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Lignopolymers as viscosity-reducing additives in magnesium oxide suspensions

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Graphical Abstract:

Highlights:

- Model cementitious suspensions of magnesium oxide were made to test the flow properties of a new class of additive.
- These new lignopolymer additives have been custom synthesized for examination of the impact of polymer architecture on viscosity.
- Lignin-PAm was observed to significantly decrease viscosity at a low concentration below the current industrial additive concentration.
- Addition of a commercial polycarboxylate ether superplasticizer was shown to have the largest decrease in viscosity at the highest concentrations tested.
- Lignin-PAm chains with 17- grafted lignin side-chains are more effective for viscosity reduction at low concentrations than 2- grafted side chains.

Abstract

Lignopolymers are a new class of polymer additives with the capability to be used as dispersants in cementitious pastes. Made with kraft lignin cores and grafted polymer side-chains, the custom-synthesized lignopolymers were examined in terms of the molecular architecture for viscosity reducing potential in inert model suspensions. Lignin-poly(acrylic acid) (LPAA) and lignin-polyacrylamide (LPAm) have been found to vary the rheology of magnesium oxide (MgO) suspensions based on differences in chain architecture and particle-polymer interactions. A commercial comb-polymer polycarboxylate ester was compared to LPAA and LPAm at 2.7 mg/mL, a typical dosage for cement admixtures, as well as 0.25 mg/mL. It was found that LPAm was a more effective viscosity reducer than both LPAA and the commercial additive at low concentrations, which was attributed to greater adsorption on the MgO particle surface and increased steric dispersion from PAm side-chain extension. The influence of chain adsorption and grafted side-chain molecular weight on rheology was also tested.

Keywords: Colloids, Cement, Rheology, Structure-Property Relationships, lignin, superplasticizer, comb-polymer adsorption

Introduction

Portland cement, the main constituent in concrete for structural applications, relies on polymer additives to disperse particles and reduce viscosity to improve workability [1,2]. For this goal polymer surfactants have evolved over the years from lignosulfonates to fully synthetic comb-polymers that are currently used due to their non-reactivity with concrete constituents and to meet the continual demand for better cement pouring and pumping [3,4]. The sulfonate group chemistry of the lignosulfonates inhibits cement hydration, which can result in improperly cured concrete with subsequently poor mechanical properties [3]. Despite the non-reactivity and renewal resource of the lignin component of lignosulfonates, synthetic comb-polymers were adopted as a replacement to lignosulfonates due to their non-reactivity. Superplasticizer comb-polymers typically have a poly(acrylic acid) (PAA) main-chain with either poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA) grafted side-chains and are known as

polycarboxylate ethers (PCEs) [5–10]. When added to alkaline cementitious mixtures, the PAA backbone becomes negatively charged and electrostatically adsorbs to the cement particles with side-chains extending into the water. These conventional superplasticizers are thought to prevent particle aggregation due to steric repulsion between side-chains on neighboring particles, but high concentrations of these superplasticizers (at least 2 mg/g cement) are needed to achieve this effect [8,9]. The molecular architecture of comb-polymer additives has been explored and tailored for cement dispersion [7,11–14], but no new polymeric architectures have been extensively tested and recommended as alternatives to the current comb-polymers.

Furthermore, the analysis of a superplasticizer's efficiency in improving cement workability has been irregular when conducted with empirical concrete-based tests, such as slump cones, which are unable to quantify the rheology of the paste [2,15]. These methods have left gaps in the understanding of how polymer additives impact the many stages of cement processing during mixing, pouring, pumping, and placement. Rheometry of cements and model cementitious suspensions has consisted of many analyses, but connections between the macroscopic flow, polymer architecture, and polymer interactions have yet to be fully developed [16]. Herein we apply shear rate ramps to assess the pouring and placement of cementitious pastes along with creep tests (applied shear stress) as an analog for the pumping of cements. These rheometry methods provide detailed information on the polymer-particle flow dynamic that is unavailable from slump tests.

Magnesium oxide (MgO) suspensions have been used by both colloidal scientists and cement researchers [11,13,17,18] to delineate the flow characteristics of cementitious pastes during short-term handling and placement. This model system is a simplified simulation of Portland cement with a uniform and unreactive particle composition. The physical interactions between particles and polymer can be investigated without the interference of the hydration reaction in cements [11,13]. Although cement particles do undergo reactions upon mixing, MgO suspensions are employed to examine only the initial flow behavior without consideration of the longer-time effect of hydration. The particle size distribution of MgO can be tuned to match that of ordinary Portland cement [18], and MgO portrays similar surface chemistry to calcium silicate in cement [1]. However, the particle composition of the MgO suspensions leaves out the

formation of hydration phases that interact with superplasticizer adsorption and effectivity [13,15]. This aspect is not addressed herein but may be examined in future studies.

