Lignopolymers as viscosity-reducing additives in magnesium oxide suspensions

Lisa R. Murray [a], Chetali Gupta [b], Newell R. Washburn [c,d,*], Kendra A. Erk [a,*]

[a] School of Materials Engineering, Purdue University, 701 West Stadium Ave., West Lafayette, IN 47907, USA
[b] Department of Materials Science & Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, USA
[c] Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, PA 15213, USA
[d] Department of Biomedical Engineering, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, PA 15213, USA

HIGHLIGHTS

- Lignopolymers have been synthesized as new superplasticizers for cement.
- Lignopolymers were tested in model cementitious suspensions of magnesium oxide.
- Comparisons with leading polycarboxylate ether (PCE) dispersant were performed.
- At low concentrations, lignin-polyacrylamide was more effective than PCE.
- Lignin-polyacrylamide was more effective at higher grafting densities than low.

GRAPHICAL ABSTRACT
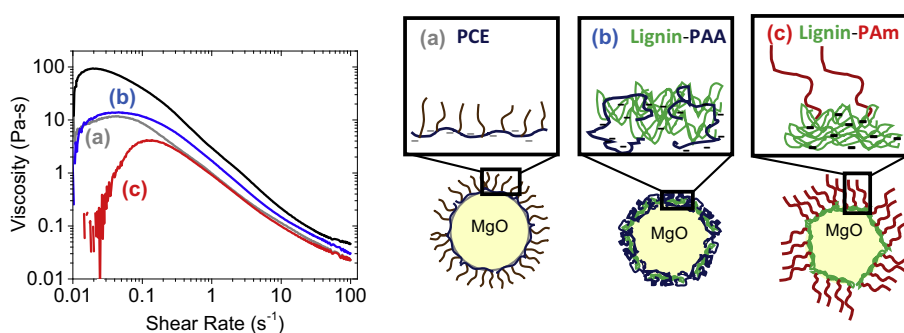
ABSTRACT

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.

© 2015 Published by Elsevier Inc.

* Corresponding authors at: Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, PA 15213, USA (N.R. Washburn), School of Materials Engineering, Purdue University, 701 West Stadium Ave., West Lafayette, IN 47907, USA (K.A. Erk).
E-mail addresses: lnielse@purdue.edu (L.R. Murray), cgupta@andrew.cmu.edu (C. Gupta), washburn@andrew.cmu.edu (N.R. Washburn), erk@purdue.edu (K.A. Erk).

1. 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, [12,14] 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], 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 cementitous 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.

2. Materials

2.1. 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 and 1.7.

2.2. 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 ~1000 g/mol [16]. Dialysis was performed to separate small molecular weight species from the PCE [16].

2.3. 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].

2.4. 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

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	5000	17
LPAm-17-10k	PAm	10,000	17