LigniOx lignins – High performance concrete plasticizers and versatile dispersants

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Abstract

A simple and economic alkali-O2 oxidation (LigniOx) process has been developed for the production of concrete plasticizers and versatile dispersants from technical lignins. Previously, soda and kraft lignin based LigniOx lignins have been shown to have great potential to serve the traditional lignosulfonate markets, and to compete even with more expensive synthetic products. Here, the latest results of successful use of kraft, organosolv and hydrolysis lignin based LigniOx solutions for mortar plasticization in comparison to several commercial lignosulfonates and synthetic superplasticizers are presented. To widen the range of applications of LigniOx lignins, high performance for dispersing of special carbon black into aqueous solutions, used e.g. in paints, inks and various coatings is demonstrated.

1 Introduction

Dispersants are widely used for suspending colloidal particles in cosmetics, paints, pharmaceuticals, oil drilling mud, cement, and ceramic applications. Besides lignosulfonates, mainly synthetic polymers are used as dispersants in these applications. For substituting the current non-biodegrable polymers with bio-based (less expensive) materials, technical lignins have been modified in several ways (e.g. by sulfomethylation, oxidation, carboxymethylation, grafting with PEG, hydroxymethylation/propylation and sulfonation, fractionation, enzyme utilization) to convert them into water soluble dispersants. Despite the encouraging results, the modification procedures seemed to be industrially unattractive and the property-performance relationships for lignin-based dispersants case dependent [1].

LigniOx technology, recently developed by VTT, is a simple and cost-efficient alkali-O2 oxidation process for conversion of technical lignins to ready-to-use products for concrete plasticization, i.e. cement dispersing, or versatile dispersants [2,3]. The LigniOx process can be integrated into the biorefineries, or operated in stand-alone units e.g. by chemical industry. The oxidation is active toward phenolic hydroxyls (PhOH) and introduces acidic groups into the lignin polymer, while retaining its polymeric structure. Depending on the oxidation conditions, (especially pH), the negative charge and molar mass of lignin can be adjusted in a controlled way. The previous studies on mortar and concrete plasticization have demonstrated that the soda and kraft LigniOx lignins have great potential to compete with lignosulfonates in their traditional markets, and even with synthetic products. LigniOx lignins have also shown high dispersing performance of several inorganic pigments, such as TiO2, colour pigment, and CaCO3, used e.g. in paints [4,5]. Currently, the oxidation technology is optimized for several different lignin raw materials [6].

In this study the very recent results of applying kraft, organosolv and hydrolysis lignin based LigniOx lignins as plasticizers in mortar are presented. The adsorption tendency of the LigniOx lignins on cement surface is discussed. In addition, the dispersing performance of LigniOx lignins in special carbon black, used e.g. in latex paint pigmenting, conductive coating, water based inks, textile printing pastes, and aqueous graphite dispersions, is demonstrated.

2 Experimental

Industrial lignin raw materials provided by Metsä Fibre, CIMV and St1 were used (Table 1).

Table 1. Industrial lignin raw materials, characteristics, and sample coding.

Lignin	Origin	Characteristics	Coding
Kraft	Softwood	Rich in PhOH, low carbohydrate content	KL
Organosolv	Wheat straw	Relatively rich in PhOH	OSL
Hydrolysis	Softwood	Low PhOH, high carbohydrate content	HL

Oxidations of different lignin raw materials were performed under the range of conditions reported in [2,3].

The plasticizing performance of kraft, organosolv and hydrolysis lignin based LigniOx solutions was evaluated in mortar. Mortar was prepared using a standard sand mixture, Portland cement (CEM I, 52.5N, Megasementti by Finnsementti), and water. Plasticizer was added in the mix in the end of the preparation. Dosage of 0,6 wt% (active matter) of cement was used. Few drops of de-airing agent (Tributylfosfate, TBF) was used in all tests. The fluidity of the mortar was measured using Haegermann flow table (Ø 300 mm) method and a mold with a diameter of 100 mm. Flow value represents the spread (diameter) of mortar. Commercial polycarboxylate ether (PCE) and sulfonated naphthalene (SNF) based superplasticizers and lignosulfonate (LS) based plasticizers were used as references. Commercial products were dosed based on dry matter reported on the containers, LigniOx solutions based on lignin content measured by UV280.

