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Use of a Lignin-Based Admixture for Tailoring the Rheological Properties of Mortars for 3D Printing

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Abstract. Efforts toward decarbonizing construction materials and industrial processes related to cement and concrete can be aided via multifaceted approaches that target alternative admixtures as well as precision control of fabrication. Chemical admixtures for water reduction have played a crucial role in the development of advanced concrete mixtures. Newer biomass processing techniques developed for aviation fuel production from corn stover biomass produce a more reactive lignin byproduct that is suitable for chemical modifications to mimic the properties of polycarboxylate ether admixtures with a smaller carbon footprint. The present study examines the use of lignin-based water-reducing admixture in cement pastes and mortar mixtures for 3D printing. The experimental program explores the use of different dosages of lignin-based admixture to produce 3D-printed samples with appropriate extrudability and buildability. The rheological characterization was performed to determine the flow curve of various mixtures. Finally, the heat of hydration of cement pastes was monitored via isothermal calorimetry to assess the impact of lignin-based admixtures on the hydration process of cement. The results of this study indicate that the use of biomass by-products, such as lignin-based admixtures have great potential to effectively control the fresh-state properties of cement-based materials.

Keywords: Bio-based admixtures, Corn stover, Water-reducing admixture, Rheology, Lignin.

1 Introduction

Concrete is the most used construction material in the world, and accounts for up to 8% of annual anthropogenic CO_2 emissions. Specialized applications of concrete for construction such as high-strength and 3D-printable concretes require significantly lower amounts of water, drastically reducing flowability. Thus, use of chemical admixtures such as superplasticizers (SPs) have become vital to customize the flow characteristics (i.e., workability) by increasing plasticity of these concretes [1]. Most modern commercial SPs are polycarboxylate ethers (PCEs), however, their carbon intensive synthesis from petrochemicals makes the search for green SPs an exciting frontier in decarbonizing concrete and its consideration in LCA analysis to quantify their impacts in the overall CO_2 emissions [2]. Lignin, the second most abundant biopolymer, is an attractive feedstock for bio-based SPs. Oxidation, sulfonation, and grafting with additional molecular species are examples of techniques to enhance functionality of the lignin polymer to improve performance in cementitious systems. Lignosulfonates, byproducts from sulfite pulping processes, have been used as plasticizers since the 1930s[3]. Unmodified, these biopolymers can drastically decrease viscosity in Portland cement pastes and mortars [4]. While lignosulfonates were effective in cement systems, they are not competitive with commercial PCEs at similar dosages. Chemically modified lignosulfonates have been successful in further increasing plasticizing ability [5].

However, global decline in lignosulfonate production coupled with increases in alternative lignin sources has made Kraft, soda, and biorefinery lignins increasingly attractive feedstocks for SP production. Grafting and oxidation techniques on various alternative lignin sources have become common in the search for carbon neutral SPs. Grafting polyacrylamide, poly(methacrylic acid), and polyaniline to lignin has been shown to exhibit superplasticizing behavior, comparable with lignosulfonates and other commercial SPs. However, oxidation techniques have the advantage of avoiding fossil-fuel derived additives entirely and promote formation of anionic carboxylate species within the lignin polymer. Different oxidants have been applied to various types of lignins and shown to drastically increase the carboxylate functional group content of these lignins, making them viable plasticizers that perform similarly to commercial PCEs, albeit at higher dosages [6]. Regardless of processing methods, low-carbon, lignin-based admixtures have a promising future in decarbonization of concrete.

Here, we present the characterization of a lignin-based water-reducing admixture (LigWRA) derived from a novel biorefinery lignin byproduct derived from sustainable aviation fuel production [7]. The lignin was subjected to rapid oxidation using an alkaline hydrogen peroxide process to enhance carboxylate content and improve its suitability for use as a cement additive. We systematically investigated the performance of this admixture within a cementitious system, assessing its impact on 3D printability, rheological properties, and heat of hydration with respect to a commercial high range water reducing admixture (ComWRA). This study constitutes an initial analysis that provides valuable insights into the potential of utilizing lignin-derived additives for enhancing the fresh-state properties and sustainability of cement-based materials.

2 Materials and Methods

The effect of ComWRA and LigWRA on cement-based mixtures was assessed via printability tests, rheological characterization, and isothermal calorimetry tests. The materials used in the present study include Type IL ordinary portland cement (OPC) compliant with ASTM C595, sand with a maximum particle size of 0.6 mm, a viscosity modifying admixture (VMA), and water, in addition to the LigWRA and ComWRA.