To explore the potential of a renewable material as a superplasticizer, new lignin-based polymers have been synthesized and tested for their flow properties in model cementitious suspensions. Previous results demonstrated that polyacrylamide-grafted kraft lignin significantly decreased the yield stress of Portland cement pastes to levels comparable with commercial polycarboxylate superplasticizers [19]. The processing characteristics are explored with rheometry for delineating the role of chain chemistry and architecture in reducing viscosity. With magnesium oxide (MgO) model suspension rheometry and chain characterization, the lignopolymers are shown to be a functional alternative to fully synthetic superplasticizers. Rheometry demonstrates that these lignopolymers can lower viscosity at concentrations below the current industry standards and that the tuned side-chain molecular weights also serve to improve viscosity reduction.

Materials

Lignopolymer Synthesis and Characterization

Lignopolymers were synthesized according to the procedures outlined in [19] for acidified (anionic) kraft lignin cores with grafted polymer chains. Kraft lignin with an estimated molecular weight of 25,000 g/mol without polymer side-chains was also prepared and used for comparison. Three lignopolymers with grafted polyacrylamide (PAm) chains were synthesized with different numbers of grafted PAm chains and different degrees of polymerization. From GPC analysis of cleaved chains using the method reported in [19], there were approximately two grafted chains and nearly 17 grafted chains for the two compositions. A lignopolymer with PAA chains was also synthesized. Table 1 displays the estimated molecular weights and the effective number of grafted chains for each lignopolymer. All PDIs were between 1.6 – 1.7.

Table 1: Estimated number and molecular weights of grafted side-chains for different synthesized lignopolymers

Sample Name	Grafted Polymer	Estimated Molecular Weight of grafted polymer (g/mol)	Estimated Number of grafted chains per lignin core
LPAA-2-10k	PAA	10,000	2
LPAm-2-10k	PAm	10,000	2
LPAm-17-5k	PAm	5,000	17
LPAm-17-10k	PAm	10,000	17

Commercial Comb-Polymer

A commercial PCE, ADVA 190 (Grace Construction) was treated and used as a comparison to the synthesized lignopolymers. The PCE in ADVA 190 is a ~20,000 g/mol comb-polymer PCE with an anionic PAA backbone and approximately 15 poly(ethylene oxide) (PEO) side-chains of ~1,000 g/mol [16]. Dialysis was performed to separate small molecular weight species from the PCE [16].

Magnesium Oxide

Magnesium oxide powder (MagChem P-98 pulverized) was used as received from Martin Marietta Magnesia Specialties (Baltimore, MD) with an average particle size of 3.8 μm . The particle size distribution was found to have 84.1% of the particles less than 10 μm and only 0.41% of the particles less than 1 μm in diameter [16].

Suspension Fabrication

A 0.42 water:MgO weight ratio was selected in order to correlate the suspension particle loading to that of a common Portland cement [15]. Suspensions were made with either 0.25 or 2.7 mg/mL PCE, kraft lignin, LPAA, or LPAm varieties. The higher concentration of 2.7 mg/mL was selected because it is within the range of the manufacturer's recommended levels for polymer additives (195–980 mL/100 kg cement). An order of magnitude lower concentration of 0.25 mg/mL was chosen for comparison.

Suspensions were made by first dissolving either the PCE or the lignopolymer in water. To fully dissolve, lignopolymers required 20 minutes of sonication followed by stirring

overnight. PCE dissolved after a few minutes of stirring. Afterwards, MgO was added gradually with ongoing stirring and shaking to evenly disperse the particles. Sonication was applied for 5 minutes after the completion of suspension fabrication and 5 minutes before testing with constant stirring overnight in-between sonication.

Methods

Rheometry

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 (24 mm vane diameter, 2 mm gap, 19.35 mL sample volume) was used to avoid wall slip [2,20]. Wall slip was found to have influenced the Couette rheometry of 0.42 water:MgO suspensions when previously tested with ultrasonic speckle velocimetry [21], which prompted the use of the vane fixture. Preshear was applied before all tests by shearing the suspension at 500 s^{-1} for 30 seconds, followed by a 10 s pause in the rotation before starting the test to ensure no residual stresses. Due to the hydrodynamic forces during the rheometry no particle sedimentation was observed. All tests were conducted with fresh sample. Shear rate was increased from 0.01 to 100 s^{-1} to simulate the behavior during 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 the rheology during pipe flow and pouring.

