCMs and portland cement. A head-to-head comparison between LPAM, lignosulfonates and PCE was performed to understand how the different mechanisms of each one of them impact their performance. Lignosulfonates were used as a point of comparison as they are commercially used as superplasticizers.

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#### 10.2 Experimental

The detailed procedure for the synthesis of LPAM can be found in Section 2.1. The representative chemical structures of LPAM, lignosulfonates and PCE are shown in Figure 10.2.1. Rheometry, adsorption, zeta potential and calorimetry were used to evaluate how the three plasticizers perform when portland cement is mixed with high surface area ASCMs. The Rietveld analysis of Type I/II portland cement along with XRD for kaolin and zeolite can be found in Appendix C.



Figure 10.2.1. Chemical structure of the (a) lignosulfonate, (b) PCE and (c) LPAM

# 10.3 Results

The primary mechanism for plasticization of cement paste by admixtures is through adsorption onto the mineral surfaces. The affinity of LS, PCE, and LPAM for kaolin and clinoptilolite zeolite was determined by measuring the residual superplasticizer in the supernatant decanted from the samples after centrifugation by TOC. These measurements were then normalized against the mineral's nitrogen accessible surface area and are reported in Figure 10.3.1. For all three plasticizers measured, a monotonic increase in mass adsorbed was observed as function of increasing concentration. For both kaolin and clinoptilolite, LPAM had the highest adsorption, followed by PCE and LS. The mass adsorbed at lower concentrations for all three plasticizers was similar and within the error range of each other. However, at the highest concentrations measured, LPAM showed significantly increased adsorption compared to PCE and LS. The mass adsorbed by LS seemed to have a delayed response, as it showed a low adsorption value until a concentration of 2 mg/mL, after which it steadily increased. This is consistent with reported behavior of lignosulfonates, as higher concentrations are needed to observe significant plasticization effect [15]. It is interesting to note that there were no significant differences in concentration-dependent adsorption for LS for both kaolin and zeolite, suggesting a lack of specific interactions between these mineral surfaces and LS.

For both the lignin-based samples, LPAM and LS, a plateau value was not observed in the TOC data, which suggests that the mineral continues adsorbing the admixture or that the lignin is capable of aggregating or accumulating, perhaps in layers. The LPAM adsorbed significantly more than the LS which indicates that the grafting promotes admixture binding, which is due to the reduction in aggregation in the grafted samples compared to lignin itself. This suggests that the preferential adsorption to these mineral surfaces of LPAM is due to the kraft lignin core, which is rich in carboxylate groups but has few sulfonate groups. However, direct comparisons will be required to establish this given the contributions of the polyacrylamide grafts to the interactions with cementitious particle surfaces [90].



Figure 10.3.1. Adsorption data for all the admixtures in each mineral phase normalized to surface area (a) kaolin (BET =  $18.02 \pm 0.0080 \text{ m}^2/\text{g}$ ), (b) zeolite (BET =  $28.22 \pm 0.1672 \text{ m}^2/\text{g}$ )

In order to elucidate electrostatic effects when the admixtures adsorb on the mineral, the zeta potential was measured. The zeta potential for mineral suspensions immediately following addition of the admixture is shown in Figure 10.3.2. Most samples had zeta potential magnitudes greater than 40 mV, which predicts that they form semi-stable solutions [20], [88]. It can be seen that at all dosage ranges the LPAM sample has the lowest zeta potential compared to the other

admixtures, which suggests that the dispersant effects observed for this admixture were not primarily due to electrostatic stabilization.

In theory, the greatest zeta potential should correspond to the admixture that produces the most stable dispersion. This corresponds to the admixture that has the highest adsorption to the mineral surface and hence would have the greatest effect on slump spread. According to the data in Figure 10.3.2, lignosulfonates should produce stable solutions as they impart the largest zeta potentials. However the opposite was observed. This is believed to be attributable to the lower adsorption affinity of the lignosulfonates to the surfaces of the minerals, as seen in Figure 10.3.1. The large value of the zeta potential can be attributed to the contribution that non-adsorbed lignosulfonates make in solution [89], [90], [126]. The non-adsorbed admixtures in solution have been previously reported to have competing effects on cement-paste slump, which could increase slump through lubrication effects or decrease it through increasing particle-particle interactions [127]. Clearly the effect depends sensitively on the chemical environment in the cement paste and its surrounding solution, but these zeta potential results provide some insight into the relative effectiveness of these superplasticizers. It must also be noted that zeta potential alone cannot be used to predict reductions in slump due to aggregation since the strength of steric interactions were different for these admixtures, with LS having relatively low contributions and PCE and LPAM having relatively high contributions.



Figure 10.3.2. Zeta potential value for when the admixture is added to each mineral phase (a) kaolin and (b) zeolite

The effects of LS, PCE, and LPAM on workability of the cement paste were measured as a function of mineral dose rate by mass of cement by using mini-slump spread tests. These were performed at admixture concentrations of 0.5 mg/mL (0.025 wt.%) and 5 mg/mL (0.25 wt.%).

These values were compared to the effects on neat portland cement paste to provide information on interactions between the admixtures and the two minerals. The slump spread values were converted to yield stress,  $\tau_0$ , using equation 15.

Figure 10.3.3 shows the effect of these admixtures on portland cement paste without any mineral addition. It is seen that LS had modest effects on the yield stress, but PCE and LPAM appeared to have much more significant impact. This is consistent with the primary application of lignosulfonates being as water-reducing agents but not imparting the large gains in slump that are associated with PCE's. The reduction of yield stress observed with LPAM suggests that this grafted nanoparticle architecture can be effective in improving flowability. Interestingly, LPAM induced the lowest yield stress at lower concentrations and had a similar effect at high concentrations.





When portland cement was blended with kaolin or zeolite, similar trends were observed but with lower reductions in yield stress compared to superplasticizer-free cement blends. At 0.25 wt. %, LPAM produced the lowest yield stress for both kaolin and zeolite as seen in Figure 10.3.4(a) and (b), respectively. LPAM adsorbed strongly to both surfaces at both concentrations, which correlated with the increases in slump spread and reductions in calculated yield stress. As seen in Figure 10.3.1(b) PCE had a slightly higher adsorption than LPAM for the lower concentration range for zeolites, which correlates with the slightly lower yield stress observed for PCE in Figure 10.3.4 (b). This validates the correlation between higher adsorption of the admixture to

the mineral and improvements in dispersion. The significant decrease in yield stress with LPAM dosage observed suggests that there are strong steric interactions taking place between the particles, which was not observed in the case of LS. It is proposed that the polyacrylamide grafting of kraft lignin increased its effects on the workability of mineral-blended cement. These observations are corroborated with previously published studies that suggest side chains are necessary for improved workability due to their steric interactions [23], [21], [92], [96], [128]. Otherwise, the admixture needs to be added above saturation level, which may result in some non-adsorbed polymer that may improve workability [127]. In conclusion, these data show that LPAM provides reductions in yield stress and that these are found at ten-times lower dosage than the recommended dosage for current superplasticizers.



Figure 10.3.4. Effect of admixtures on yield stress at low and high polymer dosage of cement pastes containing (a) kaolin and (b) zeolite

To further probe the interactions of LPAM and PCE with the kaolin and zeolite minerals, rheometry experiments were performed using a vane fixture and measuring the viscosity as a function of strain magnitude at constant oscillation frequency. From the representative rheology results shown in Figure 10.3.6, the data for the mineral-containing pastes showed fluctuations in the viscosity/strain behavior, compared to the relatively consistent or smooth viscosity curves measured in portland cement pastes, as shown in Figure 10.3.5. This suggests that the dispersion of these mineral-blended portland cement pastes may have been incomplete, possibly due to flocculation under shear. However, the magnitude of the fluctuations was reduced at higher admixture concentrations, which supports associating phenomenon with reversible aggregation phenomena of cement and minerals that can be controlled through the addition of dispersants. For the kaolin rheology, as seen in Figure 10.3.6 (a) at low admixture concentration, it appears

that neither PCE (green) nor LPAM (red) significantly affect the viscosity compared to the admixture-free sample (blue curve). This changed when the polymer concentration was increased, as seen in Figure 10.3.6 (c), and PCE resulted in a 5-fold reduction in viscosity and reduction in fluctuations of the viscosity curve. For zeolite at low admixture concentrations, the LPAM had a pronounced effect in the viscosity profile as seen in Figure 10.3.6 (b). At high concentration PCE seemed to have a larger effect on the viscosity similar to kaolin as shown in Figure 10.3.6 (d). This is similar to what was observed in portland cement paste in Figure 10.3.5. At low concentration it appeared that LPAM had a greater effect whereas at higher concentration PCE was more effective at improving paste flow. The trends observed in the viscosity plots are in qualitative agreement with the yield stress values calculated at low concentrations for both kaolin and zeolite. However, at higher concentrations the yield stress trends suggest that for kaolin, LPAM imparted the lowest yield stress, not PCE.



Figure 10.3.5. Effect of admixtures on portland cement paste viscosity (a) low admixture dosage (0.025 wt. %) and (b) high admixture dosage (0.25 wt. %)



Figure 10.3.6. Effect of admixtures of mineral-cement paste viscosity ( $\eta'$ ) (a) Kaolin at low admixture dosage (0.025 wt. %), (b) Zeolite at low admixture dosage (0.025 wt. %), (c) Kaolin at high admixture dosage (0.25 wt. %) and (d) Zeolite at high admixture dosage (0.25 wt. %)

In developing new plasticizing agents with practical applications, it is necessary for the admixture to not affect the cement hydration reactions significantly. In order to test the effects of LPAM on the mineral-cement blends isothermal calorimetry was performed. This technique is useful for understanding how interactions between admixtures, minerals, and cement influence early cement hydration kinetics. The results for blends of kaolin and zeolite with cements are shown in Figure 10.3.7; results for the portland cement (PC) paste without admixtures or mineral additions are also plotted for comparison. The main exotherms around 6 h and 12 h, which can be attributed to the hydration of the alite or tricalcium silicate (C<sub>3</sub>S) and tricalcium aluminate (C<sub>3</sub>A) phases in the portland cement, respectively, are both significantly influenced by the presence of the minerals [129]. The kaolin appears to delay the onset of the initial C<sub>3</sub>S reaction by approximately 1.5 h, while increasing the heat released associated with the reaction of the aluminate phase by nearly 70% when no admixtures are used, compared to the portland cement alone. The zeolite, meanwhile, appears to accelerate the C<sub>3</sub>S reaction by nearly 2 h, while

increasing the heat released by the aluminate reaction by approximately 40% when no polymer admixtures were used. The increase in heat evolved by the aluminate reaction is consistent with the high aluminosilicate contents and relatively high surface area of both the kaolin and natural zeolite. Increases in cumulative heat evolved were observed for both minerals, occurring at or near the onset of reaction for the zeolite and beyond 12 h for the kaolin (as seen in Figures 10.3.7 (d) and (b) respectively), compared to the neat pastes.

Generally, the admixtures had minimal effects on the hydration of both minerals, which is generally desirable since predictable behavior is preferred in practice. The exception observed is for the zeolite mixture at high admixture concentration, for which both admixtures increased the peak heat release observed 12 h following addition of water. In particular, this peak (corresponding to the hydration of the  $C_3A$ ) shows an increase of approximately 20% and an acceleration of approximately 30 min relative to the zeolite paste without admixtures. The same peak in the kaolin mixtures, meanwhile, lacks this increase in height and, in fact, shows a slight deceleration of approximately 30 min when LPAM was used.



Figure 10.3.7. Effect of admixtures on mineral-cement hydration. (a) Heat flow rate and (b) cumulative heat of kaolin mixtures at low (0.025 wt. %) and high (0.25 wt. %) admixture

dosages; (c) Heat flow rate and (d) cumulative heat of zeolite mixtures at low (0.025 wt. %) and high (0.25 wt. %) admixture dosages

Although both minerals are rich in alumina and have a notable effect on the aluminate phase hydration, it appears as though the PCE and LPAM interact more strongly with the zeolite than with the kaolin. This may be possibly related to the unique structure of the natural zeolite, which enables it to be used in ion-exchange reactions, potentially altering hydration kinetics by either binding with ions in the admixture during initial mixing or adsorbing ions from the solution during hydration [130]. It is also possible that mineral dispersion and water absorption play roles. Further research is needed to understand the mechanism by which the kaolin and clinoptilolite interact with the chemical admixtures explored in this study.

PCE showed a similar behavior to LPAM and continually adsorbed on the kaolin and zeolite surface. The hydration data shown in Figure 10.3.7 (a) and (c) can be rationalized using the adsorption trends. Figure 10.3.7 (a) showed that there was a delayed response in the hydration data for the early time points compared to the hydration data for zeolite shown in Figure 10.3.7 (c) where there is an increased response in the early time points. As seen in Figure 10.3.1, the slope of the curve for PCE decreases as the concentration increases suggesting some saturation. The slope for zeolite is significantly lower compared to that of kaolin, which suggests that the high surface area of kaolin is continually adsorbing the PCE resulting in a delayed reaction, whereas the zeolite is reaching saturation due to its porous structure resulting in an accelerated response at high concentrations.

These results present a complex picture of interactions between cement, mineral, and polymer admixtures. In its hydrating state, the paste is viewed as finely divided minerals suspended in a complex medium based on portland cement that is initially rapidly dissolving and remineralizing. Suspension of finely divided minerals in a concentrated solution generated by cement particle dissolution, but maintaining fluidity requires also inhibiting association of the kaolin and zeolite particles with themselves or with portland cement constituents. Macroscopic properties such viscosity and yield stress are determined by flocculation of the mineral and cement species, and polymeric admixtures reduce these through mediating particle-particle interactions. The most effective mechanism is based on steric inhibition of aggregation by pendant polymer grafts, which is the basis for PCE function. In contrast, LS primarily functions

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through increasing electrostatic repulsion between particles, although the high ionic strength of the cement pore solution can screen these interactions making it less effective than steric repulsion. Both mechanisms require adsorption onto the particle surfaces, but non-adsorbed polymers can reduce aggregation through depletion stabilization, which is based on concentration gradients at small particle separations resulting in an osmotic pressure that stabilizes non-aggregated states. However, this mechanism tends to be significantly less effective than ones based on adsorption, so it is expected that polymer adsorption should correlate more strongly with viscosity and yield stress rather than changes in zeta potential.

Polymer admixtures such as PCE have been optimized for portland cement, and the interactions with the spectrum of ASCM's are poorly understood. In aqueous suspensions of kaolin and zeolite used in this work, PCE actually displayed comparable adsorption as LS at 5 mg/mL, and both were lower approximately half the value of LPAM. It is interesting to note that none of the polymers displayed signs of reaching a plateau adsorption value even at values of 0.25 mg per m<sup>2</sup>/g at solution concentrations of 4 mg/mL. In contrast, PCE on portland cement generally reaches saturation of adsorbed polymer below 0.2 mg/per m<sup>2</sup>/g at solution concentrations of 0.5 mg/mL [130]. This continued adsorption on the ASCM surface suggests that even when normalized for BET surface area there are additional adsorption sites or modes on these materials.

At doses of 0.5 mg/mL, LPAM had comparable adsorption with LS and PCE but imparted the lowest values for cement pastes containing either kaolin or zeolite. Interestingly, higher dosages of LPAM led to further reductions in yield stress on cement pastes containing kaolin but did not for those containing zeolite despite having nearly identical specific adsorption on both minerals at a solution concentration of 5 mg/mL. This suggests that the LPAM mechanism of dispersion in zeolite in portland cement paste is primarily due to the fraction adsorbed at low admixture concentrations, while in kaolin additional LPAM results in further plasticization. In contrast, PCE was less effective at plasticizing both minerals at low admixture concentrations in yield stress. Despite the lower affinity of PCE for the minerals at higher concentration, it is assumed that the dominant plasticization mechanism is steric interactions due to adsorbed polymer. However, given the comparable size of PCE and LPAM, the more effective plasticization by the latter could be due to the greater molecular weight of the grafts polymer, although this does not explain the

anomalous concentration dependence for LPAM, which had been reported in pure portland cement paste [21]. Another possible explanation is LPAM functions more through depletion stabilization, although this is difficult to reconcile with the significant reduction in yield stress due to the addition of LPAM.