LigWRA was prepared from corn stover black liquor produced at NREL [7]. Lignin was isolated from black liquor through sulfuric acid precipitation followed by repeated centrifugation and water washing prior to drying via lyophilization. Lignin was oxidized using hydrogen peroxide (H_2O_2) in alkaline conditions (pH 13−14), at 80°C for 1 hour using molar ratios of 0.77 for $NaOH/H_2O_2$ and 2.85 for H_2O_2/lignin. The reaction mixture was dialyzed (0.5−1 kDa) overnight and lyophilized forming the proposed LigWRA powder that was then dissolved in water at a weight ratio of 30%.

The experimental program focused on characterizing the effects of increasing dosages of ComWRA and LigWRA on the fresh properties of cement-based systems (**Table 1**). All mixtures had a constant water-to-cement ratio (w/c) and VMA content. For the printability assessment, the sand-to-cement ratio (s/c) was kept constant. For rheology and heat of hydration tests, cement paste specimens were prepared separately.

Table 1. Experimental program for the assessment of water-reducing admixtures.

Mixture ID	w/c	s/c	WRA Type	WRA %	VMA %
Control	0.35	0.75	-	-	0.05
ComWRA 0.2%	0.35	0.75	ComWRA	0.2	0.05
ComWRA 0.5%	0.35	0.75	ComWRA	0.5	0.05
ComWRA 0.8%	0.35	0.75	ComWRA	0.8	0.05
LigWRA 0.2%	0.35	0.75	LigWRA	0.2	0.05
LigWRA 0.5%	0.35	0.75	LigWRA	0.5	0.05
LigWRA 0.8%	0.35	0.75	LigWRA	0.8	0.05

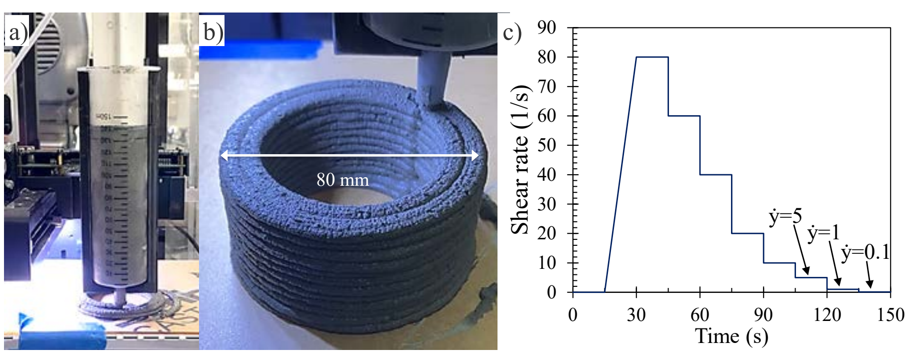

Fig. 1. a) 3D-printing system for mixture development; b) assessment of extrudability and buildability of mixtures; c) rheological protocol for determination of flow curve.

The 3D-printed elements were produced in a Hyrel 30M printer (22.5 x 20 x 20 cm^3 build volume) equipped with a 150 cm^3 syringe with a 6-mm nozzle opening and a printing speed of 600 mm/min (**Fig. 1a**). The filament was designed with a 3-mm height and 6-mm width. Printability and buildability of the mixtures were assessed by producing single-wall and double-wall cylindrical specimens with 80-mm diameter (**Fig. 1**). The rheological characterization was performed on a Bohlin Gemini HR Malvern Nano Rheometer with a parallel plate configuration (40-mm diameter and 1-mm gap) set at 25°C. Cement paste specimens were mixed for 5 minutes and placed on the bottom plate, followed by the application of the 1-mm gap and removal of excess material. **Fig. 1c** illustrates the protocol used to determine the mixtures' flow curve. Finally, the effects of the use of the ComWRA and LigWRA on the evolution of heat of hydration were assessed using an 8-channel isothermal calorimeter (TAM Air, TA Instruments) to determine the hydration kinetics of cement pastes after 100 hours, and the thermal indicator of setting time of the cement paste according to ASTM C1679-19.