Sedimentation Study

Suspensions were allowed to sit in graduated cylinders for one week to observe the volume of sedimented particles and supernatant, the supernatant above the sedimented particles. 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 [13,22]. To evaluate the viscosity of the supernatant that resulted from settling particles, separate suspensions were

centrifuged at 1,000 RPM for 2 minutes in order to extract the supernatant. Viscosity measurements of the supernatant at 1 s^{-1} were made to correlate the adsorption of chains to the rate of particle sedimentation.

Additional Suspension Characterization

The pH of lignopolymers, kraft lignin, and commercial PCE comb-polymer were measured with a pH meter calibrated with pH buffers. Readings were taken both with and without MgO at a concentration of 2.7 mg/mL. Zeta potential was measured for all suspensions with a Nanosizer nano-z (Malvern Instruments) with the Smoluchowski model [16]. Disposable capillary cells held MgO particles with size less than $10\text{ }\mu\text{m}$ in aqueous suspension at low concentrations to avoid noise interference. The four lignopolymers and the PCE were tested with and without MgO particles. Samples sat for 2 minutes before testing and then were equilibrated at 25°C for 1 minute before testing [16,23]. Dynamic light scattering (DLS) was also performed with the Nanosizer nano-z (Malvern Instruments) at a 173° scattering angle. Kraft lignin was tested at a 5 mg/mL concentration in water in a glass cuvette. Total organic carbon (TOC) measurements were conducted to record the adsorption of lignopolymer, kraft lignin, and commercial PCE to the MgO particle surface. A GE InnovOX TOC analyzer was used to test 0.25 and 2.7 mg/mL lignopolymer concentrations for polymer adsorption onto MgO particles.

Results and Discussion

MgO suspensions containing 0.25 mg/mL admixture

The suspensions with 0.25 mg/mL polymer had peak viscosities that were nearly an order of magnitude lower than that of the control suspension in viscosity curves (Figure 1a) for the lignopolymers, acidified lignin, and commercial PCE. LPAm suspensions maintained the lowest viscosities over the ramped shear rate. Of the LPAm lignopolymers, LPAm-17-10k had the lowest viscosity by only a slight margin. Creep experiments (Figure 1b) revealed that kraft lignin and LPAA-2-10k reached the greatest shear rates for 0.25 mg/mL while the PCE resulted in the second-lowest shear rate over time, second only to the control which did not flow at the 5 Pa of applied shear stress (Figure 1b). LPAm-17-10k maintained the greatest observed shear rate of the LPAm suspensions with LPAm-17-5k and LPAm-2-10k with intermediate shear rates. The

magnitude of shear rates demonstrated the ease of flow under applied shear stress with low recorded shear rates serving as an indication of strong resistance to flow and high shear rates as a sign of the ease of pipe flow. LPAm appeared to be a more effective dispersant at 0.25 mg/mL compared to LPAA and PCE due to its strong viscosity reduction along with its improved creep measurements over the commercial comb-polymer.

Figure 1: Viscosity curves for suspensions with 0.25 mg/mL lignopolymer with inset plot with linear scale (a) and creep tests at 5 Pa for 0.25 mg/mL suspensions (b) for the control suspension (black), LPAA 2-10k (blue), kraft lignin (green), PCE (grey), LPAm-17-5k (pink), LPAm-2-10k (red), and LPAm-17-10k (dark red). It should be noted that the control suspension did not flow at 5 Pa.

LPAm's viscosity reduction may be attributed to the extension of PAm chains into the water while the lignin core was electrostatically adsorbed to the MgO particle (Figure 2). Shown in Table 2, pH varied between the polymers with and without MgO. Kraft lignin was the most acidic (3.0) followed by LPAA-2-10k (3.45). The remainder of the polymers maintained slightly acidic or neutral pH and all polymer solutions became alkaline upon addition of MgO. The pH of the suspensions showed that LPAA had a lower pH in water with and without MgO than LPAm, which serves as evidence for the deprotonation of the carboxylic acid groups on PAA, which is expected in alkaline conditions [9,10,24,25]. De-protonated PAA chains should be electrostatically attracted to the slight positive charge of the MgO surface, whereas neutral PAm chains can extended into the water [26,27].

Figure 2: Schematic of the proposed adsorption conformation of LPAm and LPAA on MgO particles.