The effects on the viscosity of the cement pastes containing varying concentration of PCE were similar for those with and without mineral additions. In pastes containing kaolin or zeolite, increasing concentrations of PCE decreased both the fluctuations in the measured viscosity as well as the magnitude. The former are attributed to transient aggregation of the mineral additives and the latter are attributed to and overall reduction in interaction strength between constituents in the paste. The reductions in viscosity fluctuations were observed following addition of 5 mg/mL LPAM to the paste containing zeolite but the fluctuations were still observed in both formulations containing kaolin and the zeolite formulation with 0.5 mg/mL LPAM.

While viscosity and yield stress of suspensions are both related to aggregation, viscosity is more sensitive to small-scale aggregates while yield stress requires percolation and network formation [131]. A possible reconciliation of the difference in effect of PCE and LPAM is PCE functions as a true dispersant with increasing concentration resulting in monotonic increases in adsorption onto particles and concomitant reductions in aggregation, which are recorded as decreases in viscosity and yield stress of both the mineral and portland cement constituents in these blended materials. In contrast, LPAM could provide partial disaggregation at lower concentrations, resulting in lower yield stresses but not viscosities. Increasing concentration of LPAM does appear to improve dispersion of kaolin and zeolite but may form microaggregates of portland cement constituents that do not contribute to the yield stress but do contribute to the viscosity. Further studies are required to elucidate the microstructural basis of LPAM effects, but it clearly has potent effects in cement.

# 10.4 Conclusion

High surface area minerals such as kaolin and zeolite can significantly reduce workability when blended with portland cement. In this study, a novel polyacrylamide-grafted kraft lignin LPAM was demonstrated to improve the workability of both mineral formulations. Based on adsorption and zeta potential data, a mechanism in which both adsorbed and solutionphase superplasticizers contributed to improving flowability of pastes with LPAM or PCE, although the performance at low concentrations of LPAM were significantly improved.

In contrast, LPAM had significantly good performance than lignosulfonates and the grafting of a small amount of hydrophilic polymer present results in improved dispersant properties. Zeta potential along with slump tests showed that the charge present on the lignin core along with side chains of the LPAM allows for both electrostatic and steric interactions to improve the workability of these blends. It is proposed that PCE and LPAM have distinct mechanisms of plasticization, which allows LPAM to have significant effects on the workability of these blends at ten-times lower dosage than currently commercially used admixtures. In conclusion the study indicates that LPAM can be used as an effective admixture for reactive, high surface area minerals.

## 11. Poly(ethylene glycol)-grafted lignosulfonate superplasticizers

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## 11.1 Introduction

As seen previously, out of crosslinked nanoaggregates of kraft lignin and polyacrylamide prepared via FRP, the CRP molecular architecture resulted in large increases in slump spread of portland cement paste that were nearly comparable to commercial PCE formulations at low concentrations, demonstrating that similar mechanisms of plasticization could be achieved using synthetically modified lignin. However, CRP can be a complex, expensive method for polymer grafting, and requires preparing lignin macro initiators in non-aqueous solvents.

Lignosulfonates are a leading superplasticizer for cement and concrete, but their mechanism of plasticization is primarily electrostatic. Compared to kraft lignin, lignosulfonates have improved electrostatic repulsion and hydrophilicity due to the high concentration of sulfonate groups, and they find broad use in concrete. Despite the continued importance of lignosulfonates, PCE's are used more frequently [29]. While lignosulfonates do not naturally provide significant steric repulsion, this is clearly an important mechanism for effective plasticization of cement slurries [127], [132]. However, lignosulfonates are only soluble in water making it impossible to use CRP to increase steric interactions. Given the importance of lignosulfonates in plasticizing portland cement paste, it was of considerable interest to develop a method for preparing similar polymer-grafted constructs.

In this study, lignosulfonate was grafted with monofunctional, low molecular-weight poly(ethylene oxide) as an alternate approach to CRP, while maintaining polymer-grafted nanoparticle architecture. Grafting of low molecular weight PEG to lignosulfonates would enhance the steric interactions while maintaining the strong native electrostatic interactions and hydrophilicity.

#### 11.2 Experimental

A simple PEG grafting reaction, shown in Scheme 2.3.2.1 was used to prepare the final product. The detailed procedure for synthesis can be found in Section 2.3. The representative chemical structures for lignosulfonate and PEG-grafted lignosulfonate is shown in Figure 11.2.1. Lignosulfonate was compared head to head with lignosulfonate grafted PEG at 0.3, 0.4 and 0.5 wt. %. Rheometry and adsorption were performed on paste to evaluate the plasticizers. Microstructural analysis along with calorimetry was performed on LSPEG samples to understand in detail the affects on hydration chemistry. The Rietveld analysis of Type I/II portland cement can be found in Appendix B.



Figure 11.2.1. Representative chemical structures for a) lignosulfonate and b) PEG-grafted lignosulfonate.

# 11.3 Results

## 11.3.1 LSPEG characterization

The degree of PEG grafting (reported as average number of PEG chains per lignin particle) was measured using <sup>1</sup>H NMR and found to be 1.9, which increases the molecular weight of the LS by only 10%. The state of charge of LS and LSPEG were assessed by zeta potential measurements. At a pH value of 12 and a concentration of 4 mg/mL, PEG-grafted lignosulfonates had a surface charge of -52.4 mV and non-PEG-grafted lignosulfonates had a surface charge of -46.5 mV.

	Zeta Potential (mV)	Degree of PEG	Molecular weight
		grafting	(g/mol)
LS	-46.5	0	$2.0 \times 10^4$
LSPEG	-52.4	1.9	$2.2 \times 10^4$

Table 11.3.1. Properties for PEG-grafted and non-PEG-grafted lignosulfonates

## 11.3.2 Adsorption

Changes in lignosulfonate affinity for cement particles due to PEG grafting were assessed by adsorption measurements, and the results are shown in Figure 11.3.2.1 In suspensions of portland cement, the LS isotherm increased monotonically as a function of solution concentration but never reached saturation, consistent with previous observations [88], [99]. In contrast, the amount of adsorbed LSPEG was lower than that of LS throughout most of the concentration range measured, increasing until it reached a plateau value at 4 mg/mL, which is similar to values for some PCE compositions [88]. The adsorption behavior of LS has been attributed to the formation of a multi-layer structure in which sulfonate groups primarily mediate interactions with the particle surface and non-polar aromatic and aliphatic components of the LS structure drive aggregation at the interface [99]. This indicates that steric interactions at even low degrees of PEG grafting are sufficient to significantly alter interactions between lignosulfonate particles at cement interfaces [110]. It is also interesting to note that the adsorbed amount of LSPEG was 25% greater than LS at 0.25 mg/mL, while at all higher concentrations more LS adsorbed to the surface. This suggests that the intrinsic affinity of LSPEG for the cement was greater than that of LS, since surface aggregation is more likely to contribute to the amount adsorbed. Clearly, PEG grafting of lignosulfonate did not abolish the affinity for cement particle surfaces and may have enhanced it.

Given the similar zeta potentials of LS and LSPEG, sulfonate-mediated interactions with cement particles are important for LSPEG. The primary difference is in the formation of what is thought to be a monolayer of LSPEG instead of a multilayer coating of LS. The monolayer coating of LSPEG was confirmed by calculating the total surface area of the cement particles available and using the concentration of adsorbed LSPEG. In studies of PCE adsorption onto type I portland cement saturation of cement particle surfaces by polymethacrylic acid, it was

observed that at concentrations below 1.0 mg/mL and incorporation of PEG-grafted monomers increased the saturation concentration depending on the fraction of PEG-grafted monomers by up to five-fold [23]. In studies performed at constant PEG grafting density in PCE but varying the graft molecular weight, the adsorption of LSPEG is most similar to the PCE having PEG with n = 90, which suggests that either the disorganized molecular structure of LSPEG or the lower affinity of sulfonate groups for cement particle surfaces than carboxylate groups is modulating the interactions [99], [110]. In this comparison, it is interesting to note that saturation was reached even by non-PEG-grafted polycarboxylate whereas LS continued to adsorb even after reaching monolayer coverage. This supports the idea that multilayer formation is mediated by hydrophobic domains in the LS structure, so PEG grafting is having an even more dramatic effect on adsorption behavior than in PCE systems.



Figure 11.3.2.1. TOC data showing adsorbed amount of superplasticizer (ppm/mg of cement) as a function of concentration.

# 11.3.3 Assessments of workability

The slump spread and the slump height were recorded for each sample and the results are shown in Figure 11.3.3.1. The dotted lines represent the slump-spread range measured in the lab for commercially available PCEs. As expected, ordinary portland cement without added superplasticizer had the lowest slump spread and height change. In general, as more

superplasticizer was added to the cement paste, the slump spread and slump height increased, and overall the largest difference was observed for 0.5 wt. % LSPEG. The slump height difference increased from 2.6 cm for neat OPC to 4.7 cm for 0.5 wt. % LSPEG. The 0.3 and 0.4 wt. % PEG-grafted lignosulfonate had about 30% larger slump spread values than formulations with non-PEG-grafted lignosulfonate. The 0.5 wt. % PEG-grafted lignosulfonate had a 15% increase in slump spread compared to the non-PEG-grafted. The difference was much more prominent at lower dosages but still significant at higher dosages. This concentration-dependent difference suggests that especially about 0.4 wt. % LSPEG functions more like PCE than LS in plasticizing cement pastes.

The significant increases in fluidity is consistent with the hypothesis that steric interactions, such as those in PCE, are more effective in inhibiting flocculation than electrostatic mechanisms, such as those for unmodified LS, in high ionic strength environments like cement paste. Previous studies in adsorption of superplasticizers on cement particles have shown that the effect on the fluidity of the cement paste is dependent on the type and amount of superplasticizer used. In a study by Hanehara et al., the effect on fluidity of cement paste was measured for two superplasticizers with different dispersing mechanisms. PCE was compared to naphthalene sulfonic acid, which relies primarily on electrostatic interactions. No improvement in fluidity was measured until a naphthalene sulfonic acid dosage of 0.8 wt. % whereas polycarboxylate ethers showed a measureable increase in fluidity at 0.2 wt. % dosage [133]. This shows that the pendant groups provide steric effects, which are much stronger at low concentrations compared to electrostatic effects. In comparing LSPEG to LS, it is suggested that in PEG-grafted ligonosulfonates, steric effects become the dominant plasticization mechanism and the sulfonate groups primarily function to mediate particle interactions. Without the PEG side chains, polycarboxylates have been shown to induce rapid setting of cement pastes, possibly due to the strong affinity of carboxylates for calcium ions [88], [109]. Lignosulfonates also show a strong affinity for calcium ions, resulting in a formation of a calcium salt of the lignosulfonate incorporated into the polymer matrix of the hydrated grain [134]. The mechanism of LSPEG function is proposed to be strong adsorption to particle surfaces mediated by electrostatic interactions and steric repulsion of particle flocculation but clearly rapid setting is not observed for unmodified LS.



Figure 11.3.3.1. Slump spread and slump height difference for different concentrations of LS and LSPEG in cement pastes. For comparison, the slump spread values for a commercial PCE formulation are shown as dashed lines representing superplasticizer concentrations of 0.17 wt. % (lower) and 0.3 wt. % (upper).

Water reduction is a critical function of admixtures for the preparation of high-strength cementitious materials, allowing similar workability at lower water content [133]. Defined as the percent reduction in water that has the same slump value as a reference water/cement ratio in neat cement or concrete, a mid-range water-reducing agent is defined as approximately 8% water reduction and a high-range water-reducing agent is defined as having values ranging from 12-30%. While the presence of aggregate can significantly impact the water-reduction values in concrete relative to cement, measurements in cement are still valuable for understanding the interplay between plasticization and the volume fraction of particles in suspension. The plasticization of OPC pastes was further confirmed by the data in Figure 11.3.3.2, where the water/cement ratio was varied while holding the dosage constant at 0.4 wt. %. As expected, the slump spread increased as the w/c ratio increased for both LS and LSPEG. However, at 0.3 w/c ratio it is shown that LSPEG has close to twice the slump spread of LS and OPC and a corresponding water reduction of approximately 25-30%.



Figure 11.3.3.2.Slump spread for PEG-grafted and non-PEG-grafted lignosulfonates at different water/cement ratios and a constant superplasticizer dosage of 0.4 wt. %.

To further understand the rheological behavior of the paste, an oscillatory strain sweep was performed. In Figure 11.3.3.3 is shown the real part of the viscosity as a function of strain magnitude. All formulations exhibited shear-thinning behavior, and the viscosity data followed the same concentration trends as the slump data. At constant superplasticizer concentration, the PEG-grafted lignosulfonates had lower viscosity than the non-PEG-grafted versions, particularly at low strains where the difference was nearly a factor of four. However at higher strains, the trends are reversed as ordinary portland cement without any superplasticizer has the lowest viscosity as seen in Figure 11.3.3.3(a). This may be due to changes in the pore-solution viscosity due to non-adsorbed superplasticizer, but interactions between adsorbed polymers could also increase friction in the deflocculated state. However, at lower strains the viscosity of the cement paste was clearly lower in the formulations containing LSPEG than LS.

$(a)_{1000}$	—OPC			(b)	Sample	$\eta_{0.05\%}(Pa.s)$	$\eta_{50\%}(\text{Pa.s})$
(s					OPC	879.19	3.76
<u>Ба</u> 100					0.3 LS	685.89	5.73
osity					0.3 LSPEG	603.2	6.21
NISC 10	-				0.4 LS	402.38	6.29
Real					0.4 LSPEG	151.74	7.98
1	ļ,				0.5 LS	370.36	9.64
(	).05 0 C	5 Dscillation strai	5 50 in (%)		0.5 LSPEG	139.48	15.04

Figure 11.3.3.3. Real viscosity ( $\eta'$ ) of all the samples tested versus oscillation strain (%) (a) line plot (b) tabulated values.

Sample	Low Strain (0.05%)	High Strain (50%)
OPC	7.28	4.37
0.3 LS	7.09	4.99
0.3 LSPEG	6.89	4.8
0.4 LS	6.85	4.89
0.4 LSPEG	6.33	4.77
0.5 LS	6.81	4.87
0.5 LSPEG	5.98	5.11

Table 11.3.3.1. Intrinsic viscosity values for LS and LSPEG (in wt. %) in cement paste

In order to understand the nature of the dispersion as a result of the enhanced steric interactions provided by LSPEG, the intrinsic viscosity was fitted to the data with the help of the Krieger-Dougherty analysis. The analysis along with an explanation of the different parameters is shown in equation 16 in Section 9.3.2. In order to fit the rheology data shown in Figure 11.3.3.3 to the Krieger-Dougherty equation a constant  $\phi_M$  value of 0.5245 was used for both shear magnitudes, and was optimized based on a  $\phi$  value of 0.51, which was calculated for a 0.40 w/c ratio. The intrinsic viscosity values fitted for both low (0.05%) and high (50%) values are shown in Table 11.3.3.1. The values fitted at the lower strain explain more about the nature of the dispersion at the initial flocculated state of the system, whereas the higher strain explains more about the pore solution. The PEGylated lignosulfonates had the lowest intrinsic viscosity values compared to the lignosulfonates and control. As the concentration of the LSPEG increased the intrinsic

viscosity value decreased, suggesting that LSPEG reduced flocculation compared to the non-PEGylated lignosulfonate, which was also suggested by the slump data. It is interesting to note that at the higher strains this was not the case as the intrinsic viscosity of the PEGylated samples was higher than the non-PEGylated ones. This can be explained due to the possible increase in elasticity of the pore solution due to the dissolved polymers present. Due to the addition of significant amounts of LSPEG, it is possible that the elasticity of the paste increased resulting in higher intrinsic viscosity values only at higher strains, when the polymer does not have sufficient relaxation time at this strain rate. This would need to be further confirmed using the elastic modulus obtained from the oscillatory strain sweep.