Adsorption tendency of kraft lignin based LigniOx lignins on cement (CEM I, 52.5, Megasementti) surface was studied using a fast in-house method [7]. The method is based on quantifying the un-adsorbed amount of plasticizer by UV-measurement from the liquid phase separated from the cement paste (W/C 0.4) by centrifugation. Commercial sulfonated naphthalene (SNF) based superplasticizer and lignosulfonate (LS 2) were studied as references.

The dispersing performance of the oxidized kraft and hydrolysis based samples (LigniOx-KL 3 kDa, LigniOx-KL 7 kDa, LigniOx-HL 20 kDa) was evaluated in Special Carbon Black (CB) (Orion Engineered Carbons). The dispersion prepared using high shear mixing (Omni mixer Sorvall, OCI instruments) contained 10 wt% of CB pigment in water (including LigniOx solution or commercial products). Dispersant dosages 0,25 - 2,5 wt% (active matter) of pigment were used. The viscosity of the pastes was measured as a function of shear rate using AR-G2 rheometer (Texas Instruments) at 25°C. Commercial polyacrylic acid (PAA) and lignosulfonate (LS) based dispersants were used as references.

3 Results and discussion

3.1 Mortar plasticization

Strong dispersion capabilities of organosolv lignin (OSL) based LigniOx solutions was verified in addition to kraft lignin (KL) based LigniOx samples (Figure 1). Both the kraft and organosolv lignin based LigniOx solutions provided better plasticization performance compared to the commercial polycarboxylates (PCE) and sulfonated naphthalene (SNF) references. Hydrolysis lignin (HL) based LigniOx solutions were also showing rather good performance, and nearly comparable with some of the synthetic references.

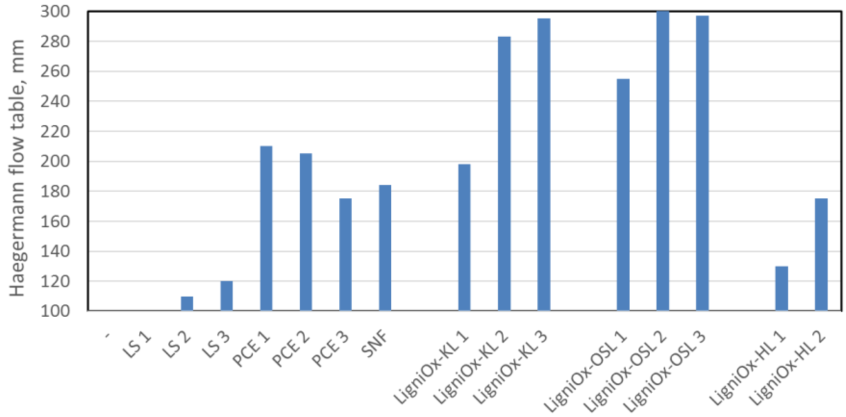

Figure 1. Haegermann flow in fresh mortar plasticized with commercial (super)plasticizer products (LS, PCE, SNF) and kraft, organosolv, and hydrolysis lignin based LigniOx. Dosing 0,6% (based on lignin content) of cement. Defoamer used.

3.2 Adsorption on cement particles

Concrete superplasticizers are reported to work either by electrostatic or steric repulsion between individual cement particles to achieve a full dispersion. The negatively charged functional groups of the superplasticizer, sulfonic and carboxylic groups, adsorb on the active sites (calcium aluminate) of the cement particles giving them a negative charge, which leads to the electrostatic repulsion between the particles. The branched structure of the PCE superplasticizer achieves steric repulsion by forcing the cement particles apart [8]. Steric repulsion is known to be more effective in dispersion compared to electrostatic repulsion. In the case of lignosulfonates, it is postulated that the dispersing effect is mainly due to the electrostatic repulsion between the cement particles [9].

In previous studies, it has been shown that alkali-O2 oxidation (LigniOx) of lignin yields highly carboxylated lignin [10]. To gain understanding of the working mechanism of LigniOx lignins, their adsorption on ordinary Portland cement as a function of dosing was quantified and compared to selected commercial plasticizers (Figure 2). Adsorption of sulfonated naphthalene based product (SNF) and lignosulfonate (LS 2), showed rather similar behaviour as a function of the plasticizer dosing: the adsorbed amount increased steadily as increasing the dosing up to 0,5%, where after it was still increasing in lesser extent as increasing the dosing up to 1,0%. In the case of the LigniOx plasticizers, the maximum adsorption was reached already with the dosing of 0,5% on cement. The adsorption behaviour of the studied plasticizers could be interpreted using Langmuir isotherm equation with rather high correlation [7]. Based on this initial study, it can be postulated that the working mechanism of LigniOx lignins is somewhat similar to that of the commercial plasticizers.