3 Experimental Results

3.1 Effect of Admixtures on the Printability of Mortar Mixtures

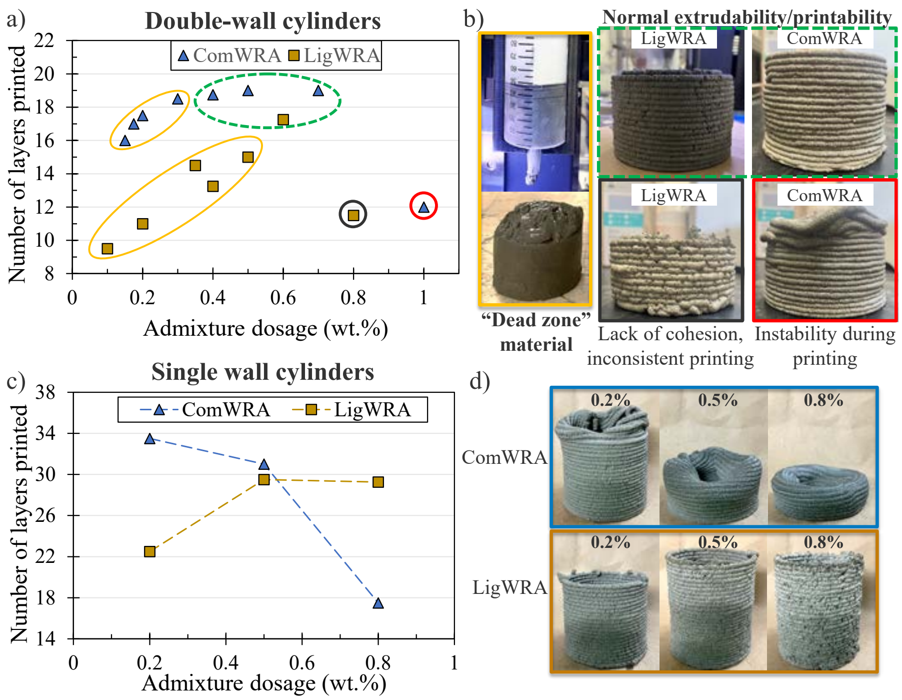

Fig. 2. Results of extrudability/buildability assessment of mortar mixtures.

An initial calibration of mixture development was performed to identify the s/c and particle size that could satisfy the extrudability of mortars through a 6-mm nozzle. An iterative process indicated that a s/c of 0.75 and max particle size of 0.6 mm were appropriate for further printing experiments along with a combination of VMA and the respective water reducing admixture (i.e., ComWRA or LigWRA) studied. **Table 1** shows the mixtures assessed during the experiments; additional dosages were explored during 3D-printing to identify printability changes in more detail. **Fig. 2a–b** illustrate the printability performance of double wall cylinders to assess the extrudability of the mixtures using a syringe system, and single-wall cylinders (**Fig. 2c–d)** used to evaluate the stability of thin-wall elements as a function of increasing WRA dosages in the mixtures. The effect of the ComWRA and LigWRA was evaluated by increasing their dosages in the range of 0.15-1.0 wt.% and 0.1%-0.8%, respectively. At lower dosages, the mixtures exhibited bleeding, as evidenced by slightly more fluid, unstable initial layers and drier, stiffer layers toward the end of the printing; this phase separation created a "dead zone" in the syringe followed by the obstruction of the plunger. For ComWRA, this phenomenon was observed with dosages up to 0.3%, compared to dosages up to 0.5% for LigWRA. Increasing dosages gradually reduced the magnitude of the "dead zone," allowing for a higher number of layers to be printed as the material gained fluidity. For ComWRA, dosages from 0.4%–0.7% allowed for complete extrusion of the material and reached the highest number of layers; however, even at 0.7%, high fluidity in the layers caused instability and buckling. For LigWRA, the best extrudability results were found at a dosage of 0.6%, after which an adverse reaction of the lignin was observed on the characteristics of the filament, causing a breakdown of the filaments during printing and a stark decrease in cohesion between layers.

Additionally, single-wall cylinders were printed to assess the buildability of selected dosages of material. For ComWRA a dosage of 0.2% allowed the printing of 34 layers before failure, and a higher dosage decreased the stability of the hollow cylinders, resulting in buckling after 31 and 17 printed layers (0.5% and 0.8%). For LigWRA, a lower dosage (0.2%) allowed printing of 23 layers before failure due to formation of a "dead zone." Further increasing LigWRA dosage improved the printability to 29 and 28 layers (0.5% and 0.8%), with an appropriate filament quality; at a dosage of 0.8%, the filaments showed poor quality and discontinuities throughout the printing process.