Figure 11.3.3.4 (a) Storage modulus (G') and (b) tan  $\delta$  values at different oscillation strains for 0.4 wt. % LS and LSPEG.

To further probe the viscoelastic nature of these pastes, the storage and loss modulus of each superplasticizer concentration were measured as a function of strain magnitude at constant frequency of 1 Hz. The storage modulus (G') reflects elastic responses while the loss modulus (G") reflects viscous dissipation, thus providing complementary information on the properties of the cement paste. In rheology, tan  $\delta$  represents the ratio of the loss modulus to the storage modulus, providing a measure of the relative viscous and elastic responses of a material. In the plots of G' as a function of strain magnitude shown in Figure 11.3.3.4 (a), and at low strains the storage modulus is nearly independent of strain magnitude but decreases almost linearly at higher strains. Similarly, at low strains, OPC and formulations containing LS or LSPEG all have similar values for tan  $\delta$  that decrease rapidly until a critical strain of *ca.* 1%, suggesting the

elastic response dominates until the applied stress field results in yielding of the paste. For higher strains, tan  $\delta$  increases monotonically as a function of strain magnitude, but the OPC paste plateaus at a value near 1 while those containing LS or LSPEG have tan  $\delta$  values ranging from 1.2-1.4, as shown in Figure 11.3.3.4 (b), suggesting the viscous response is dominating. The value of G' at low strains is lowest for the formulation containing LSPEG, consistent with the steric effects exerted by adsorbed LSPEG on the surface of the cement particles, which could reduce the cohesive strength of the particle network. At higher strains, the storage modulus for both the LS and LSPEG formulations is higher than that of OPC, which implies that the adsorbed superplasticizers may impart slightly greater residual elasticity in the deflocculated state relative to the viscous responses as also suggested by the Krieger-Dougherty analysis. Overall the rheology results are consistent with the slump data in indicating that LSPEG effectively plasticizes OPC.

#### 11.3.4 Assessment of workability in mortar

To explore the effects of LSPEG in the presence of aggregate, mini-slump tests were performed on mortar composed of 25% portland cement and 75% sand at w/c of 0.5. Competitive adsorption onto aggregate surfaces can result in a lower amount of effective superplasticizer, which reduces the workability of the paste [135]. Due to the complex chemical structure of lignosulfonates they have avid adsorption onto cement particle surfaces, but no steric interactions which is why very high concentrations are necessary [126]. In preliminary tests, a similar trend was observed in slump tests on mortar as in OPC, and the results are shown in Figure 11.3.4.1. However, while the samples containing LS had a monotonic increase in slump values, the LSPEG samples had the highest slump spread and slump height difference at 0.4 wt. % LSPEG. This suggests that increasing the concentration beyond 0.4 wt. % of PEG-grafted lignosulfonates resulted in an additional interaction involving the aggregate that requires further study.



Figure 11.3.4.1. Slump spread and slump height difference for superplasticizers in mortar pastes at different concentrations (in wt. %).

Polycarboxylate ethers are the most effective superplasticizer due to their enhanced steric interactions, and recent studies have tried to mimic this by grafting polymers onto lignite backbones [136]. This is have proven to be quite effective as the ionic strength of the cement pore solution is well above the limit for coagulation [36]. As a result, electrostatic interactions alone are not sufficient to provide high levels of plasticization. By grafting PEG onto lignosulfonates, the steric effects of this commonly used superplasticizer were enhanced. Addition of these steric groups increased the slump spread of mortar pastes by 20% when compared to the non-PEG-grafted lignosulfonates. However, the significant increase in slump values observed in mortar indicates that PEG grafting of lignosulfonate could be an effective strategy for improving the performance of this important superplasticizer.

## 11.3.5 Compressive strength development and microstructure

From the paste studies it has been demonstrated that LSPEG acts as an effective superplasticizer comparable to that of PCE due to its enhanced steric interactions compared to lignosulfonates. However, lignosulfonates are known to have retardation effects, resulting in a delay of early-age strength [137]–[139]. In order to see the effects of retardation on early-age strength on LSPEG the compressive strength of four different concentrations of LSPEG was tested at 1, 3 and 7 days.

The results of the compressive strength testing are shown in Table 11.3.5.1. Retardation effects are expected to affect the 1-day compressive strength the greatest. Up to 0.4 wt. % LSPEG there did not appear to be any impact of retardation as the 1-day strength is 60% greater than the control with 0 wt. % LSPEG. At 0.8 wt. % LSPEG however, there seems to be a significant effect of retardation as the compressive strength was lower than the control. Also during the testing of the sample, the sample was deforming in shape as the force was applied. This shows that the retardation effects of LSPEG on cement strength are concentration dependent but only above a critical concentration. By three days the retardation appeared to have no impact on the compressive strength, as the value for 0.8 wt. % LSPEG was actually greater than the other formulations. This suggests that there is some preferential interaction occurring with either one of the clinker phases responsible for strength tricalcium silicate (C<sub>3</sub>S) or tricalcium aluminate (C<sub>3</sub>A) at high concentrations of LSPEG. Lignosulfonates have been shown previously to have preferential interactions with both C<sub>3</sub>S and C<sub>3</sub>A [137]. Similarly for 7-day compressive strength, the greater the concentration of LSPEG the greater the strength gains were observed. It is interesting to note that for 0.8 wt. % LSPEG the final 7-day compressive strength was 32% greater than the control. This further suggests that there is a preferential reaction of the LSPEG with  $C_3S$  or  $C_3A$  as the slope for the progression of strength over time is the greatest.

Sample	1 day (psi)	3 day (psi)	7 day (psi)
0.0 wt. % LSPEG	$1487.5 \pm 28.4$	$2562.5 \pm 42.6$	$3459.2 \pm 21.3$
0.2 wt. % LSPEG	$2327.5 \pm 40.3$	$2594.1 \pm 31.5$	$3615.0 \pm 24.1$
0.4 wt. % LSPEG	$2437.5 \pm 47.5$	$2666.2 \pm 17.4$	$3890.8 \pm 24.2$
0.8 wt. % LSPEG	940 ± 15.7	2821.3 ± 39.4	4577.5 ± 25.3

Table 11.3.5.1. Compressive strength values with increasing concentration of LSPEG

From Table 11.3.5.1 it can be seen that even minimal amount of added LSPEG results in an increase in compressive strength. As mentioned previously, an increase in compressive strength is generally attributed to a higher degree of hydration, which results in a decreased porosity [133], [140]. In Section 7.3 it was shown that LSPEG is interfacially active, which may result in it preferentially occupying the paste-air interface hence affecting the porosity. In order to explore this further, nano-CT was performed on 0 and 0.8 wt. % LSPEG at 1 and 3 day time points.

In order to use computed tomography to reconstruct the microstructure of the sample, 601 radiographs were taken of each sample at high resolution and then reconstructed using Avizo 3D reconstruction software. Due to the complex structure but similar chemical makeup of all the hydrated products of the cement paste, it is impossible to accurately predict the hydrated phase based on the intensity of the radiograph. In addition, over time the degree of hydration of all these products changes, two different phases with varying degrees of hydration can appear as the same on the radiograph further making it impossible to distinguish. Since in this study the central focus was to understand how LSPEG affected the porosity of the sample, the sample was decided into three phases namely; brightest, gel and pore phase. The samples were thresholded based on the intensity in the grey scale radiograph. A sample with a higher atomic number (Z) would have a higher attenuation coefficient and hence have a brighter intensity compared to that of air.

Ortho slices for all four samples from the nano-CT data can be seen in Figure 11.3.5.1, along with the percentage of each phase in Table 11.3.5.2. From the ortho slices it can be seen that there are significant differences between the control and 0.8 wt. % LSPEG, suggesting that the presence of LSPEG in the paste is affecting the amount and degree of hydration of each phase present. This would be difficult to quantify using Rietveld analysis due to the varying crystal structures present for each hydrated phase. However, the Ca:Si ratio was verified for all the phases using energy-dispersive spectroscopy (EDS) while taking SEM images of each samples. The SEM images are shown in Figure 11.3.5.2. EDS was run on ten arbitrary spots that were chosen for each image, and for each sample ten images were taken at different locations. For the 1-day samples, LSPEG appeared to have a larger grain size compared to the control, and also a significant decrease in porosity. This was confirmed by the particle size distribution performed on the SEM images shown in Figure 11.3.5.3. For both 1 and 3 day LSPEG had a higher particle size distribution compared to the control. Nano-CT data shown in Table 11.3.5.2, also confirmed this data as the brightest phase of LSPEG is close to double that of the control. The porosity of the LSPEG on the other hand was three times less than that of the control sample. This suggests that the interfacial activity of LSPEG results in a decrease in the porosity. In the 3-day data, the brightest phase is again significantly greater than the control, and the porosity is similar to that of 1-day LSPEG. Whereas for the control there is a significant drop in porosity over the two days, which is generally expected [141]. This further confirms that the interfacial activity of LSPEG is responsible for the decrease in porosity. It is interesting to note

that the porosity for three-day control is 5.36%, which is slightly greater than 5.11% of LSPEG but the three-day compressive strength of LSPEG is significantly higher than control. This suggests that the porosity % alone does not completely describe the strength gains seen with LSPEG. These strength gains can either be attributed to the brightest and gel phase or the pore size distribution. Since it is impossible to accurately predict the chemical composition of the brightest and gel phase, the pore size distribution was examined.



Figure 11.3.5.1. Reconstructed ortho slices of (a) 1-day	, (b) 3-day control, (c) 1-day LSPEG and
(d) 3-day LSPEG	

Table 11.3.5.2. Percentage of each phase calculated from tomography data

Sample	Brightest Phase (%)	Gel Phase (%)	Pore Phase (%)
Control – 1 day	18.48	62.67	18.85
Control – 3 day	13.23	81.65	5.36

0.8 wt. % LSPEG -	31.77	61.83	6.4
1 day			
0.8 wt. % LSPEG -	26.59	68.04	5.11
3 day			



Figure 11.3.5.2. SEM images of 1-day (a) control and (b) LSPEG samples



Figure 11.3.5.3. Particle size distribution for (a) 1-day and (b) 3-day sample for both 0.0 and 0.8 wt. % LSPEG

The pore size distribution is shown below in Figure 11.3.5.4 (a) and (b) for both 1-day and 3-day samples. As seen from the values shown in Table 11.3.5.3, LSPEG had the lowest pore percentage, which was attributed to the LSPEG interfacial activity and is further confirmed by the pore size distribution data. Both samples at time points had a majority of pores below 10 nm,

which are generally the porosity, associated with the hydrated phases and mainly affects the shrinkage [142]. As shown in both Figure 11.3.5.4 (a) and (b) the histogram for LSPEG shown in blue is shifted to the left compared to the control samples for both 1 and 3 days. The control sample has a much more wider distribution. For the 3-day sample the majority of the pore size distribution was below the 50-60 nm range, which suggests that these are medium size capillaries. For the control sample however, there were capillaries beyond that range which suggests the presence of large capillaries, which can be deleterious to strength [142]. This confirms that the LSPEG not only influences the porosity but also the types of pores that are formed in the system.



Figure 11.3.5.4. Pore size distribution for (a) 1-day and (b) 3-day sample for both 0.0 and 0.8% LSPEG

## 11.3.6 Isothermal calorimetry

The issue of retardation due to PEGylated lignosulfonates requires further investigation. Generally a high dosage of lignosulfonates is needed to improve workability, and the retardation scales with concentration. The mechanism is associated with lignosulfonate adsorption onto particle surfaces, which interferes with hydration reactions involving dissolution and remineralization [15], [143]. In order to gain understanding into whether PEG-grafted lignosulfonates also affect these reactions, isothermal calorimetric measurements were performed, and the results are shown in Figure 11.3.6.1. The samples were allowed to equilibrate for 45 min then were measured over the course of 120 h to characterize the acceleration and retardation periods.



Figure 11.3.6.1. Isothermal calorimetry data for LSPEG at 0.0, 0.2, 0.4 and 0.8 wt. % of added superplasticizer at a 0.40 water to cement ratio

Evidence of retardation in samples containing LSPEG is seen in the extended dormant period. As the concentration of LSPEG increased, the curves seemed to shift more to the right. The major hydration peak that is noticed in Figure 11.3.6.1 is the alite (C<sub>3</sub>S) reaction. A shoulder follows this major peak and this is generally associated with the renewed dissociation of  $C_3A$  resulting in the formation of ettringite, which is responsible the setting of the cement paste [127], [128]. As the percentage of LSPEG in paste was increased the formation of ettringite shoulder becomes the dominant peak and keeps shifting to the right. The increase in the intensity of the ettringite peak is clearly shown for 0.2 wt. % and 0.4 wt. % LSPEG. This suggests that LSPEG is primarily interacting with the  $C_3A$  peak and might be responsible for the strength gains. The phenomena of an accelerated formation of ettringite are characteristic to lignosulfonates to a lesser extent and have been previously reported in literature [17], [129]. The shift of the hydration peaks to the right also suggests a delay in set time of the paste. There is a possibility that LSPEG is resulting in good dispersion of C<sub>3</sub>A due to the enhanced steric interactions resulting in it being available to interact with the C<sub>3</sub>S and further maximize the strength development as proposed by Alexander et al and further result in gains in compressive strength seen in Table 11.3.5.1 to a greater extent than non PEGylated lignosulfonates [144]. However, for the 0.8 wt. % LSPEG sample the ettringite peak completely disappears. It is possible that the ettringite peak overlapped with the

 $C_3S$  hydration peak. The normalized heat flow curves shown in Figure 11.3.6.1 (b) follow the same trend as the heat of hydration curves in terms of delay, but the overall maximum heat flow is higher for both 0.2 wt. % and 0.4 wt. % LSPEG compared to the control. This maximum value generally corresponds to a quicker and greater extent of silicate hydration, which is essential since a higher degree of silicate hydration is known to impact the compressive strength [145]. In general, LSPEG does experience retardation as the concentration increases but with an enhanced gain of strength.

#### 11.3.7 Performance of LSPEG in Concrete

LSPEG has shown to be a significant strength enhancer in cement and viscosity modifying agent for both cement and mortar. In collaboration with Bryan Materials Group in Pittsburgh, PA, LSPEG was tested in concrete in a 13.6 kg (30.0 lbs) cement system with added fine and coarse aggregate. The objective of these tests was to ensure that LSPEG works as an effective viscosity modifier and strength enhancer in the presence of aggregate. The slump, air content and compressive strength were measured for different LSPEG concentrations and the data are shown below in Table 11.3.7.1.