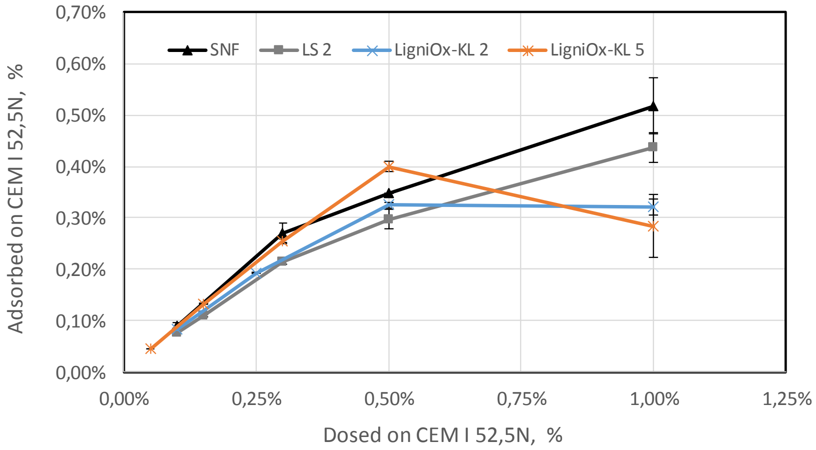

Figure 2. Adsorption of commercial plasticizers (SNF, LS 2) and kraft lignin based LigniOx on cement surface as a function of dosing.

3.3 Carbon black dispersing

LigniOx-KL samples with molar masses of 3 and 7 kDa and LigniOx-HL with Mw of 20 kDa showed all high dispersing performance in special carbon black when using dosing of 2,5% (Figure 3, left). The viscosity values were measured just after preparing the dispersion and after 7d.There was no changes seen after the storage period. Better dispersing performance of LigniOx lignins over synthetic commercial reference was supported also by microscopy and particle size analyses.

Differences in the performance between the tested LigniOx samples were seen when decreasing dosing down to 0,75% (Figure 3, right). The 7 kDa LigniOx-KL sample was still showing high performance, while the other LigniOx samples as well as the lignosulfonate reference (LS) could not retain the viscosity as low. To confirm that 0,75% was not overdosing for synthetic reference (PAA), 0,25% dosing was tested. At dosage of 0,25%, PAA showed even higher viscosity than at 2,5 or 0,75%.

The results highlight that the oxidation conditions must be optimized according to the specific end-uses to provide high-performance LigniOx products for each lignin type. Regarding the new end-uses of LigniOx lignin, performance in the actual formulated end-product (paints, coatings or inks), and the co-effect with all the other ingredients should be demonstrated.

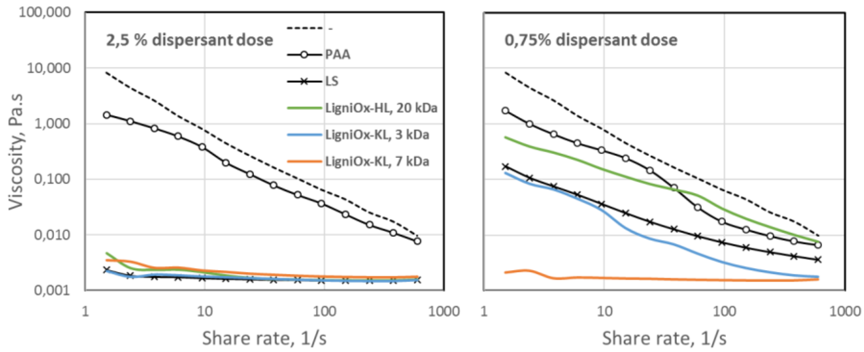

Figure 3. Viscosity of special carbon black dispersion with commercial dispersants (PAA, LS), kraft (LigniOx-KL 3 & 7 kDa) and hydrolysis lignin (LigniOx-HL 20 kDa) based LigniOx. Dosing 2,5 & 0,75% of carbon black.

4 Conclusions

LigniOx oxidation technology converts various industrial lignin raw materials to high-performing plasticizers and versatile dispersant. In addition to kraft lignin, it was shown that organosolv and hydrolysis lignin based LigniOx solutions have high dispersing performance in cementitious material. Kraft and hydrolysis lignin based solutions also efficiently dispersed special carbon black in water, which further opens new application possibilities for LigniOx lignins.

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