3.2 Effect of Admixtures on the Rheology of Cement Pastes

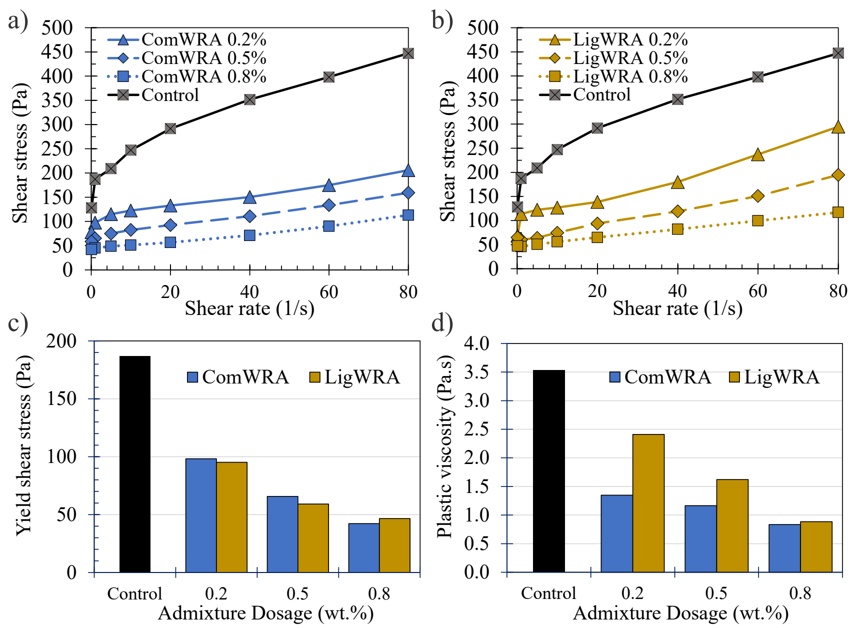

Fig. 3. Flow curves of mixtures with a) commercial admixture, b) lignin-based admixture. Parameters derived from curve-fitted to Bingham model: c) yield stress, d) plastic viscosity.

Fig. 3 shows the results of the flow curve obtained for the selected mixtures assessed in a parallel plate setup. ComWRA and LigWRA results at different dosages are compared with the plain OPC paste at the same w/c to illustrate the effectiveness of different dosages. Paste behavior was characterized by obtaining the best fitting Bingham model, thus obtaining the yield stress and plastic viscosity of the mixtures. **Fig. 3c** shows a comparable effect of LigWRA to ComWRA in reducing the yield stress of pastes at different dosages. However, comparing the effect on plastic viscosity **(Fig. 3d)**, ComWRA has a more significant impact on the estimated viscosity at different dosages.

3.3 Hydration Reactions for WRAs via Isothermal Calorimetry

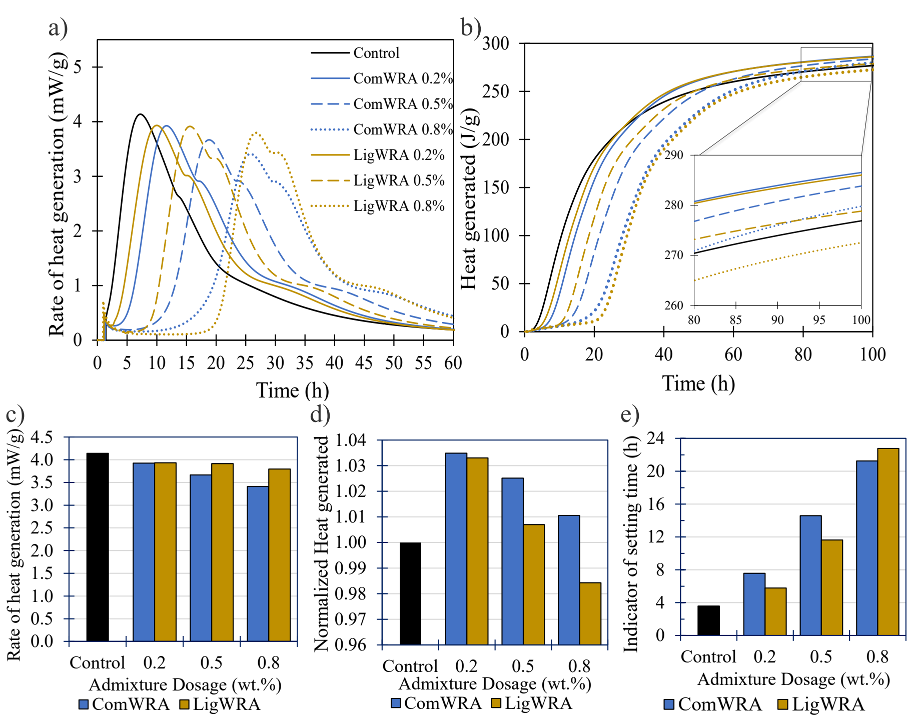

Fig. 4. Effect of admixtures on a) Hydration of cement pastes; b) Heat generation (100 hours); c) magnitude of main peak of hydration; d) total heat of (100 hours); e) indicator of setting time.