The effect of a range of concentrations of LSPEG from 0.2 to 0.6 wt.% was examined in concrete paste. The amount of cementitious material throughout the experiments remained constant, but the amount of water was modified to keep a six-inch slump, which is required in most commercial applications. Mix 1 was the control mix with the absence of LSPEG, and the air content was measured to be 1.6%, using the gravimetric method in accordance with ASTM C138. In mix 2, 0.2 wt.% of LSPEG was added to the system, and as seen from the data below the air content jumped to 6.1% along with a slump increase of two and half inches. Due to the high air content, the mix design did not harden properly and as a result had a lower compressive strength compared to the control for all the time points measured. In general, the air content for most mix designs are limited to between 1.5% and 3.0% due to strengthening issues and the higher the air content, the greater the slump is [146]. To bring the air content down, a standard defoamer was added to the mix design. Mix 3 contained the same specifications as mix 2 with added defoamer, which lowered the air content to 2.9% while maintaining a six and half inch slump. By adding the defoamer, the slump of the system was impacted but this helped the system

gain strength and there was a 1000-psi increase in the compressive strength for all time points when compared to the control. A similar trend was noted for the rest of the mix designs shown in Table 11.3.7, as the amount of LSPEG added increased, there was a significant increase in compressive strength and despite the added defoamer and the low air content, it was hard to main a six-inch slump. The effect of the increase in concentration of LSPEG on the compressive strength is not as clear because there is also a decrease in the water/cement ratio to maintain the six-inch slump, which inherently leads to higher strength. LSPEG showed a minimum of 20% reduction in water between mix design 1 and 7. The actual reduction is probably much larger, as there is a two and half inch difference between the slump of mix design 1 and 7. The data also suggests that above 0.4 wt. % of LSPEG, the mechanism of viscosity reduction is changing. This can be attributed to the non-adsorbing polymers in the pore solution. According to the adsorption measurements shown in Figure 11.3.2.1, 0.08 wt.% LSPEG completely saturated the cement surface. At a concentration of 0.4 wt.% LSPEG, theoretically there should be enough to saturate the surfaces of both fine and coarse aggregate; and have some non-adsorbing polymers floating in solution. Adsorption measurements on aggregate would need to be performed to confirm this. The non-adsorbing polymers present in mix design 6 and 7 might be resulting in lubrication effects, which would explain the sudden jump in the slump values. Finally, the data presented in Table 11.3.7 suggests that LSPEG shows strength enhancing and viscosity modifying behavior in concrete paste also and can be used in conjunction with other construction chemicals such as defoamers.

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Water/Cement	0.48	0.48	0.478	0.453	0.437	0.422	0.397
LSPEG (wt.%)	0.0	0.2	0.2	0.3	0.4	0.5	0.6
Slump (in)	6.50	9.00	6.50	6.75	6.50	8.50	9.00
Air (%)	1.6	6.1	2.9	1.9	1.9	1.7	1.8
3-Day (psi)	3770	N/A	4600	5220	5570	6120	5670
7-Day (psi)	4480	3540	5580	6370	6840	7560	7690
28-Day (psi)	5810	4110	6840	7590	8220	8850	9020

Table 11.3.7.1. Performance of LSPEG in concrete mix designs

# 11.4 Conclusion

PEG grafting of lignosulfonates results in improved plasticization and dispersion properties compared to base lignosulfonates. Using TOC and zeta potential measurements, it was demonstrated that PEG-grafted lignosulfonates plasticize the cement using a different mechanism compared to unmodified lignosulfonates based on steric effects. These steric interactions enhanced workability assessed by rheometric and slump measurements and also increased compressive strength. PEGylated lignosulfonates provided significantly enhanced viscosity reduction and lower yield stress compared to lignopolymers synthesized using CRP. This study shows that PEGylated lignosulfonates can be used as effective strength enhancers and viscosity modifying agents in cement, mortar and concrete. Further studies are required to elucidate the interplay between lignin characteristics, including molecular weight and charge density, and polymer-grafting variables, such as graft density and molecular weight, but this approach appears to be promising for improving the dispersing power of lignosulfonates.

#### 12. Effects of PEGylated lignosulfonate superplasticizer on metakaolin/OPC blends

\*Calorimetry experiments were performed by Kurtis group at Georgia Institute of Technology

## 12.1 Introduction

Metakaolin is one of the few SCMs that does not negatively affect the mechanical properties of the cement and instead provides some added benefits such as an increase in durability in contrast to other SCMs, such as kaolin [147]. Metakaolin is a fine aluminosilicate material that has high pozzolanic activity (50-55% SiO<sub>2</sub> and 40-45% Al<sub>2</sub>O<sub>3</sub>) and is produced by the calcination of kaolin clays at 700 °C. The reactivity of metakaolin has been linked to its content of pentacoordinated aluminum ions that are formed during calcining. The addition of 10% or less by weight to cement can produce relatively large increases in strength, impermeability and ductility [24], [147], [148]. Mixes containing less than 10% metakaolin have resulted in a 20% increase in compressive strength at 1 day and 40% at 28 days. The increase in compressive strength is a result of the densification of the microstructure of the paste, which is due to the pozzolanic and hydration reactions taking place leading to greater impermeability and enhanced cyclic freeze-thaw stability of the materials [149], [150].

Due to the improved durability and mechanical strength of metakaolin-cement pastes, there is increased interest to see whether plasticizers could decrease the viscosity of the paste, while maintaining the mechanical properties making it more conducive to commercial applications. Hydration effects on the rheological behavior of cement pastes alone have been studied in detail over the past few decades [127], [129], [151]. As a result, several different plasticizers have been explored extensively to improve cement paste rheology and their effects on other physical properties [29], [145]. In comparison to cement pastes, the hydration chemistry of metakaolin is not very well understood, which can lead to unexpected effects on rheology in a blended metakaolin-cement paste [152]. Consequently this makes it difficult to understand and predict how plasticizers will affect the blended metakaolin-cement. In this study, attempts are made to understand the rheology of metakaolin paste and the effect of LSPEG and PCE on paste rheology.

#### 12.2 Experimental

Metakaolin-cement pastes of up to 30 wt. % (metakaolin:OPC) were prepared in accordance with ASTM C305. Rheometry, calorimetry and hydration studies were performed to understand how the LSPEG impacts the metakaolin-cement paste. In particular, rheology was only performed to examine the initial effects of the polymers on the flocculation of the metakaolin-OPC paste within the first 5 min after mixing. Two concentrations of LSPEG were tested (0.4 g and 0.8 g) with a comparison to PCE. The metakaolin was characterized by measuring the BET surface area and XRD.

#### 12.3 Results

#### 12.3.1 Metakaolin characterization

The metakaolin powder was characterized using XRD and the trace can be found in Appendix C. The BET surface area of the metakaolin powder was measured to be 12.7153,  $\pm 0.0427 \text{ m}^2/\text{g}$ .

### 12.3.2 Metakaolin – OPC paste rheology

Particles in cement clinker are attracted to each other due to the colloidal interactions that occur between them during the hydration process. The steric interactions imparted by PCE and LSPEG help reduce the strength of colloidal interactions and allow for viscosity reduction. However, metakaolin does not have the same strong colloidal interactions as clinker particles. Despite having a large surface area, they have a much lower yield stress, which is due to the percolation of early reaction products rather than colloidal interactions. Metakaolin paste alone can therefore be seen as a semi-dilute suspension of non-Brownian, non-colloidal and non-deformable particles in a highly viscous Newtonian fluid. As a result of the difference in particle-particle interactions, there is uncertainty over how plasticizers that primarily rely on steric interactions will perform [153]. However, for most commercial applications, metakaolin is used as a blend with cement and it is generally less than 30% by weight [24]. Metakaolin and OPC blends have a significant increase in surface area, which includes both the colloidal and non-colloidal

interactions making it difficult to disperse. In addition, there is a density difference between metakaolin and cement that can lead to sedimentation. In order to effectively disperse such a system it is essential to provide steric interactions for the colloidal interactions, lubrication effects for the dispersion of the early reaction products and good adsorption to both metakaolin and cement and control over pore solution viscosity to prevent sedimentation.

In this study high concentrations of both LSPEG and PCE (0.4 and 0.8 wt. %) were tested on 10% metakaolin and cement blends. Due to the lack of significant steric interactions of LS, it was not examined in this head to head comparison. These two concentrations were chosen, because 0.4 wt. % of polymer was above the concentration needed to saturate the cement particle as seen from Figure 11.3.2.1. The actual concentration needed to saturate the cement particle is 0.08wt. % of polymer. The lower concentration of 0.4 wt.% allowed for enough polymers in solution to also coat the metakaolin particles, which have a higher surface area than the cement particles. The higher concentration of 0.8 wt. % allowed for an abundance of non-adsorbing polymer floating in solution. There have been many studies showing that non-adsorbed polymers contribute to lubrication effects and decrease slurry viscosity by depletion flocculation [127]. Also higher concentrations of polymer would also result in an increase in the elasticity of the system and possibly reduce sedimentation effects. The viscoelastic behavior of the two polymers in the blends was analyzed to understand the state of the dispersion and its mechanism.

The viscosity of the polymer samples in OPC alone and metakaolin-OPC blend were measured as a function of oscillation strain and are shown in Figure 12.3.2.1 (a) and (b) respectively. This comparison allowed delineation of the effects of metakaolin on the system. Figure 12.3.2.1 (a) shows the effect of the polymers on the viscosity of OPC alone. As the concentration of PCE increased the viscosity of the paste decreased. However, for LSPEG as the concentration increased there was an increase in viscosity at lower oscillation strain but then the sample shear thinned resulting in a decrease in viscosity. This increased viscosity at lower strains is hypothesized to be a sign of flocculation between the LSPEG particles possibly due to increased elasticity. The increased elasticity can be attributed to the abundance of non-adsorbing polymers in the paste. In the metakaolin-OPC blends shown in Figure 12.3.2.1 (b) the effects of concentration were clearer. The blend itself had a viscosity value of 4000 Pa.s, four times that of OPC alone. The viscosity curves were grouped based on the concentration, the 0.4 wt. % for both PCE and LSPEG had similar to values to each other and then the 0.8 wt.% were also together. As

the concentration for both polymers increased the viscosity decreased. The viscosity reductions associated with the lower concentration can be attributed to the adsorbed polymers, and the higher concentration to the non-adsorbing polymers. None of the samples sedimented significantly, which suggested that the polymers were interacting strongly with both metakaolin and cement and preventing extensive aggregation. However, the shapes of the curves for both the polymers were very different. The LSPEG samples experienced a decrease in viscosity with an increase in oscillation strain, suggesting that the sample was shear thinned. Whereas, the PCE samples did not have such a significant decrease, suggesting more elastic behavior of the sample.



Figure 12.3.2.1 Real viscosity as a function of oscillation strain for LSPEG and PCE in (a) OPC and (b) metakaolin-OPC blend.

To further understand the state of dispersion, Krieger-Dougherty analysis was performed on the viscosity data at two different strains high (50%) and low (0.05%). The intrinsic viscosity for both blends is tabulated in Table 12.3.2.1. The intrinsic viscosity values for the OPC paste showed significant shear thinning as shown by the difference between the low and high strain values. However, when superplasticizers were added the difference between the high and low strain intrinsic viscosity was much smaller, suggesting a dominant elastic behavior. This behavior is amplified in the metakaolin-OPC blend. Especially at higher concentrations, the difference between the high and low strain values was minimal. At 0.8 PCE the high strain intrinsic viscosity value is higher than the low strain, which confirms the elastic behavior seen in Figure 12.3.2.1.This can be attributed to the non-adsorbed polymers present in the paste. The PCE sample might have had a stronger elastic behavior in pore solution due to the strong hydrophilicity of the polymer itself. The second virial coefficient, A<sub>2</sub> is a good indication of the

hydrophilicity as it is a measure of the strength of solute-solvent interactions [154]. The coefficient for both LSPEG and PCE was measured using vapor pressure osmometry and were 1900 and 9200 mol.mL/g<sup>2</sup> respectively. The  $A_2$  coefficient of PCE was five times greater than LSPEG, which explains the elasticity seen in the viscosity data and the Krieger-Dougherty analysis. This would result in higher concentrations of LSPEG having a lower intrinsic viscosity compared to PCE. At the lower concentrations PCE and LSPEG have very similar high strain values again confirming the trends seen in the viscosity data.

Table 12.3.2.1. Intrinsic viscosity values for LSPEG and PCE in OPC and metakaolin-OPC blend

	OPC		Metakaolin-OPC Blend		
	Low Strain (0.05%)	High Strain (50%)	Low Strain (0.05%)	High Strain (50%)	
OPC	8.42	5.13	9.58	6.32	
0.4 LSPEG	3.23	2.9	7.39	5.22	
0.8 LSPEG	3.99	3.34	4.29	3.87	
0.4 PCE	3.92	3.46	6.44	5.32	
0.8 PCE	3.23	2.91	4.62	4.67	

To understand more about the effect of the superplasticizers of the viscoelastic behavior of the paste, the tan  $\delta$  values were plotted for each blend. The data for OPC and metakaolin-OPC blend are shown below in Figure 12.3.2.2. By adding metakaolin to OPC paste, the total solid content increased, which starts hydrating and forming a combination of colloidal and non-colloidal interactions. This results in an increased elastic contribution due to network formation. For the majority of the oscillation strain measured the response is primarily elastic. As the oscillation strain increased to 30% the blend started to deform past the yield point and resulted in a viscoelastic paste. The tan  $\delta$  values for LSPEG and PCE were measured for both blends and are shown below in Figure 12.3.2.3 (a) and (b) respectively. In Figure 12.3.2.2, the metakaolin-OPC blend had a critical strain of about 3.8% above which the paste disaggregates and starts to flow. When comparing this critical strain to the data shown in Figure 12.3.2.3 (b), it can be seen that by the addition of any amount or superplasticizer this critical strain is shifted to lower values. This suggests that the energy required to break these interactions is decreasing by the

addition of superplasticizers. Both 0.4 and 0.8 LSPEG had similar critical strain values and they also followed a similar pattern. The higher concentration of LSPEG however had a more elastic response compared to the lower concentration, which can be due to the flocs being formed between the particles. On the contrary, for PCE the higher concentration had a higher critical strain than the lower one. This suggests that the bonds in the 0.8 PCE are much more elastic which is expected due to its strong hydrophilic behavior. Overall, both 0.8 LPSPEG and PCE have similar viscoelastic behavior, however 0.8 LSPEG is significantly less elastic than PCE.



Figure 12.3.2.2. Tan  $\delta$  versus oscillation strain for OPC and metakaolin-OPC blend



Figure 12.3.2.3. Tan  $\delta$  versus oscillation strain for LSPEG ad PCE in (a) OPC and (b) metakaolin-OPC blend

12.3.3 10 wt. % Metakaolin-OPC blend

To examine macroscopic effects on the rheology, the slump spread was measured for metakaolin-cement pastes. The slump height and slump spread were measured for each sample

and are shown in Figure 12.3.3.1. The concentration of PCE was kept constant at the recommended dosage, whereas LS and LSPEG were measured at 0.4 wt. % as shown in Figure 12.3.3.1 (a and b) and at 0.8 wt. % as shown in Figure 12.3.3.1 (c and d). Three different w/cm (water/cementitious) ratios were tested: 0.4, 0.45 and 0.5. These ratios were decided based on the amount of metakaolin added to the paste. At 0.4 wt. % for all the w/cm ratios PCE had the highest slump spread and slump height difference. LSPEG had significant improvement over the non-PEGylated LS over all w/cm ratios. The addition of any superplasticizer increased slump relative to the control sample. At 0.8 wt. %, non-PEGylated and PEGylated lignosulfonate had larger slump than recommended dosage of PCE with close to a 50% improvement in slump over control. The difference in slump spread between LS and LSPEG was significant at lower w/cm ratios compared to higher ones. At 0.5 w/cm, there is not a significant difference in LS and LSPEG. Also, all three superplasticizers had a slump over 10 cm, which is consistent with a significant reduction in yield stress of the paste. The effect of three superplasticizers at 0.40 and 0.45 w/cm ratio on the paste is of more importance, as that is the most commonly used w/cm ratio. Figure 12.3.3.1, suggests that LSPEG is comparable to PCE at 0.4 wt.%, but has a significant increase in slump at 0.8 wt.%. This behavior is characteristic of lignosulfonates, as generally higher dosage is needed to achieve improvement in workability [26]. However, as previously seen in Figure 11.3.3.1 the LSPEG adsorbs to the cement surface as a monolayer due to the steric interactions of the PEG compared to LS, which adsorbs as a multilayer. The increase in slump as a function of concentration for LSPEG suggests that the metakaolin interacts differently with the LSPEG compared to OPC. This can be attributed to the preferential interactions with increased amount of aluminosilicates present in the metakaolin-OPC blend as mentioned in Section 11.3.5.