Relative polymer charge, determined by zeta potential measurements, played a strong role in the polymer adsorption and particle stabilization. The zeta potential magnitude (Table 2) was less than 12 mV for MgO as well as the three LPAm polymers whereas PCE, kraft lignin, and LPAA-2-10k had higher magnitude zeta potentials. LPAA-2-10k demonstrated a decrease in zeta potential magnitude by 11.2 mV upon addition of MgO but all three LPAm samples had slight changes in zeta potential when MgO was added, with changes ranging from 2.7 to 0.33 mV. The greater zeta potential magnitude of LPAA-2-10k is attributed to the anionic charges along the deprotonated PAA side-chains. LPAm polymers have lower magnitude zeta potentials (-6.0 to -8.3 mV) due to the anionic charge of kraft lignin core with uncharged PAm chains partially screening the negative charges. This finding also suggests that PAA chains were adsorbed to the particle surface while PAm chains extended into the water due to the more negative zeta potential of the LPAA upon interacting with MgO (-26.1 mV) than that of LPAm (-5.7 to -11.0 mV) (Figure 2). However, zeta potential alone cannot be used to predict aggregation due to the presence of steric interactions in the system. It is hypothesized that the difference in side-chain conformation between PAA and PAm leads to their different levels of aggregation and thus impacts their viscosity-reducing ability. The difference in grafted side-chain conformation between the collapsed PAA and the extended PAm may have influenced the

effective steric repulsion between particles and be responsible for the superior performance of the three LPAm varieties over LPAA in rheometry tests.

Table 2: pH and zeta potential data for admixtures

Sample	pH without MgO	pH with MgO	Zeta potential without MgO (mV)	Zeta potential with MgO (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-2-10k	3.45	10.4	-14.9	-26.1
LPAm-2-10k	6.63	10.6	-7.6	-8.2
LPAm-17-5k	7.19	10.4	-8.3	-11.0
LPAm-17-10k	7.03	10.9	-6.0	-5.7

To further examine the impact of adsorption and viscosity-reducing ability of LPAm at low concentrations, sedimentation tests were conducted. Suspensions were allowed to settle in a graduated cylinder to measure the ratio of supernatant to the total suspension volume, shown in Figure 3. Maximum sedimentation rates, volume fraction of supernatant at the end of the test, and the viscosity of supernatant were analyzed as indications of sedimentation speed, degree of particle separation from the water, and impedance to sedimentation (Table 3). Of the 0.25 mg/mL concentrations the PCE, LPAA-2-10k, and the control suspension carried out the most-gradual sedimentation whereas LPAm suspensions were the most rapid along with kraft lignin (Figure 3). LPAm-17-10k reached its final sedimented volume fraction of 0.65 after only ~3 hours while LPAm-17-5k and LPAm-2-10k required ~33 hours and nearly 167 hours were needed before LPAA-2-10k and PCE approached their final sedimentation volume fraction of 0.65. Additionally, the sedimentation rate was much more rapid (max of 0.67 mL/min) for the viscosity-reducing LPAm suspensions than LPAA-2-10k and PCE (Table 3). The swift sedimentation of the LPAm suspensions indicates that there was little interference between the

stabilized particles within the fluid. It should be noted that sedimentation of suspensions was not observed for the rheometry testing due to the pre-shear and ongoing hydrodynamic forces from the applied shear rate or shear stress.

A comparison of the centrifuged water viscosities taken from centrifuged suspensions may offer an explanation for the swift sedimentation of LPAm stabilized particles (refer to Table 3). It is well known that Stokes' Law relates the viscosity of the continuous medium (here, water containing non-adsorbed polymer) to the velocity of particles settling due to gravity [28], especially when the particle diameter exceeds 1 μm and Brownian motion is not influential [22]. It is suggested that the low supernatant fluid viscosity of the LPAm-17-10k suspension (0.011 Pa•s) promoted fast particle sedimentation as result of a relatively low concentration of non-adsorbed chains in the suspension. A large volume of non-adsorbed polymers would be expected to increase the viscosity of the supernatant and therefore reduce the rate of gravity-induced sedimentation. LPAm-17-5k (0.086 Pa•s) and LPAm-2-10k (0.061 Pa•s) also sedimented rapidly and are suspected to have a low concentration of non-adsorbed chains which lead to longer times to reach the final sediment volume fractions than LPAm-17-10k. It is therefore believed that the LPAm-17-5k and LPAm-2-10k adsorbed more strongly than the PCE and LPAA-2-10k which were slow to settle. Similar trends have been observed for other comb-polymer additives in settling studies [29]. However, greater fluid viscosities were observed for the neat MgO suspension (0.157 Pa•s) and LPAA-2-10k (0.186 Pa•s) which may explain the relatively slow sedimentation rates in Figure 3 due to an increased concentration of non-adsorbed LPAA-2-10k (0.17 mg/mL). Likewise, the PCE suspension with 0.062 mg/mL free polymer sedimented slowly with the possibility of free chains delaying particle settling.