Fig. 4 shows the results of isothermal calorimetry tests, including rate of heat generation, cumulative heat, and indicator of setting time for ComWRA and LigWRA specimens. There is a drastic effect of increasing dosages of both ComWRA and LigWRA on the thermal power curve, producing a significant delay in the onset of the acceleration period of hydration. Still, the cumulative heat generated after 100 hours performs similarly to the control specimen (plain OPC). Additionally, when comparing the performance of the commercial (ComWRA) and lignin based (LigWRA) admixtures at same dosages, at 0.2% dosage, the peak of heat of hydration is identical, while for higher dosages the use of LigWRA has a lower impact in the peak rate of heat as compared to the ComWRA (**Fig. 4c**). For total heat of hydration generated after 100 hours, all specimens except 0.8% LigWRA have a slightly higher cumulative heat of hydration compared to the control case (plain OPC) (**Fig. 4d**). Finally, the estimated indicator of setting time shows that specimens with 0.2% and 0.5% LigWRA have a significantly shorter setting time when compared to the ComWRA counterparts. However, at 0.8% dosage, the LigWRA specimens have a longer setting time than the ComWRA specimen (**Fig. 4e**).

4 Discussion

The preliminary results from tests performed on the proposed lignin-based admixture show its potential for use in cement-based systems and 3D-printing applications and comparative performance as a commercial water reducing admixture at the same dosages. While the extrudability/printability experiments indicate the need for higher dosages of LigWRA to overcome the creation of a "dead zone" in the syringe, chemical modification of the lignin-based admixture successfully influenced the workability of cement pastes and mortar to behave akin to the ComWRA. We hypothesize that the increase in anionic functionality of the bulky lignin molecule served to both increase electrostatic binding with cement particles and sterically hinder agglomeration of cement particles, similar to the effect from PCEs. These benefits facilitate the extrusion process by significantly modifying cement flowability characteristics, which is supported by rheology experiments.

From the flow curve results, it is possible to observe that like ComWRA, LigWRA has a similar effect on decreasing the yield stress of cement pastes for the different dosages evaluated. However, a different behavior was observed in terms of the decrease in the plastic viscosity with respect to the control sample. At dosages of 0.2% and 0.5%, LigWRA shows a limited effect on reducing the viscosity compared to ComWRA. This is a reduction of 32% for LigWRA vs. 62% for ComWRA at 0.2% dosage, and 54% for LigWRA vs. 67% for ComWRA at 0.5% dosage; a 0.8% dosage causes a similar decrease in viscosity of LigWRA-75% vs. 76% for ComWRA. These results support the issues observed during the extrusion. ComWRA produces a drastic decrease in viscosity of the mixtures at lower dosages, which allows for a lower pressure applied on the material, avoiding excessive bleeding and dead zone formation in the extruder. Conversely, the limited effect on viscosity of LigWRA at lower dosages can be related to the resistance of the mixture to be deformed by the displacement of the plunger and effectively directed to the nozzle opening, causing an increase in pressure of the bulk mixture, bleeding, and excessive torque required from the motor. Additionally, tests performed on mixtures with different w/c indicate similar trends with respect to appropriate dosage and a lower impact of LigWRA materials on the delay of setting time when compared to ComWRA. Finally, for the effects of LigWRA on setting time, the main objective is to satisfy the requirements for admixtures given by ASTM C494, thus for current results, lower dosages around 0.2% of LigWRA are permitted to be considered as a water reducing set retarding admixture.

5 Conclusions

Our results present a preliminary characterization of a novel water-reducing admixture derived from an industrial byproduct for applications in cement-based systems. We conclude that the developed lignin-based admixture (LigWRA) can modify the fresh-state characteristics of cement-based systems, thus influencing the printability of mortar mixtures. Further analysis showed that LigWRA has a significant impact on the yield stress, at the same level as a commercial superplasticizer (ComWRA) used for comparison; however, its low impact on the viscosity could have influenced the extrudability at lower dosages, affecting the extrudability of mixtures with the syringe system used. LigWRA showed lower setting times compared to ComWRA at different dosages; still, only lower dosages (up to 0.2%) could be further explored to satisfy ASTM standards for chemical admixtures in concrete. Further research aims to explore the refinement of rheological response and the effects on mechanical performance and durability.

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