Figure 12.3.3.1. (a) Slump height and (b) slump spread for 0.4 wt.% plasticizer dosage for LS and LSPEG. (c) Slump height and (d) slump spread for 0.8 wt.% plasticizer dosage for LS and LSPEG

In addition to slump tests, rheology was performed on the samples to understand the effect of superplasticizers on viscosity. Rheology was performed at the lowest w/cm ratio, 0.4 for LSPEG and PCE. The viscosity data as a function of oscillation strain is shown in Figure 12.3.3.2. The control sample had the highest viscosity value over all strains, which was expected. Samples with 0.8 LSPEG had the lowest viscosity over all the strains followed by PCE and then 0.4 LSPEG. The same trend was observed with slump tests. All the samples showed non-Newtonian behavior, but PCE and 0.8 LSPEG showed significant shear-thinning behavior with some elastic response at higher strains as seen in Section 12.3.2. LSPEG had a ten-fold decrease in viscosity to PCE at lower strains. This significant decrease in rheology was not prominent from slump tests. The rheology data suggests that the PEGylation of lignosulfonates results in an improvement in workability and can be used in metakaolin-cement pastes as an effective viscosity reducer.



Figure 12.3.3.2. Real viscosity versus oscillation strain for 10 wt. % metakaolin (MK)-cement pastes

It is important to ensure that the superplasticizer does not significantly impact the formation of hydration products. This was measured using isothermal calorimetry for up to 70 h after mixing and the hydration curve is shown in Figure 12.3.3.3. The control sample has one peak that is split into two around 9-10 h. The first peak corresponds to the hydration of  $C_3S$  phase and nucleation of portlandite and the second peak is associated with the reaction of the  $C_3A$  phase [25]. The PCE sample has a similar curve shape to the control, except the formation of the phases is delayed by 1-2 h. The 0.4 LSPEG and 0.8 LSPEG curves on the other hand have a single peak, which is different than the control and PCE sample. This suggests that there is a difference in the mechanism of hydration. The 0.4 LSPEG sample was shifted by about 10 h from the control and 0.8 LSPEG was shifted by 30 h from the control, which suggests that the LSPEG is strongly interacting with the metakaolin. Also the change in the shape of the peak can suggest the decrease in the formation of portlandite, and the C<sub>3</sub>A reaction dominating. The decreased formation of portlandite would result in a higher compressive strength. It is also interesting to note that from Figure 12.3.3.4, the cumulative heat of hydration of 0.4 and 0.8 LSPEG samples is lower than the other two samples.



Figure 12.3.3.3. Hydration curves versus time for 10 wt.% metakaolin (MK)-cement pastes



Figure 12.3.3.4. Cumulative heats of hydration for 10 wt. % metakaolin (MK)-cement pastes

To understand how this calorimetry behavior would affect the hydration products, XRD was conducted on all the samples and is shown in Figure 12.3.3.5. Overall, looking at the XRD traces the same peaks was present for all samples, which shows that the same hydration products are being formed. This was not expected as based on the hydration data; the absence of some peaks was expected for the LSPEG sample compared to PCE and the control. Since one of the most significant properties influenced by metakaolin is the hydration of the clinker, two of the most significant hydrate phases were followed up in detail using the XRD traces. These hydrate

phases are ettringite (E) and portlandite (P) and can be seen in Figure 12.3.3.5 [155]. The normalized intensities of these phases for all samples are also shown in Table 11.3.4.1. The XRD traces were normalized against the intensity and as seen there is no significant difference between the three samples in the formation of ettringite and portlandite. An evolution study in the future would need to be performed for these phases to quantify the difference in the formation of these phases.



Figure 12.3.3.5. XRD curves for 10 wt. % metakaolin (MK)-cement pastes

12.3.4 30 wt. % Metakaolin-OPC blend

The slump height difference and slump spread were measured for each sample and are shown in Figure 12.3.4.1. Only two w/cm (water/cementitious) ratios were tested (0.55 and 0.6), as the metakaolin-cement paste did not flow below 0.55 w/cm. At 0.4 wt. % for all the w/cm ratios PCE had the highest slump spread and slump height difference. LSPEG did not have significant improvement over the non-PEGylated LS over all w/cm ratios. For 0.4 wt. %, at 0.55 w/cm there was no improvement in slump for LS and LSPEG over the control. PCE only had a slight improvement in slump. At 0.8 wt. %, PEGylated lignosulfonate had improved performance

compared to all the samples at both 0.55 w/cm and 0.6 w/cm. There was greater than a 50% improvement in slump over the rest of the samples at 0.60 w/cm. This is inconsistent with the data observed at 10 wt. % metakaolin pastes, as LSPEG had significant differences in flow behavior at lower w/cm ratios. Also, LSPEG imparted significantly larger slump than LS, which was not observed for 10 wt. % metakaolin pastes. This suggests that there is a different adsorption behavior for the LSPEG at both concentrations for 30% metakaolin-OPC blends compared to 10%. Additional adsorption experiments at different metakaolin loading need to be performed to understand this interaction.



Figure 12.3.4.1. (a) Slump height and (b) slump spread for 0.4 wt.% plasticizer dosage for LS and LSPEG. (c) Slump height and (d) slump spread for 0.8 wt.% plasticizer dosage for LS and LSPEG

Rheology was performed at 0.6 w/cm for LSPEG and PCE. The viscosity data as a function of oscillation strain are shown in Figure 12.3.4.2. The control sample had the highest viscosity value over all strains, which was expected. 0.8 LSPEG had the lowest viscosity over all the strains. Both PCE and 0.4 LSPEG were had very similar viscosity values. PCE had a lower viscosity at lower strains and 0.4 LSPEG had a lower viscosity at higher strains. The same trend was observed with slump tests. All the samples showed non-Newtonian behavior, 0.4 LSPEG

showed the most significant shear thinning behavior followed by 0.8 LSPEG and PCE. LSPEG had a ten-fold decrease in viscosity compared to PCE and a hundred-fold decrease compared to metakaolin-cement paste. The viscosity reduction was also prominent in the slump tests, unlike 10% metakaolin blends. It is also interesting to note that the elastic behavior is not as prominent in the viscosity curves as seen in the 10% metakaolin-OPC blend. This suggests that for 30% metakaolin-cement blends, there was a significant increase in surface area and 0.8 wt.% LSPEG was only saturating the surface with a minimal amount of non-adsorbing polymer in the solution. Overall, the rheology data measured supports the data from slump tests very well. This suggests that PEGylation of lignosulfonates can provide significant improvement in workability in 30% metakaolin-cement pastes.



Figure 12.3.4.2. Real viscosity versus oscillation strain for 30 wt. % metakaolin (MK)-cement pastes

The hydration curve for the samples is shown in Figure 12.3.4.3. The data from the control sample are not shown in the Figure 12.3.4.3 because it had a very high rate of heat evolution compared to the other samples. The control sample had a hydration curve shape to that of the PCE sample despite the higher cumulative heat of hydration. The formation of the phases in the PCE sample is delayed by 1-2 h. It is important to note that the shape of the peak is different for the 10 wt. % and 30 wt. % metakaolin. For the 30 wt. % sample the peak on the left is
significantly lower and appears to look like a shoulder rather than two peaks as seen in the 10 wt. % sample. It has been previously reported in literature that metakaolin decreases the formation of portlandite, which is possibly why the intensity of the peak is lower [25], [156]. The presence of the shoulder significantly diminishes for the 0.4 LSPEG and 0.8 LSPEG samples. The difference in peak shapes for the LSPEG samples is consistent with the data observed for the 10 wt. % metakaolin paste, suggesting a different mechanism of hydration. The 0.4 LSPEG sample was shifted by about 2 h from the control and 0.8 LSPEG was shifted by 15 h from the control. This is significantly lower than 8 and 20 h respectively that were observed for the 10 wt. % metakaolin paste. This provides evidence that the reactivity of metakaolin and LSPEG is increasing as the amount of metakaolin in the paste increases. Also the change in the shape of the peak can suggest the decrease in the formation of portlandite, and the C<sub>3</sub>A reaction dominating. It is interesting that the cumulative heat of hydration for 0.4 and 0.8 LSPEG is very close to that of PCE as seen in Figure 12.3.4.4, unlike in the 10 wt. % metakaolin-cement pastes. This further confirms that the LSPEG is reacting with the metakaolin, which results in the production of more heat. XRD was conducted on all the samples and is shown in Figure 12.3.4.5 along with a detailed look at the ettringite (E) and portlandite (P) phase. The same peaks were present for all samples, which shows that the same hydration products are being formed. Again, this was not expected, as there is a significant change in the peak shape as shown in Figure 12.3.4.3 between all three samples. However, the relative intensity of these peaks is different and the normalized intensities for ettringite and portlandite are shown in Table 11.3.4.1. The normalized intensities of ettringite and portlandite in 30% metakaolin-cement paste is compared to 10% metakaolincement paste. As seen from Table 11.3.4.1, as the content of metakaolin increases there is no significant difference in the normalized intensity of ettringite, but there is a decrease in the formation of portlandite for all the samples. The decrease in the formation of portlandite was also observed in the hydration curves. The difference in magnitude of the intensity of portlandite and ettringite between LSPEG, PCE and control is minimal, making it difficult to confirm any preferential reactions. However, a time evolution study in the future highlighting the formation of ettringite and portlandite phase would be helpful to understand this.



Figure 12.3.4.3. Hydration curves versus time for 30 wt.% metakaolin (MK)-cement pastes



Figure 12.3.4.4. Cumulative heats of hydration for 30 wt. % metakaolin (MK)-cement pastes



Figure 12.3.4.5. XRD curves for 30 wt. % metakaolin (MK)-cement pastes

Table 12.3.4.1 Comparison of peak intensity of ettringite and portlandite for 10% and 30% metakaolin (MK)-cement pastes

10% Metakaolin (MK)-cement pastes						
	Control	0.4 LSPEG	0.8 LSPEG	0.325 PCE		
Ettringite	0.00069	0.00059	0.00055	0.00073		
Portlandite	0.00177	0.00142	0.00145	0.00133		
30% Metakaolin (MK)-cement pastes						
	Control	0.4 LSPEG	0.8 LSPEG	0.325 PCE		
Ettringite	0.00058	0.00075	0.00085	0.00053		
Portlandite	0.00079	0.00069	0.00082	0.00083		

### 12.4 Conclusion

Slump tests and rheology experiments verified that PEGylation of lignosulfonates effectively reduces the viscosity of metakaolin cement blends of up to 30%. The importance on non-adsorbing polymers in the pore solution was also examined for metakaolin-OPC blends. From the slump tests, it can be noticed that both LS and LSPEG interact differently with metakaolin compared to OPC. Also due to the shift in the shape of the hydration curves, it is hypothesized that LSPEG has a preferential interaction with the C<sub>3</sub>A component, which in turn is affecting the

hydration reactions and possibly the compressive strength. As seen from the XRD curves the hydration products are consistent with all samples. However, it is clear from these data that LSPEG can be used as an effective superplasticizer for metakaolin-OPC blends.

#### 13. Commercialization with NSF I-Corps program

The goal of the NSF I-Corps program is to learn more about entrepreneurship that will help university technologies along the path of commercialization. The I-Corps team consisted of a PhD student, principal investigator and an industry mentor. The program uses customer interviews to validate different aspects of the business model canvas. The business model canvas has nine different aspects to it namely; customer segments, value propositions, channels, customer relationships, revenue streams, key resources, key activities, key partners and cost structure. The nine different aspects were populated with hypothesis of how the technology would commercialize. Customer interviews were then used to validate these hypotheses and modify them as necessary. Each one of the nine segments are briefly explained in terms of a business below:

- Customer segments: The different groups of people or organization an enterprise aims to reach and serve.
- Value propositions: The bundle of products and services that create value for a specific customer segment.
- Channels: How a company communicates with and reaches its customer segment to deliver a value proposition.
- Customer relationships: The types of relationships a company establishes with specific customer segments.
- 5) Revenue streams: The cash a company generates from each customer segment.
- 6) Key resources: The most important assets required to make a business model work.
- 7) Key activities: The most important things a company must do to make its business model work
- 8) Key partnerships: The network of suppliers and partners that make the business model work.
- 9) Cost structure: All costs incurred to make the business work.

Throughout the program, I had a chance to interview over sixty people in the span of four weeks from different companies and different backgrounds that work in dispersant related fields. During this process, we were able to populate the business model canvas, modify it according to our customer discovery and finally narrow down who the customer for such a technology would be. We went through different business model canvas iteration every week. The first 20-30 interviews conducted taught us more about some of the products they use in each one of the markets we were considering and their respective drawbacks. In the remaining 40 interviews conducted, despite being different markets there was repetition in the key features desired by an ideal dispersant. These repetitive ideal features were then used to populate the value proposition section of the business model canvas. The final business model canvas reflecting the input from the customer discovery is shown in Figure 13.1. For lignin-based surfactants, the original target customer base included and not limited to coatings, agrochemicals, concrete and cosmetics. However, through the customer discovery process we were able to narrow it down to cementitious applications.



Figure 13.1. Final business model canvas for the commercialization of LSPEG.

During the customer interviews we came across a couple of companies that would serve to be early adopters of our technology. After learning what some of the ideal attributes companies were looking for, we tried to modify our technology to fit some of them. After doing so, we partnered with Bryan Materials Group in Pittsburgh, PA, one of the companies we interviewed, to validate our technology. In order to be able to test our technology, we needed to establish a cost structure and ensure that the final product was worth the cost. The cost of the raw materials (\$1.8/kg), along with up-scaling production costs (\$5000/18 gallon reactor) was accounted for to estimate a cost of about < \$10.00 for a gallon, which is only a little cheaper than the current superplasticizers available. The revenue stream comprised of selling this superplasticizer to cement distributors or partnering with a construction chemical company.

To test the technology, LSPEG was first scaled up in a commercialization facility in multi-gallon reactors. Bryan Materials Group first validated our technology on site with concrete and looked for air entrainment, slump and strength to ensure there were no adverse effects when aggregate and sand were mixed into the cement paste, as most of the work done in lab was with cement paste and that we delivered most of our value propositions. They then helped us identify more specific applications for LSPEG based on the results and production cost for roller compacting concrete applications. Overall, the business model canvas process helped us identify a very specific market for our lignin-based surfactants that we were initially unaware of. It also helped us identify different parts of commercializing a technology that we would have not considered until much further down the line. This help us identify potential problems we may face and address them early on such as our key partners and resources. For lignin-based surfactants for cementitious applications, we initially thought that we could use lignosulfonates manufactured from any company. However, while updating the canvas we realized that our key resource needed to be Borregaard a lignotech company, as they are the only company that produces the type of lignosulfonate we need for PEGylation to achieve the desired properties. This allowed to us to plan ahead and make sure that Borregaard was a key partner in this commercialization process. We are currently working on up-scaling the production of LSPEG to have enough for a pilot scale testing.