Figure 3: Sedimentation results for 0.25 mg/mL for the control suspension (black), LPAA-2-10k (blue), kraft lignin (green), PCE (grey), LPAm-17-5k (pink), LPAm-2-10k (red), and LPAm-17-10k (dark red).

Of the 0.25 mg/mL LPAm polymers, LPAm-17-10k resulted in the lowest viscosity of the control suspension (Figure 1a) with further evidence given by the lowest supernatant fluid viscosity (0.011 Pa·s) of the three suspensions. The measured shear rate of LPAm-17-10k was greatest for the creep tests (Figure 1b) of the three LPAm samples, and also had the lowest magnitude zeta potential (-6.0 mV alone, -5.7 mV with MgO, Table 2) of the lignopolymers. Therefore, of the three LPAm polymers, it is believed that LPAm-17-10k has the most chains extending into the slipping plane and effectively diluting the negative charge of the lignin core, which make the 17 grafted side-chains and the ~10,000 g/mol side-chain molecular weight the optimal molecular characteristics of the lignopolymers studied for use at 0.25 mg/mL.

Table 3: Maximum sedimentation rates, and particle volume fraction at end of sedimentation tests along with the viscosity of supernatant taken from centrifuged suspensions.

Sample	Concentration (mg/mL)	Maximum Rate of Sedimentation (mL/min)	Sediment Volume Fraction	Viscosity of Centrifuged Water at 1 s⁻¹ (Pa•s)
Control Suspension	--	0.125	0.64	0.157
PCE	0.25	0.125	0.67	0.117
	2.7	0.125	0.68	0.064
Kraft Lignin	0.25	0.33	0.65	0.128
	2.7	0.375	0.80	0.016
LPAA-2-10k	0.25	0.125	0.73	0.186
	2.7	1.50	0.70	0.062
LPAm-2-10k	0.25	0.50	0.66	0.061
	2.7	0.50	0.69	0.0173
LPAm-17-5k	0.25	0.25	0.64	0.086
	2.7	0.25	0.74	0.001
LPAm-17-10k	0.25	0.67	0.65	0.011
	2.7	0.50	0.77	0.002

TOC adsorption results (Table 4) also gave insights to differences in the adsorption of PCE and lignopolymers to particle surfaces. Although physical adsorption of polymer is often treated as a static occurrence, it should be noted that the polymers most likely undergo desorption and resorption along the surface of the particle [30]. TOC data are reported and analyzed in terms of the average, steady-state levels of adsorbed polymer on the particles during the constant adsorption-desorption process. The extent of polymer adsorption at 0.25 mg/mL displayed the following trend: LPAm-17-10k > LPAm-2-10k > PCE > LPAA-2-10k > LPAm-17-5k > kraft lignin. Supernatant viscosity was near zero for LPAm-17-10k (see Table 4), which is also consistent with the TOC data. Furthermore, increased supernatant viscosity occurred for LPAm-2-10k, PCE, and LPAA-2-10k which have greater amounts of non-adsorbed chains than LPAm-17-10k. However, the kraft lignin and LPAm-17-5k did not fit the trend.

Despite their different molecular architectures, viscosities of the commercial PCE and LPAA-2-10k suspensions are similar over the ramped shear rates (Figure 1a) which is attributed to low adsorption (75.3 and 32.6%, respectively) at the 0.25 mg/mL concentration. Non-adsorbed LPAA and PCE may have retarded particle settling due to chain-particle friction and resulted in increased supernatant viscosities. During rheometry tests, aggregation of the free chains or depletion-induced flocculation may have increased the viscosity and reduced effective steric repulsion.