#### 14. Conclusions

#### 14.1 Conclusion

Throughout this study different experiments were conducted to understand the interfacial activity of lignin at different interfaces. First the surfactant properties of polymer-grafted lignin were examined for different architectures and hydrophilic grafted polymers at the air-liquid and liquid-liquid interface. The goal was to understand and improve the interfacial activity of lignin. It was concluded that the hydrophobicity of the lignin core was primarily responsible for the properties observed in polymer-grafted lignin. The polymer grafts added hydrophilicity to the hydrophobic core, and all polymer-grafted lignin compositions were soluble in water at 1 mg/mL. All of the polymer-grafted lignin irrespective of architecture showed the presence of a critical concentration, past, which there was minimal decrease in surface tension. Non-modified lignin did not show any such properties and had a slow linear decrease as a function of concentration at the air-liquid interface. The presence of critical concentration is important for surfactant behavior as at this concentration the partitioning of the surface competes with formation of aggregates in the bulk solution [3].

Polymer grafting of lignin also helped produce stable emulsions for extended periods of time that is consistent with polymer grafted nanoparticles. The polymer grafts provided stability due to the steric repulsion between grafts, preventing droplet flocculation and subsequent coalescence. The polymer-graft lignin nanoparticles showed some interesting properties that were unexpected which were attributed to the lignin core interaction and conformation of the polymer grafts. From all the experiments it was clear that the native lignin dominates the properties of these PGLNs, which results in very interesting properties. It was seen that fewer grafts resulted in higher interfacial activity, which further confirms the importance of the core. The polymer grafts enhanced these properties by improving the interfacial activity resulting in higher stability and less aggregation [157]. It was also confirmed that a "grafting-from" architecture is necessary to achieve high levels of interfacial activity. For all the samples tested, kraft lignin was more surface active than the lignosulfonates and PEG grafts had improved interfacial properties over PAM and PAA. Throughout the experiments, it was seen that these polymer-grafted lignin surfactants can be tuned for a variety of applications by changing the

graft density, degree of polymerization, graft polymer and ionic strength, which makes them quite versatile.

These modified lignin surfactants were then tested for dispersant applications in high ionic strength cementitious systems. For cementitious systems, due to the increased charge it was necessary to use dispersants both with electrostatic and steric repulsion. The "grafting-from" architecture helped with steric repulsion for LPAM and LPAA but only at low concentrations. First, both LPAM and LPAA were tested in a model cementitious system of MgO to understand how this new architecture helped dispersion. Second, they were tested in portland cement and compared to the nano-cross linked aggregates. The nano-cross linked architecture did not seem to provide any steric or electrostatic repulsion and resulted in aggregates [21]. The dispersion mechanism for LPAM and LPAA mimicked that of commercial dispersants at low concentrations but did not provide enough viscosity reduction at high concentrations. This was attributed to the presence of flocculated particles of LPAM and LPAA, which were also observed when the surfactant behavior of these samples was being examined. This was confirmed using the Keiger-Dougherty equation in the case of cementitious systems. LPAM and LPAA both also provided good dispersion in much more complex blends of ASCM and portland cement.

PEGylated lignosulfonates were also tested for dispersion of cement due to the enhanced steric and electrostatic repulsion of lignosulfonates compared to kraft lignin. A similar dispersion mechanism to commercial dispersants was noted over different concentrations. This type of dispersion mechanism was confirmed with rheology, as there was increased elastic behavior at lower strains and residual effects at higher strains. The amount and type of adsorption profile also provided some insight for an effective dispersion mechanism. It was noticed that high adsorption leads to enhanced dispersion, and based on steric interactions the polymer could either have a monolayer adsorption or a multilayer adsorption. Monolayer adsorption was common for polymer-grafted lignin systems with significant contributions from steric hindrance. LSPEG also showed no change in the phases being formed and significant improvement in mechanical strength. This is possibly due to the preferential adsorption of the polymer to the airsolid interface as a result of the increased interfacial activity of lignosulfonates as seen from the dispersion. It was also observed that the PEG length did not have an affect on the dispersion properties and was primarily needed for steric effects, which could be due to the

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narrow range of graft lengths tested. LSPEG similar to LPAM and LPAA also provided good dispersion in complex blends of ASCM and portland cement.

In conclusion, architecture of polymer-grafted lignin is critical for leveraging the native interfacial activities of lignin. Due to the native surface activity of the lignin core, it is essential to not completely cover the surface with polymers either by increasing the graft density or the graft length. As a result, it was noticed that grafting density had a greater impact on interfacial properties compared to degree of polymerization in the case of LPAA and LPAM. In the case of PEGylation the lowest graft length (900) of PEG was used as it is hypothesized that the longer graft lengths collapsed onto the core resulting in decreased interfacial activity and the grafting density was maintained at 1.4. The low grafting density compliments the native interfacial activity of lignin with added hydrophilicity. The type of polymer used to graft onto the lignin core seemed to impart its native properties to the system. For instance, PEG showed enhanced steric interactions, PAA collapsed onto the core to shield the charge and PAM showed both charge and steric effects. The overall hydrophilic-liophilic balance of the polymer-grafted lignin is important based on the applications. For dispersant applications, polymer grafting of lignosulfonates with PEG was preferred, whereas for emulsifying applications, kraft lignin is preferred with either PAA or PAM. In summary, the "grafted-from" architecture results in improved interfacial activity at the air-liquid, liquid-liquid and liquid-solid interface.

#### 14.2 Future Work

Work done during the scope of this thesis was limited to showing how the molecular architecture affected dispersant properties. However, the whole spectra of dispersant properties were not examined. When examining how LSPEG affected the strength of the cement, the particle was considered as one phase rather than looking at its individual effects on the different cement components; C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF. This would be a good future experiment, as it would help understand how LSPEG affects the hydration of each one of these phases. It would be beneficial to use a combination of in-situ XRD and Nano-CT to be able to see when the new hydrated phases are forming and how it impacts the microstructure development. This would be helpful to understand the hydration process, as Rietveld analysis alone cannot predict the different phases formed due to the constantly changing and complicated crystal structures. In addition, this would

help to confirm whether LSPEG has preferential interactions with  $C_3A$  as mentioned in Chapter 11 and 12, which lead to strength development. These findings will then help predict the behavior of LSPEG in different types of portland cements. Until now, only Type I/II portland cement has been considered, but if LSPEG does have a preferential intereaction with  $C_3A$  it would be of great use in Type III, early age strength cements. Finally it would be helpful to see how LSPEG performs in other ASCMs such as kaolin and zeolite. This would help create a portfolio of the potential uses of LSPEG in different systems and help with the commercialization process.

Another area that requires some future work is to understand the hydration process of metakaolin and its impact on paste rheology. In this scope of this thesis, only the effects on paste rheology for the first 5 min after mixing were considered. In the first 5 min, the rheology is predominantly shear thinning, however previous studies in the literature have shown that shear thickening is more commonly observed. It would be interesting to note how the behavior changes with time when allowed to run for longer and how the non-adsorbing polymers interact with the hydrating network of colloidal and non-colloidal interactions. It is also necessary to confirm that LSPEG has no deleterious effect on the strength of metakaolin-OPC blends.

My current thesis work helped explain how the surfactant properties of polymer-grafted lignin affect its dispersant properties in different cementitious blends. This work can be used as a template and extended to understand how different architectures and chemical functionalities affects dispersion properties and extend it to a variety of dispersant systems with varying solid loading, ionic strength and viscosity requirements. A simple dispersant system such as magnesium oxide will be used as a starting system. This study would be extremely helpful when working with new systems to understand what factors affect the rheological properties. The first step would be to build a database with at minimum of ten different polymers and measure their various effects on magnesium oxide. These ten different polymers have varying functionalities and similar molecular weight that have been shown in previous studies to have good dispersive properties. First, different physical properties of these polymers will be measured in an aqueous solution such as molecular weight, charge, radius and viscosity. Then properties such as viscosity, charge, sedimentation rate, and adsorption are measured when the polymer is added to the magnesium oxide paste. These properties would be measured at three different polymer concentrations and three different magnesium oxide particle loadings. With the help of pair plots

these would then be used to relate the physical properties and chemical functionalities of the polymer to measured properties of the magnesium oxide paste. This would help clearly identify what properties are responsible for viscosity reduction. Currently, there is a lot of speculation of what properties affect the system and most of them are not characterized for the same system and concentration. Once this global minimization problem has been addressed, and relationships between polymer and paste properties have been developed, machine learning will then be used to predict how a given polymer with a different architecture or functionality would perform in a model system. This would be very useful for formulation science as constantly in industry paste ionic strength or rheology needs to be changed and this would minimize the numerous experiments that need to be performed to understand that.

# 15. Appendices

## 15.1 Appendix A – Surfactant properties

Sample	Concentration	Surface tension	Viscosity (cP)
-	(mg/mL)	(dynes/cm)	
LPAM-17-50	1	66	
	2	64	
	4	64	
	10	64	1.1
	50	55	1.5
LPAM-17-100	1	66	
	2	69	
	4	68	
	10	67	1.5
	50	62	2.0
LPAM-2-50	1	70	
	2	70	
	4	67	
	10	62	1.2
	50	58	2.3
LPAM-2-100	1	69	
	2	69	
	4	63	
	10	63	1.6
	50	62	33
LPAA-17-50	1	64	
	2	62	
	4	62	
	10	54	11
	50	47	15
LPAA-17-100	1	60	
	2	56	
	4	52	
	10	47	12
	50	45	1.2
LPAA-2-50	1	68	
	2	67	
	4	66	
	10	50	13
	50	47	1.5
LPAA-2-100	1	69	1.0
	2	69	
	-	07	

Table 15.1.1 Surfactant properties of LPAM and LPAA

4	66	
10	49	1.6
50	42	1.8

15.2 Appendix B - XRD Characterization of cement and MgO

## XRD characterization of phases

Each cement phase was synthesized using either sol gel or solid state synthesis. Each phases was characterized using X-ray diffraction and was compared to the JCPDS standard. The grey circle represents the characteristic peaks. The composition of portland cement was determined using Rietveld analysis and a goodness of fit of 9.56 and is shown in Table 15.2.1



Figure 15.2.1. XRD pattern of MgO phase (JCPDS: 45-0946)



Figure 15.2.2. XRD pattern of C<sub>2</sub>S phase (JCPDS: 20-0237)



Figure 15.2.3. XRD pattern of C<sub>3</sub>S phase (JCPDS: 42-0551)



Figure 15.2.4 XRD pattern of C<sub>3</sub>A phase (JCPDS: 38-1429)



Figure 15.2.5 XRD pattern of C<sub>4</sub>AF phase (JCPDS: 87-1229, with other impurities)

Component	Composition (%)
Alite	56.1
Arcanite	0.2
Bassanite	0
Belite	21.1
Brownmillerite	13.2
Calcite	0
Lime	0.5
Periclase	5.5
Portlandite	0.1

Table 15.2.1 Composition of Type I/II Portland cement

15.3 Appendix C - XRD Characterization of ASCM



Figure 15.3.1 XRD pattern of Kaolin (JCPDS:29-1488)



Figure 15.3.2 XRD pattern of Zeolite (JCPDS:85-1767)



Figure 15.3.3 XRD pattern of Metakaolin (JCPDS:39-0222)

## 16. References

- [1] H. Chung and N. R. Washburn, "Chemistry of lignin-based," *Green Mater.*, pp. 137–160, 2012.
- [2] S. M. Notley and M. Norgren, *Lignin : Functional Biomaterial with Potential in Surface Chemistry and Nanoscience*. 2008.
- [3] C. Gupta and N. R. Washburn, "Polymer-grafted lignin surfactants prepared via reversible addition-fragmentation chain-transfer polymerization," *Langmuir*, vol. 30, no. 31, pp. 9303–9312, 2014.
- [4] J. D. Gargulak and S. E. Lebo, "Commercial use of lignin-based materials.," *Lignin Hist. Biol. Mater. Perspect.*, vol. 742, no. Figure 1, pp. 304–320, 2000.
- [5] L. Struble and G.-K. Sun, "Viscosity of Portland cement paste as a function of concentration," *Adv. Cem. Based Mater.*, vol. 2, no. 2, pp. 62–69, 1995.
- [6] T. Tomita and T. Hirata, "Dispersant using kraft lignin and novel lignin derivative," US11663536, 2010.
- [7] H. Homma, S. Kubo, T. Yamada, K. Koda, Y. Matsushita, and Y. Uraki, "Conversion of Technical Lignins to Amphiphilic Derivatives with High Surface Activity," *J. Wood Chem. Technol.*, vol. 30, no. 2, pp. 164–174, 2010.
- [8] V. Hornof and R. Hombek, "Surface-active agents based on propoxylated lignosulfonate," J. Appl. Polym. Sci., vol. 41, no. 910, pp. 2391–2398, 1990.
- [9] H. Sixta, *Handbook of Pulp*. Weinheim, Germany: Wiley-Interscience, 2006.
- [10] B. Saake and R. Lehnen, "Lignin," *Ullmann's Encyclopedia of Industrial Chemistry*. 2007.
- [11] C. Schuerch, "The solvent properties of liquids and their relation to the solubitlity, swelling, isolation and fractionation of lignin," J. Am. Chem. Soc., vol. 74, no. 20, pp. 5061–5067, 1952.
- [12] R. Alen, *Basic chemistry of wood delignification*. Finland, 2000.
- [13] J. J. Meister, "Modification of Lignin," J. Macromol. Sci. Part C Polym. Rev., vol. 42, no. 2, pp. 235–289, 2002.
- [14] W. O. S. Doherty, P. Mousavioun, and C. M. Fellows, "Value-adding to cellulosic ethanol: Lignin polymers," *Ind. Crops Prod.*, vol. 33, no. 2, pp. 259–276, 2011.
- [15] M. Y. A. Mollaht, P. Palta, T. R. Hess, R. K. Vempati, D. L. Cockef, M. Yousuf, and A. Mollah, "Chemical and physical effects of sodium lignosulfonate superplasticizer on the hydration of Portland cement and solidification/stabilization consequences," *Cem. Concr.*, vol. 25, no. 3, pp. 671–682, 1995.
- [16] P. Mehta and P. J. Monteiro, *Concrete: Microstructure, Properties and Materials*, Fourth. Mc-Graw Hill, 2006.
- [17] T. Danner, H. Justnes, M. Geiker, and R. A. Lauten, "Phase changes during the early hydration of Portland cement with Ca-lignosulfonates," *Cem. Concr. Res.*, vol. 69, pp. 50– 60, 2015.
- [18] H. Lou, H. Lai, M. Wang, Y. Pang, D. Yang, X. Qiu, B. Wang, and H. Zhang, "Preparation of Lignin-Based Superplasticizer by Graft Sulfonation and Investigation of the Dispersive Performance and Mechanism in a Cementitious System," *Ind. Eng. Chem. Res.*, vol. 52, no. 46, pp. 16101–16109, Nov. 2013.
- [19] I. Amanto, "Concrete solutoins," *Nature*, vol. 494, pp. 3–4, 2013.
- [20] H. M. Yang, M; Neubauer, C.M.; Jennings, "Interparticle Potential and Sedimentation

Behavior of Cement Suspensions," Adv. Cem. Based Mater., vol. 7355, no. 96, pp. 1–7, 1997.

- [21] C. Gupta, M. J. Sverdlove, and N. R. Washburn, "Molecular architecture requirements for polymer- grafted lignin superplasticizers," *Soft Matter*, vol. 11, pp. 1–9, 2015.
- [22] J. Plank, C. Schroefl, M. Gruber, M. Lesti, and R. Sieber, "Effectiveness of Polycarboxylate Superplasticizers in Ultra-High Strength Concrete: The Importance of PCE Compatibility with Silica Fume," *J. Adv. Concr. Technol.*, vol. 7, no. 1, pp. 5–12, 2009.
- [23] J. Hot, H. Bessaies-Bey, C. Brumaud, M. Duc, C. Castella, and N. Roussel, "Adsorbing polymers and viscosity of cement pastes," *Cem. Concr. Res.*, vol. 63, no. October 2012, pp. 12–19, 2014.
- [24] K. E. Kurtis, "Benefits of Metakaolin in HPC," HPC Bridg. Views, no. 67, pp. 6–9, 2011.
- [25] F. Lagier and K. E. Kurtis, "Influence of Portland cement composition on early age reactions with metakaolin," *Cem. Concr. Res.*, vol. 37, no. 10, pp. 1411–1417, 2007.
- [26] B. H. Zaribaf, B. Uzal, and K. Kurtis, *Calcined Clays for Sustainable Concrete*, vol. 10. 2015.
- [27] J. Chiefari, Y. K. B. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, and C. South, "Living Free-Radical Polymerization by Reversible Addition - Fragmentation Chain Transfer : The RAFT Process We wish to report a new living free-radical polymer- ization of exceptional effectiveness and versatility . 1 The living character is conferred by ," vol. 9297, no. 98, pp. 5559–5562, 1998.
- [28] J. Spanswick, "Controlled / living radical polymerization," *materialstoday*, no. March, pp. 26–33, 2005.
- [29] J. Plank, E. Sakai, C. W. Miao, C. Yu, and J. X. Hong, "Chemical admixtures Chemistry, applications and their impact on concrete microstructure and durability," *Cem. Concr. Res.*, vol. 78, pp. 81–99, 2015.
- [30] B. J. de Gans, P. C. Duineveld, and U. S. Schubert, "Inkjet Printing of Polymers: State of the Art and Future Developments," *Adv. Mater.*, vol. 16, no. 3, pp. 203–213, 2004.
- [31] J. M. Harris, N. . Martin, and M. Modi, "Pegylation: A novel process for modifying pharmacokinetics," *Clin. Pharmacokinet.*, vol. 40, no. 7, pp. 539–551, 2001.
- [32] N. J. Alvarez, S. L. Anna, T. Saigal, R. D. Tilton, and L. M. Walker, "Interfacial Dynamics and Rheology of Polymer-Grafted Nanoparticles at Air-Water and Xylene-Water Interfaces," *Langmuir*, vol. 28, no. 21, pp. 8052–8063, 2012.
- [33] N. Roussel and P. Coussot, "Fifty-cent rheometer' for yield stress measurements: From slump to spreading flow," *J. Rheol. (N. Y. N. Y).*, vol. 49, no. 3, pp. 705–718, 2005.
- [34] N. Roussel, C. Stefani, and R. Leroy, "From mini-cone test to Abrams cone test: measurement of cement-based materials yield stress using slump tests," *Cem. Concr. Res.*, vol. 35, no. 5, pp. 817–822, May 2005.
- [35] H. Maag, "Fatty acid derivatives: Important surfactants for household, cosmetic and industrial purposes," *J. Am. Oil Chem. Soc.*, vol. 61, no. 2, pp. 259–267, 1984.
- [36] C. Moran, P. Clapes, F. Comelles, T. Garcia, L. Perez, P. Vinardell, M. Mitjans, and M. R. Infante, "Chemical structure/property relationship in single-chain arginine surfactants," *Langmuir*, vol. 17, no. 16, pp. 5071–5075, 2001.
- [37] W. Von Rybinski and K. Hill, "Alkyl Polyglycosides–Properties and Applications of a new Class of Surfactants," *Angew. Chemie Int. Ed.*, vol. 37, pp. 1328–1345, 1998.

- [38] P. Foley, A. Kermanshahi pour, E. S. Beach, and J. B. Zimmerman, "Derivation and synthesis of renewable surfactants," no. 41, pp. 1499–1518, 2012.
- [39] B. S. Sumerlin, "Proteins as Initiators of Controlled Radical Polymerization:Grafting-from via ATRP and RAFT," *ACS Macro Lett.*, vol. 1, pp. 141–145, 2012.
- [40] A. Carlmark and E. . Malmstrom, "ATRP Grafting from Cellulose Fibers to Create Block-Copolymer Grafts," *Biomacromolecules*, vol. 4, pp. 1740–1745, 2003.
- [41] S. Hansson, E. Ostmark, A. Carlmark, and E. Malmstrom, "ARGET ATRP for Versatile Grafting of Cellulose using various Monomers," ACS Appl. Mater. Interfaces, vol. 1, pp. 2651–2659, 2009.
- [42] P. S. Chinthamanipeta, S. Kobukata, H. Nakata, and D. A. Shipp, "Synthesis of Poly(methyl methacrylate)-Silica Nanocomposites Using Methacrylate-Functionalized Silica Nanoparticles and RAFT Polymerization," *Polymer (Guildf)*., vol. 49, pp. 5636– 5642, 2008.
- [43] J. Choi, H. Dong, K. Matyjaszewski, and M. R. Bockstaller, "Flexible Particle Array Structures by Controlling Polymer Graft Architecture," J. Am. Chem. Soc., vol. 132, pp. 12537–12539, 2010.
- [44] C. Perruchot, M. A. Khan, A. Kamitsi, S. P. Armes, T. von Werne, and T. E. Patten, "Synthesis of Well-Defined, Polymer-Grafted Silica Particles by Aqueous ATRP," *Langmuir*, vol. 17, pp. 4479–4481, 2001.
- [45] T. Shah, C. Gupta, R. L. Ferebee, M. R. Bockstaller, and N. R. Washburn, "Extraordinary toughening and strengthening effect in polymer nanocomposites using lignin-based fillers synthesized using ATRP," *Polymer (Guildf)*., vol. 72, pp. 406–412, 2015.
- [46] K. M. Askvik, S. A. Gundersen, J. Sjoblom, J. Merta, and P. Stenius, "Complexation between Lignosulfonates and Cationic Surfactants and its Influence on Emulsion and Foam Stability," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 159, pp. 89–101, 1999.
- [47] P. G. de Gennes, F. Brochard-Wyart, and D. Quere, *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves.* New York: Springer, 2004.
- [48] P. R. Gupta and J. L. McCarthy, "Lignin. XIV. Gel Chromatography and the Distribution in Molecular Size of Lignin Sulfonates at Several Electrolyte Concentrations," *Macromolecules*, vol. 1, no. 3, pp. 236–244, 1968.
- [49] B. P. Binks, "Particles as Surfactants Similarities and Differences," *Curr. Opin. Colloid Interface Sci.*, vol. 7, pp. 21–41, 2002.
- [50] R. Aveyard, J. H. Clint, and T. S. Horozov, "Aspects of the stabilisation of emulsions by solid particles: Effects of line tension and monolayer curvature energy," *Phys. Chem. Chem. Phys.*, vol. 11, pp. 2398–2409, 2003.
- [51] B. P. Binks and J. H. Clint, "Solid Wettability from Surface Energy Components: Relevance to Pickering Emulsions," *Langmuir*, vol. 18, no. 4, pp. 1270–1273, Feb. 2002.
- [52] J. Z. Du and R. K. O'Reilly, "Anisotropic Particles with Patchy, Multicompartment and Janus Architectures: Preparation and Application," *Chem. Soc. Rev.*, vol. 40, pp. 2402– 2416, 2011.
- [53] A. Walther and A. H. E. Muller, "Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications," *Chem. Rev.*, vol. 113, pp. 5194–5261, 2013.
- [54] A. B. Pawar and I. F. Kretzschmar, "Fabrication, Assembly, and Application of Patchy Particles," *Macromol. Rapid Commun.*, vol. 31, pp. 150–168, 2010.
- [55] S. A. Gundersen and J. Sjoblom, "High- and Low-Molecular-Weight Lignosulfonates and Kraft Lignins As Oil/Water-Emulsion Stabilizers Studied by Means of Electrical

Conductivity," Colloid Polym. Sci., vol. 277, pp. 462-468, 1999.

- [56] M. Ilavsky, "Effect of electrostatic interactions on phase transition in the swollen polymeric network," *Polymer (Guildf).*, vol. 22, no. 12, pp. 1687–1691, 1981.
- [57] S. Sarkanen, D. C. Teller, C. R. Stevens, and J. L. McCarthy, "Lignin. 20. Associative interactions between kraft lignin components," *Macromolecules*, vol. 17, no. 12, pp. 2588–2597, 1984.
- [58] G. Gilardi and A. E. . Cass, "Associative and colloidal behavior of lignin and implications for its biodegradation in vitro," *Langmuir*, vol. 9, no. 7, pp. 1721–1726, 1993.
- [59] O. J. Rojas and J. L. Salager, "Surface activity of bagasse lignin derivatives found in the spent liquor of soda plants," *Tappi J.*, pp. 169–174, 1994.
- [60] S. L. Hilburg, A. N. Elder, H. Chung, R. L. Ferebee, M. R. Bockstaller, and N. R. Washburn, "A universal route towards thermoplastic lignin composites with improved mechanical properties," *Polymer (Guildf).*, vol. 55, no. 4, pp. 995–1003, Feb. 2014.
- [61] P. M. Patterson and A. M. Jamieson, "Molecular weight scaling of the transport properties of polyacrylamide in water," *Macromolecules*, vol. 18, pp. 266–272, 1985.
- [62] M. Norgren and H. Edlund, "Ion Specific Differences in Salt Induced Precipitation of Kraft Lignin," *Nord. Pulp Pap. Res. J.*, vol. 18, pp. 400–403, 2003.
- [63] O. Pornsunthorntawee, S. Chavadej, and R. Rujiravannit, "Solution properties and vesicle formation of rhamnolipid biosurfactants produced by Pseudomonas aeruginosa SP4," *Colloids Surfaces B Biointerfaces*, vol. 72, no. 11, pp. 6–15, 2009.
- [64] D. J. Dong, A. L. Fricke, B. M. Moudgil, and H. Johnson, "Electrokinetic study of kraft lignin," *Tappi J.*, vol. 79, no. 7, pp. 191–197, 1996.
- [65] J. C. Berg, An Introduction to Interfaces and Colloids. World Scientific, 2009.
- [66] J. N. Israelachvili, Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems. New York: Academic Press, 1985.
- [67] R. Li, S. F. Aghamiri, D. Yang, P. Chen, and X. Qiu, "Dynamic Surface Tension and Adsorption Kinetics of Sodium Lignosulfonate Aqueous Solutions," J. Dispers. Sci. Technol., vol. 34, no. 5, 2013.
- [68] T. Saigal, H. Dong, K. Matyjaszewski, and R. D. Tilton, "Pickering Emulsions Stabilized by Nanoparticles with Thermally Responsive Grafted Polymer Brushes," *Langmuir*, vol. 26, no. 19, pp. 15200–15209, 2010.
- [69] S. A. Gundersen, M.-H. Ese, and J. Sjoblom, "Langmuir surface and interface films of lignosulfonates and Kraft lignins in the presence of electrolyte and asphaltenes: correlation to emulsion stability," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 182, no. 1–3, pp. 199–218, 2001.
- [70] W. Glasser, A. Northey, Robert, and T. P. Schultz, *Lignin:Historical, Biological and Materials Perspective*. American Chemical Society, 1999.
- [71] E. Colombo, F. Cavalieri, and M. Ashokkumar, "Role of Counterions in Controlling the Properties of Ultrasonically Generated Chitosan-Stabilized Oil-in-Water Emulsions," ACS Appl. Mater. Interfaces, vol. 7, no. 23, pp. 12972–12980, 2015.
- [72] B. W. Brooks and H. N. Richmond, "Phase inversion in non-ionic surfactant—oil—water systems—II. Drop size studies in catastrophic inversion with turbulent mixing," *Chem. Eng. Sci.*, vol. 49, no. 7, pp. 1065–1075, 1994.
- [73] B. P. Binks and S. O. Lumsdon, "Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions," *Langmuir*, vol. 16, no. 23, pp. 8622–8631, 2000.
- [74] B. P. Binks and S. O. Lumsdon, "Catastrophic Phase Inversion of Water-in-Oil Emulsions

Stabilized by Hydrophobic Silica," Langmuir, vol. 16, no. 6, pp. 2539–2547, 2000.

- [75] N. P. Ashby and B. P. Binks, "Pickering emulsions stabilised by Laponite clay particles," *Phys. Chem. Chem. Phys.*, no. 24, pp. 5640–5646, 2000.
- [76] N. Saleh, T. Sarbu, K. Sirk, V. Lowry, Gregory, K. Matyjaszewski, and R. D. Tilton, "Oilin-water Emulsions Stabilized by Highly Charged Polyelectrolyte-Grafted Silica Nanoparticles," *Langmuir*, vol. 21, no. 22, pp. 9873–9878, 2005.
- [77] D. E. Tambe and M. M. Sharma, "The effect of colloidal particles on fluid-fluid interfacial properties and emulsion stability," *Adv. Colloid Interface Sci.*, no. 52, pp. 1–63, 1994.
- [78] B. P. Binks and S. O. Lumsdon, "Stability of oil-in-water emulsions stabilised by silica particles," *Phys. Chem. Chem. Phys.*, vol. 1, pp. 3007–3016, 1999.
- [79] M. Perez, N. Zambrano, M. Ramirez, E. Tyrode, and J. L. Salager, "Surfactant-Oil-Water systems near the affinity inversion.XII. Emulsion drop size versus formulation and composition," *J. Dispers. Sci. Technol.*, vol. 23, no. 1–3, 2002.
- [80] B. P. Binks and S. O. Lumsdon, "Pickering emulsions stabilized by monodisperse latex particles: effects of particle size," *Langmuir*, vol. 17, pp. 4540–4547, 2001.
- [81] S. Simovic and clive A. Prestidge, "Nanoparticles of varying hydrophobicity at the emulsion droplet-water interface: adsorption and coalescence stability," *Langmuir*, vol. 20, no. 19, pp. 8357–8365, 2004.
- [82] Y. Matsushita, M. Imai, A. Iwatsuki, and K. Fukushima, "The relationship between surface tension and the industrial performance of water-soluble polymers prepared from acid hydrolysis lignin, a saccharification by-product from woody materials," *Bioresour. Technol.*, vol. 99, no. 8, pp. 3024–3028, 2008.
- [83] M. Kjellin and I. Johansson, Surfactants from Renewable Resources. Chichetser, UK: Wiley, 2010.
- [84] D. J. Donahue and F. E. Bartell, "The boundary tension at water-organic liquid interfaces," *J. Phys. Chem.*, vol. 56, no. 1, pp. 480–484, 1951.
- [85] J. Th and G. Overbeek, "The First Rideal Lecture. Microemulsions, a field at the border between lyophobic and lyophilic colloids," *Farady Discuss. Chem. Soc.*, vol. 65, pp. 7–19, 1978.
- [86] M. Mantler, S. Sarkanen, C. R. Stevens, and J. L. Mccarthy, "Lignin . 20 . Associative Interactions between Kraft Lignin Componentst," pp. 2588–2597, 1984.
- [87] R. J. Flatt, I. Schober, E. Raphael, C. Plassard, and E. Lesniewska, "Conformation of adsorbed comb copolymer dispersants," *Langmuir*, vol. 25, no. 2, pp. 845–855, 2009.
- [88] Y. F. Houst, P. Bowen, F. Perche, A. Kauppi, P. Borget, L. Galmiche, J.-F. Le Meins, F. Lafuma, R. J. Flatt, I. Schober, P. F. G. Banfill, D. S. Swift, B. O. Myrvold, B. G. Petersen, and K. Reknes, "Design and function of novel superplasticizers for more durable high performance concrete (superplast project)," *Cem. Concr. Res.*, vol. 38, no. 10, pp. 1197–1209, Oct. 2008.
- [89] L. R. Murray and K. A. Erk, "Jamming rheology of model cementitious suspensions composed of comb-polymer stabilized magnesium oxide particles," J. Appl. Polym. Sci., vol. 131, no. 12, pp. 1–11, 2014.
- [90] L. R. Murray, C. Gupta, N. R. Washburn, and K. a. Erk, "Lignopolymers as viscosityreducing additives in magnesium oxide suspensions," *J. Colloid Interface Sci.*, vol. 459, pp. 107–114, 2015.
- [91] Q. Ran, P. Somasundaran, C. Miao, J. Liu, S. Wu, and J. Shen, "Effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties

of concentrated cement suspensions," J. Colloid Interface Sci., vol. 336, no. 2, pp. 624–633, 2009.