Table 4: TOC adsorption onto MgO particles

Sample	Concentration	TOC Adsorption (%)	Concentration of non-adsorbed chains (mg/mL)
PCE	0.25	75.3	0.062
	2.7	91.9	0.219
Kraft Lignin	0.25	8.4	0.23
	2.7	96.8	0.086
LPAA-2-10k	0.25	32.6	0.17
	2.7	54.3	1.23
LPAm-2-10k	0.25	86.9	0.033
	2.7	82.7	0.47
LPAm-17-5k	0.25	27.3	0.182
	2.7	73.6	0.713
LPAm-17-10k	0.25	99.7	0.001
	2.7	88.3	0.316

Table 5 displays the estimated side chain density along particles based on the percentage of adsorbed chains and average particle size. It is estimated that there are only ~ 0.003 side-chains/nm² on a particle in the LPAA-2-10k suspension (order of magnitude less than the LPAm side-chain coverage), which contributed to the lack of steric interaction and less viscosity-reduction than LPAm suspensions. The ~ 0.172 PCE chains/nm² is around the same magnitude as

the 0.157 chains/nm² of LPAm-17-10k but the high surface coverage does not ensure significant steric repulsion for PCE-adsorbed particles at the 0.25 mg/mL concentration. Differences in the steric repulsion may be due to the higher molecular weight of the grafts on LPAm-17-10k than PCE. In studies on the effects of PCE architecture, it has been shown that decreasing the side-chain length increases the effective anionic charge density, which is expected to reduce adsorption of PCE onto particle surfaces [31]. The lignopolymers grafted with PAm used in the current work had much higher molecular weights than that in the PCE, but at low admixture concentrations grafting only enhanced binding affinity for MgO compared to acidified lignin and the greatest adsorbed fraction was observed in the PAm lignopolymer with highest graft density and molecular weight.

Table 5: Side-chain densities on adsorbed particle surfaces, calculated from specific surface area and polymer concentration using the TOC values of adsorbed chains [16].

Polymer	Side-chain density if using TOC adsorption results (chains/nm ²)	
	0.25 mg/mL	2.7 mg/mL
PCE	0.172	2.30
LPAA-2-10k	0.003	0.055
LPAm-2-10k	0.016	0.168
LPAm-17-5k	0.043	1.27
LPAm-17-10k	0.157	1.52

MgO suspensions containing 2.7 mg/mL admixture

Lignopolymer rheometry results displayed large differences for the polycarboxylate concentration of 2.7 mg/mL. Seen in Figure 4a, the PCE suspension had the lowest viscosity and LPAA-2-10k had the second lowest viscosity followed closely by LPAm-2-10k. LPAm-17-10k and LPAm-17-10k maintained viscosities less than the control suspension only for low shear

rates ($< 1 \text{ s}^{-1}$). The creep test at applied shear stress of 10 Pa (Figure 4b) resulted in lignopolymer suspensions with shear rates of 100-250 s^{-1} greater than kraft lignin, PCE, and the control, which demonstrated the superior ease of flow for LPAm suspensions at 2.7 mg/mL.

Lignopolymers with only two grafted chains (LPAA-2-10k and LPAm-2-10k) are the second-highest viscosity reducers regardless of the side-chain chemistry (Figure 4a). However, effective side-chain density was an order of magnitude lower for 2-side-chain polymers (LPAA-2-10k and LPAm-2-5k) than the PCE (~ 15 side-chains) and 17 side-chain LPAm polymers (Table 4). This suggests that at the 2.7 mg/mL concentration more side-chains did not result in greater particle dispersion for lignopolymers. Maximum sedimentation rates were much greater for LPAA-2-10k (1.5 mL/min) and LPAm-2-10k (0.5 mL/min) than LPAm-17-10k (0.33 mL/min) and LPAm-17-5k (0.125 mL/min) from which it may be concluded that 2 side-chain lignopolymers were more effective for particle stabilization than those with 17 side-chains at 2.7 mg/mL.

Figure 4: Viscosity curves for 2.7 mg/mL lignopolymer suspensions with linear scale insert (a) and 2.7 mg/mL lignopolymer creep tests at applied shear stress of 10 Pa (b) for the control suspension (black), LPAA-2-10k (blue), kraft lignin (green), PCE (grey), LPAm-17-5k (pink), LPAm-2-10k (red), and LPAm-17-10k (dark red).

Viscosity-reduction at the 2.7 mg/mL concentration may be interpreted in terms of the adsorption strength of the polymers on the particle surface. LPAA-2-10k has two anionic side-chains that contribute to a high charge density and the two neutral PAm chains of LPAm-2-10k

detract only a little from the charge density of the anionic lignin. Higher charge density is believed to increase adsorption strength [32,33] and it has been reported that polycarboxylates with greater charge density are more effective viscosity modifiers in high concentrations for concentrated suspensions [13]. Therefore if charge density drives the viscosity modification of the 2.7 mg/mL concentration suspensions, LPAA-2-10k would be most effective due to the anionic PAA and lignin while LPAm-2-10k has the second greatest charge density of the lignopolymers. The 17 neutral side-chains of LPAm-17-10k and LPAm-17-5k may significantly decrease the overall charge density of the lignopolymer and thus decrease their ability to modify the viscosity at the 2.7 mg/mL concentration.