- [92] L. Ferrari, J. Kaufmann, F. Winnefeld, and J. Plank, "Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements.," *J. Colloid Interface Sci.*, vol. 347, no. 1, pp. 15–24, Jul. 2010.
- [93] C. K. Schoff and P. Kamarchik, *Characterization Anlaysis of Polymers*. Hoboken, NJ: Wiley-Interscience, 2008.
- [94] J. Mewis and N. J. Wagner, *Colloidal Suspension Rheology*. New York: Cambridge University Press, 2012.
- [95] C. Autier, N. Azema, and P. Boustingorry, "Using settling behaviour to study mesostructural organization of cement pastes and superplasticizer efficiency," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 450, no. 1, pp. 36–45, 2014.
- [96] F. Winnefeld, S. Becker, J. Pakusch, and T. Götz, "Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems," *Cem. Concr. Compos.*, vol. 29, no. 4, pp. 251–262, 2007.
- [97] L. Ferrari, J. Kaufmann, F. Winnefeld, and J. Plank, "Multi-method approach to study influence of superplasticizers on cement suspensions," *Cem. Concr. Res.*, vol. 41, no. 10, pp. 1058–1066, 2011.
- [98] D. Marchon, U. Sulser, A. Eberhardt, and R. J. Flatt, "Molecular design of comb-shaped polycarboxylate dispersants for environmentally friendly concrete," *Soft Matter*, vol. 9, no. 45, p. 10719, 2013.
- [99] A. Kauppi, K. M. Andersson, and L. Bergström, "Probing the effect of superplasticizer adsorption on the surface forces using the colloidal probe AFM technique," *Cem. Concr. Res.*, vol. 35, no. 1, pp. 133–140, 2005.
- [100] C. Jayasree and R. Gettu, "Experimental study of the flow behaviour of superplasticized cement paste," *Mater. Struct.*, vol. 41, no. 9, pp. 1581–1593, 2008.
- [101] X. Peng, C. Yi, X. Qiu, and Y. Deng, "Effect of molecular weight of polycarboxylate-type superplasticizer on the rheological properties of cement pastes," *Polym. Polym. Compos.*, vol. 20, no. 8, pp. 725–736, 2012.
- [102] G. Fontani, R. Gaspari, N. D. Spencer, D. Passerone, and R. Crockett, "Adsorption and friction behavior of amphiphilic polymers on hydrophobic surfaces," *Langmuir*, vol. 29, no. 15, pp. 4760–4771, 2013.
- [103] K. Yoshioka, E. Sakai, M. Daimon, and A. Kitahara, "Role of Steric Hindrance in the Performance of Superplasticizers for Concrete," J. Am. Ceram. Soc., vol. 80, no. 10, pp. 2667–2671, 1997.
- [104] J. Ma, Z. Xie, H. Miao, Y. Huang, Y. Cheng, and W. Yang, "Gelcasting of alumina ceramics in the mixed acrylamide and polyacrylamide systems," *J. Eur. Ceram. Soc.*, vol. 23, no. 13, pp. 2273–2279, 2003.
- [105] S. Chibowski and M. Wisneiwska, "Study of electrokinetic properties and structure of adsorbed layers of polyacrylic acid and polyacrylamide at Fe 2 O 3 – polymer solution interface," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 208, pp. 131–145, 2002.
- [106] D. H. Napper, Colloid Science. New York: Academic Press, 1983.
- [107] J. M. Frostad, M. Seth, S. M. Bernasek, and L. G. Leal, "Direct measurement of interaction forces between charged multilamellar vesicles<sup>†</sup>.," *Soft Matter*, vol. 10, no. 39, pp. 7769–80, 2014.
- [108] S. Manneville, L. Becu, and A. Colin, "High-frequency ultrasonic speckle velocimetry in

sheared complex fluids," Eur. Phys. J. Appl. Phys., vol. 28, pp. 361-373, 2004.

- [109] G. H. Kirby and J. A. Lewis, "Comb Polymer Architecture Effects on the Rheological Property Evolution of Concentrated Cement Suspensions," vol. 87, no. 9, pp. 1643–1652, 2004.
- [110] R. J. Flatt and Y. F. Houst, "A simplified view on chemical effects perturbing the action of superplasticizers," *Cem. Concr. Res.*, vol. 31, no. 8, pp. 1169–1176, 2001.
- [111] R. J. Flatt, "Towards a prediction of superplasticized concrete rheology," *Mater. Struct.*, vol. 37, pp. 289–300, 2004.
- [112] K. Yamada, T. Takahashi, S. Hanehara, and M. Matsuhisa, "Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer," vol. 30, pp. 197–207, 2000.
- [113] D. Rana, G. H. Neale, and V. Hornof, "Surface tension of mixed surfactant systems: lignosulfonate and sodium dodecyl sulfate," *Colloid Polym. Sci.*, vol. 280, pp. 775–778, 2002.
- [114] Y. S. Kim and J. F. Kadla, "Preparation of a thermoresponsive lignin-based biomaterial through atom transfer radical polymerization," *Biomacromolecules*, vol. 11, pp. 981–988, 2010.
- [115] W. Zhao and J. Chang, "Sol-gel synthesis and in vitro bioactivity of tricalcium silicate powders," *Mater. Lett.*, vol. 58, no. 19, pp. 2350–2353, 2004.
- [116] G. Voicu, C. Ghitulica, and E. Andronescu, "Modified Pechini synthesis of tricalcium aluminate powder," *Mater. Charact.*, vol. 73, pp. 89–95, 2012.
- [117] J. Murata, "Flow and deformation of fresh concrete," *Mater. Struct.*, vol. 17, no. 2, pp. 117–129, 1984.
- [118] J. E. Wallevik, "Rheological porperties of cement paste: Thixotropic behavior and structural breakdown," *Cem. Concr. Res.*, vol. 39, no. 1, pp. 14–29, 2009.
- [119] N. Roussel, G. Ovarlez, S. Garrault, and C. Brumaud, "The origina of thixotropy of fresh cement pastes," *Cem. Concr. Res.*, vol. 42, no. 1, pp. 148–157, 2012.
- [120] A. Ohta, T. Sugiyama, and Y. Tanaka, "Fluidizing Mechanism and Application of Polycarboxylate-Based Superplasticizers," *Superplast. other Chem. admixtures Concr.*, vol. 173, pp. 359–378, 1997.
- [121] F. de Larrard, C. F. Ferraris, and T. Sedran, "Fresh concrete: A Herschel-Bulkley material," *Mater. Struct.*, vol. 31, pp. 494–498, 1998.
- [122] M. Cloitre, R. Borrega, F. Monti, and L. Leible, "Glassy dynamics and flow properties of soft colloidal pastes," *Phys. Rev. Lett.*, vol. 90, 2003.
- [123] N. Roussel, A. Lemaitre, R. J. Flatt, and P. Coussot, "Steady state flow of cement suspensions: A micromechanical state of the art," *Cem. Concr. Res.*, vol. 40, no. 1, pp. 77–84, 2010.
- [124] C. Gay and E. Raphael, "Comb-like polymers inside nanoscale pores," *Adv. Colloid Interface Sci.*, vol. 94, no. 1–3, pp. 229–236, 2001.
- [125] M. C. G. Juenger and R. Siddique, "Recent advances in understanding the role of supplementary cementitious materials in concrete," *Cem. Concr. Res.*, vol. 78, pp. 71–80, 2015.
- [126] S. Chandra and J. Björnström, "Influence of superplasticizer type and dosage on the slump loss of Portland cement mortars—Part II," *Cem. Concr. Res.*, vol. 32, no. 10, pp. 1613– 1619, 2002.
- [127] A. Lange and J. Plank, "Contribution of non-adsorbing polymers to cement dispersion,"

Cem. Concr. Res., vol. 79, pp. 131-136, 2016.

- [128] F. Dalas, S. Pourchet, A. Nonat, D. Rinaldi, S. Sabio, and M. Mosquet, "Fluidizing efficiency of comb-like superplasticizers: The effect of the anionic function, the side chain length and the grafting degree," *Cem. Concr. Res.*, vol. 71, pp. 115–123, 2015.
- [129] J. W. Bullard, H. M. Jennings, R. A. Livingston, A. Nonat, G. W. Scherer, J. S. Schweitzer, K. L. Scrivener, and J. J. Thomas, "Mechanisms of cement hydration," *Cem. Concr. Res.*, vol. 41, no. 12, pp. 1208–1223, 2011.
- [130] T. Nawa, "Effect of Chemical Structure on Steric Stabilization of Polycarboxylate-based Superplasticizer," *J. Adv. Concr. Technol.*, vol. 4, no. 2, pp. 225–232, 2006.
- [131] D. V Boger, "Aqueous Dispersions of Colloidal Boehmite : Structure , Dynamics , and Yield Stress of Rod Gels," *Langmuir*, vol. 14, no. 1, pp. 55–65, 1998.
- [132] S. Chandra and J. Björnström, "Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars - Part I," *Cem. Concr. Res.*, vol. 32, no. 10, pp. 1605– 1611, 2002.
- [133] S. Hanehara and K. Yamada, "Rheology and early age properties of cement systems," *Cem. Concr. Res.*, vol. 38, no. 2, pp. 175–195, 2008.
- [134] M. Bishop and A. R. Barron, "Cement Hydration Inhibition with Sucrose, Tartaric Acid, and Lignosulfonate : Analytical and Spectroscopic Study," *Ind. Eng. Chem. Res.*, vol. 45, pp. 7042–7049, 2006.
- [135] E. Sakai, K. Yamada, and A. Ohta, "Molecular Structure and Dispersion-Adsorption Mechanisms of Comb-Type Superplasticizers Used in Japan," J. Adv. Concr. Technol., vol. 1, no. 1, pp. 16–25, 2003.
- [136] M. Ilg and J. Plank, "A novel kind of concrete superplasticizer based on lignite graft copolymers," *Cem. Concr. Res.*, vol. 79, pp. 123–130, 2016.
- [137] M. Bishop and A. R. Barron, "Cement hydration inhibition with sucrose, tartaric acid, and lignosulfonate: Analytical and spectroscopic study," *Ind. Eng. Chem. Res.*, vol. 45, no. 21, pp. 7042–7049, 2006.
- [138] D. Ji, Z. Luo, M. He, Y. Shi, and X. Gu, "Effect of both grafting and blending modifications on the performance of lignosulphonate-modified sulphanilic acid-phenolformaldehyde condensates," *Cem. Concr. Res.*, vol. 42, no. 9, pp. 1199–1206, Sep. 2012.
- [139] J. Cheung, a. Jeknavorian, L. Roberts, and D. Silva, "Impact of admixtures on the hydration kinetics of Portland cement," *Cem. Concr. Res.*, vol. 41, no. 12, pp. 1289–1309, 2011.
- [140] D. Bentz, T. Barrett, I. D. la Varga, and J. Weiss, "Relating Compressive Strength to Heat Release in Mortars," *Adv. Civ. Eng. Mater.*, vol. 1, no. 1, pp. 1–14, 2012.
- [141] R. Kumar and B. Bhattacharjee, "Porosity, pore size distribution and in situ strength of concrete," Cem. Concr. Res., vol. 33, pp. 155–164, 2003.
- [142] D. A. Silva, V. M. John, J. L. D. Ribeiro, and H. R. Roman, "Pore size distribution of hydrated cement pastes modified with polymers," *Cem. Concr. Res.*, vol. 31, pp. 1177– 1184, 2001.
- [143] H. Uchikawa, D. Sawaki, and S. Hanehara, "Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste," *Cem. Concr. Res.*, vol. 25, no. 2, pp. 353–364, 1995.
- [144] K. M. Alexander, "The relationship between strength and the composition and fineness of cement," *Cem. Concr. Res.*, vol. 2, no. 6, pp. 663–680, 1972.
- [145] C. Jolicoeur and M.-A. Simard, "Chemical admixture-cement interactions:

Phenomenology and physico-chemical concepts," *Cem. Concr. Compos.*, vol. 20, no. 2–3, pp. 87–101, 1998.

- [146] B. L. Karihaloo, A. Carpinteri, and M. Elices, "Fracture Mechanics of Cement Mortar and Plain Concrete," 2006.
- [147] B. Sabir, S. Wild, and J. Bai, "Metakaolin and calcined clays as pozzolans for concrete: A review," *Cem. Concr. Compos.*, vol. 23, no. 6, pp. 441–454, 2001.
- [148] S. Wild, J. M. Khatib, and A. Jones, "Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete," *Cem. Concr. Res.*, vol. 26, no. 10, pp. 1537–1544, 1996.
- [149] R. Siddique and J. Klaus, "Influence of metakaolin on the properties of mortar and concrete: A review," *Appl. Clay Sci.*, vol. 43, no. 3–4, pp. 392–400, 2009.
- [150] V. Srivastava, R. Kumar, V. C. Agarwal, and S. F. Aai-du, "Metakaolin inclusion : Effect on mechanical properties of concrete," *J. Acad. Ind. Res.*, vol. 1, no. October, pp. 251– 253, 2012.
- [151] J. Plank and C. Hirsch, "Impact of zeta potential of early cement hydration phases on superplasticizer adsorption," *Cem. Concr. Res.*, vol. 37, no. 4, pp. 537–542, 2007.
- [152] A. Favier, J. Hot, G. Habert, N. Roussel, and J.-B. d'Espinose de Lacaillerie, "Flow properties of MK-based geopolymer pastes. A comparative study with standard Portland cement pastes," *Soft Matter*, vol. 10, no. 8, p. 1134, 2014.
- [153] A. Favier, G. Habert, J. B. D'Espinose De Lacaillerie, and N. Roussel, "Mechanical properties and compositional heterogeneities of fresh geopolymer pastes," *Cem. Concr. Res.*, vol. 48, pp. 9–16, 2013.
- [154] J. J. Schwinefus, C. Checkal, B. Saksa, N. Baka, K. Modi, and C. Rivera, "Molar Mass and Second Virial Coefficient of Polyethylene Glycol by Vapor Pressure Osmometry," J. *Chem. Educ.*, vol. 92, no. 12, pp. 2157–2160, 2015.
- [155] L. Mlinárik and K. Kopecskó, "Cement hydration in the presence of metakaolin," *Second Conf. Jr. Res. Civ. Eng.*, pp. 120–124.
- [156] P. Duxson, G. C. Lukey, and J. S. J. van Deventer, "Thermal evolution of metakaolin geopolymers: Part 1 - Physical evolution," *J. Non. Cryst. Solids*, vol. 352, no. 52–54, pp. 5541–5555, 2006.
- [157] K. S. Silmore, C. Gupta, and N. R. Washburn, "Tunable Pickering emulsions with polymer-grafted lignin nanoparticles (PGLNs)," J. Colloid Interface Sci., vol. 466, pp. 91– 100, 2016.