High admixture concentration (2.7 mg/mL) sedimentation studies revealed that all lignopolymers tested sedimented more rapidly than the 0.25 mg/mL suspensions with variance in final volumes of supernatant to total suspension volume (Figure 5). The 2-side-chain lignopolymers (LPAA-2-10k and LPAm-2-10k) sedimented most rapidly with LPAA-2-10k had the highest max sedimentation rate (1.5 mL/min), which supports the findings that the most effective lignopolymer dispersants have quicker sedimentation and low volume fraction of particles (0.70). Such a low number of grafted side-chains has been associated with greater sedimentation and particle stability at high concentrations for comb-polymer additives [29]. Kraft lignin also fits this trend with a low level of final sedimentation due to its aggregation-driven viscosity increase (0.80 volume fraction particles).

The PCE had the lowest viscosity of the suspensions at 2.7 mg/mL, which may be explained in part by the TOC data (Table 4). TOC adsorption resulted in the following trend: kraft lignin > PCE > LPAm-17-10k > LPAm-2-10k > LPAm-17-5k > LPAA-2-10k. The flow behavior of kraft lignin switched from a viscosity less than the control suspension at 0.25 mg/mL to a viscosity above the control at 2.7 mg/mL. Kraft lignin adsorbed well at the 2.7 mg/mL concentration with 96.8% adsorption, whereas at 0.25 mg/mL the adsorption was only 8.38% (Table 4). The low molecular weight of the kraft lignin without any grafted chains (~25,000 g/mol) may cause it not adsorb at low concentrations due to the disorganized molecular structure [34]. Furthermore, creep tests reveal that kraft lignin has great resistance to flow seen in the low measured shear rates (Figure 4b). Based on this observation, it is hypothesized that non-adsorbed lignin is more viscosity-reducing than adsorbed kraft lignin, with 0.23 mg/mL non-

adsorbed chains in solution for the 0.25 mg/mL total concentration and only 0.0864 mg/mL non-adsorbed chains at 2.7 mg/mL total concentration (Table 4). Aggregation may be responsible for the high adsorption of kraft lignin (96.8%) at 2.7 mg/mL due to the possibility that aggregates adsorbed more strongly to particle surfaces.

The PCE displayed a 16.6% increase in adsorption to over 90% from the 0.25 to 2.7 mg/mL concentration. For polycarboxylate superplasticizers such as PCE, increased dosage has been reported to decrease the yield stress and viscosity of pastes and has been understood as a sign of improved particle dispersion [34,35]. Furthermore, PCEs have been reported to be capable of adsorbing in layers or aggregates onto charged surfaces [36], which may also have occurred and contributed to the greater viscosity reduction of the 2.7 mg/mL PCE suspension. Viscosity reduction induced by PCE may be influenced by its strong adsorption having promoted effective steric repulsion between particles [37].

Figure 5: Sedimentation results for 2.7 mg/mL for the control suspension (black), LPAA-2-10k (blue), kraft lignin (green), PCE (grey), LPAm-17-5k (pink), LPAm-2-10k (red), and LPAm-17-10k (dark red).

Comparison of the greatest viscosity reducers for both concentrations is shown in Figure 6. The LPAm-17-10k yielded a similar viscosity-reducing performance as the high concentration PCE, demonstrating that the concentration reduction of LPAm can achieve the same results as the commercial additive.

Figure 6: Viscosity curve of 0.25 mg/mL LPA-17-10k (dark red) and 2.7 mg/mL PCE (grey) compared to the control suspension (black).

Particle Interaction Summary

Rheometry and sedimentation results are influenced by interparticle interactions that depend on the electrostatic charge along the polymer chain and the chain architecture. Lignopolymer concentration impacts the interactions among chains and particles through local osmotic differences that can lead to decreased steric repulsion due to depletion flocculation of non-adsorbed chains [30,38].

Steric repulsion is central to the concept of adsorbed polymer additives improving particle dispersion and thus the steric ability of side-chains is of utmost importance for superplasticizer design [2,4,13,39]. In principle, steric repulsion increases for longer polymer chains, but adsorbed superplasticizers have to maintain a balance between side-chain extension and particle adsorption [13,34]. The LPA-17 samples tested maintained strong adsorption that led to low viscosities at 0.25 mg/mL. As expected, kraft lignin was a good adsorbent on the particles at high concentrations but had rather ineffective steric repulsion due to the lack of side-chains and may actually have promoted coagulation.

Due to partial polymer adsorption to the particle surfaces, free polymers were present in the fluid phase of the suspensions. This results in osmotic pressure differences between two

particles that expel the free chains and bring particles closer together, a phenomenon referred to as depletion flocculation [30,38,40]. Suspensions with low polymer adsorption are particularly susceptible to depletion-induced aggregation, which can overpower the influence of the steric repulsion between adsorbed chains if there is a significant concentration of free chains [38]. It has been reported that depletion layers can occur for low and high surface coverage of adsorbed polymers [38], and depletion has been shown to aggregate 44 μm vesicles [40,41].

Superplasticizers are thought to undergo depletion flocculation due to partial polymer adsorption [34], with charged polymers being especially active in this regard [6,38]. Depletion effects may be responsible for the lower viscosity of the 2.7 mg/mL supernatant than the 0.25 mg/mL (Table 3). The rheological impact of depletion of non-adsorbed chains is currently being undertaken through our work with another model system. Contrary to depletion forces, bridging flocculation should not be considered as adsorbed chains and non-adsorbing chains coexist in the suspension, and micron-scale particles with nanoscale polymers preventing one chain from joining two particles [30]. Additionally, hydration forces are assumed not to be significant to the polymer interactions because of the short side-chains [42].

Particle sedimentation can be influenced by the viscosity of the centrifuged water which can retard particle sedimentation. For both the 0.25 and 2.7 mg/mL concentrations, lignopolymers with low suspension viscosities were found to sediment rapidly and reach a final sedimentation particle volume more quickly than suspensions with less dispersion stability. In this way sedimentation tests may be conducted to predict the influence of non-adsorbed chains on the particle friction and suspension stability [29].

Conclusions

Current comb-polymer additives improve cement workability but require higher concentrations to be effective [8,9] and their synthetic chemistry is based on petroleum-derived monomers. Lignopolymers, with lignin cores and grafted polymer side-chains, offer good viscosity reduction at lower concentrations for improved cement workability. Rheometry was used for testing lignopolymers under simulated cement processing conditions using MgO suspensions, which replicate the ionic environment of cement pastes but provide a simpler system to study that lacks the complex hydration chemistries of Portland cement. Of the two

concentrations tested, LPAm lignopolymers maintained the lowest viscosity for the 0.25 mg/mL concentration and maintained viscosities similar to the 2.7 mg/mL ADVA suspension as well (Figure 6). The side-chain chemistry factored into the viscosity of the suspension, as the neutral PAm chains promoted steric repulsion while deprotonated PAA side-chains are believed to have electrostatically collapsed onto the particles [10,25–27,43]. For the low concentration, LPAm-17-10k was slightly more effective at reducing viscosity, which is attributed to the higher grafting density of 10 kg/mol molecular weight which was more effective at reducing particle aggregation than lower grafting densities or lower graft molecular weights in LPAm-2-10k and LPAm-17-5k, respectively. Flow differences between the low and high polymer concentrations were correlated to the adsorption properties that allowed the commercial comb-polymer to improve dispersion at 2.7 mg/mL [9]. Lignopolymers tested at 2.7 mg/mL were found to have less chemistry-dependent rheology but rather correlated to the number of side-chains with two side-chains being more effective than 17.

The magnesium oxide suspensions served as an analog for examination of lignopolymers flow behavior in cement pastes [11,33,39,44]. Shear ramp curves demonstrated the ability of LPAm to reduce viscosity during mixing, while creep tests (applied shear stress) gauged the suspensions' fluidity under pipe flow. Based on our findings LPAm has potential as a cement superplasticizer at 0.25 mg/mL, which is an order of magnitude lower than the current commercial recommendations for superplasticizer dosage. Such a decrease in polymer volume would save money for the construction industry while also providing improvements to cement workability.

Our refinement of LPAm to have 17 side-chains served to further improve the suspension rheology. The increased number of side-chains with strong adsorption at a low concentration make LPAm-17-10k a desirable option for incorporation into cement mixtures, and it is recommended that future studies examine the adsorption of existing comb-polymers and look to kraft lignin cores as a greener and more effective alternative to synthetic anionic chains.

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