

## LigniOx lignins for dispersing special carbon black

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### ABSTRACT

The current study represents the excellent performance of oxidized kraft, organosolv, and hydrolysis lignins as dispersant for special carbon black (CB). The special CB dispersions were analysed at first day of preparation and after two weeks. Stable suspension of special CB was obtained with all the studied LigniOx samples, which was indicated by zeta potential, viscosity and particle size measurements. LigniOx lignins outperform the performance of the commercial polyacrylic acid and lignosulfonate-based dispersants produced for special CB.

### INTRODUCTION

Special CB is used in paints, coatings, inks, textile printing pastes, and aqueous graphite dispersions.<sup>1</sup> Special CB is not a water-soluble component. Dispersability of special CB is poor due to nonpolar and weak hydrophilic nature of the pigment surface. Consequently, it needs wetting and dispersing additives when used in the above-mentioned applications.<sup>2</sup> There is a need for bio based, low cost and sustainable method to prepare stable dispersion of special CB in aqueous system.

On the market, synthetic dispersants (*i.e.* polyacrylic acids, naphthalene sulfonate condensate and alkyl benzene sulfonates) as well as modified lignosulfonates as anionic polyelectrolytes are applied in dispersing of special CB in aqueous media. However,

synthetic dispersants are expensive and non-sustainable. For the required high performance, also lignosulphonates are typically modified, which increases their production costs<sup>3</sup>.

Lignin is the second most abundant polymer in biomass and the largest side-stream from lignocellulosic biorefineries. Nowadays, kraft pulping is the main pulping process and kraft lignin as side stream could be recovered in significant amount. Additionally, hydrolysis lignin from bioethanol production and sulphur free lignin from organosolv pulping are available in reasonable quantities. For many applications, technical lignins need to be modified, in order to improve their properties for target applications.

LigniOx technology is a simple and cost-efficient alkali-O<sub>2</sub> oxidation process for conversion of variable technical lignins to dispersing agents. Depending on the oxidation conditions, especially pH, the negative charge and molar mass of lignin can be adjusted in a controlled way.<sup>4,5</sup> LigniOx technology is currently under commercialization.<sup>6</sup>

### EXPERIMENTS

#### Materials

Special carbon black P-200Z from Penta Carbon was used. Wheat straw organosolv, softwood hydrolysis and softwood kraft lignins were oxidized by LigniOx technology. The oxidized lignins as well as

commercial polyacrylic acid (PAA) and lignosulfonate (LS) based references were used as dispersing agents for special CB. The characteristics of the dispersants used in the current study are presented in Table 1.

Table 1. Oxidized lignin and reference dispersants for special CB dispersion.

Lignin origin	Dispersant	Mw, Da	Charge density, meq/g
Kraft	LigniOx-KL	4910	-3.0
Organosolv	LigniOx-OSL	5205	-2.5
Hydrolysis	LigniOx-HL	9670	-3.4
-	LS	5800	-1.6
-	PAA	1400	n.d.

Deionized water was the solvent in the study. Special CB material (15 wt%) and dispersant (in range 2.5-30 % of special CB weight) were mixed in water and left for 15 min under paraffin at room temperature. Further, dispersion was mixed with Heidolph Diax 600 Laboratory stirrer for 2 min and with OCI Instrument Omni Mixer Sorvall for 3 min. Ready dispersion was left for 20–30 minutes in a closed container before the measurements.

#### Rheological measurements

The rheological behaviour of dispersion was measured as a function of shear rate (0,6-600 s<sup>-1</sup>) by using AR-G2 Rheometer by Texas Instruments. The measurements were conducted with a Peliter plate steel cone geometry (40 mm diameter and 2.0° angle). All rheological measurements were conducted at 25°C. The amount of paste for the rheological measurements was 600 µl. Each dispersion was measured about 30 min after preparation (1st day) and after two weeks, while storing the suspension in a closed container at room and elevated (50°C) temperature. Viscosity at a share rate of 95 s<sup>-1</sup> was followed to evaluate the dependency of viscosity and dispersant dosage.

#### Zeta potential and size measurements

The zeta potential ( $\zeta$ ) was measured by Zetasizer Nanoseries S90 (Malvern Instruments™ Ltd). Highly diluted dispersions of special CB with varying concentration of dispersant were prepared by mixing a certain amount of stock special CB dispersion in deionized water. The measurements were conducted at 25°C. The effect of LigniOx dispersants on particle size distribution of special CB P-200Z was also measured by a Malver Nanosizer S 90 instrument. Measured particle size is an intensity-based average size (diameter). Polydispersity index (PDI) was in the range of 0.1-0.4 in all measured samples.

#### RESULTS AND DISCUSSIONS

It is important to investigate the effect of LigniOx lignins and reference dispersants on the special CB dispersions. This can be achieved by following the change of zeta potential ( $\zeta$ ) with the dispersant concentration as depicted in Figure 1. The LigniOx lignins and references dispersants were tested at various dose, 2.5-30 wt% of special CB weight. The special CB in water, without any dispersant demonstrated zeta potential value of -32 mV. This indicated a negatively charged nature of the surface's oxygen-functional groups in aqueous medium. By addition of LigniOx-KL, LigniOx-OSL and reference LS – the absolute value of zeta potential strongly increased up to ~ -52 mV and in case reference PAA – zeta potential of special CB dispersion increased up to -41 mV. The LigniOx-HL had different behaviour in zeta potential measurements. This samples reached the lowest absolute zeta potential (-47 mV) at 15 wt% of dosage and then absolute zeta potential was decreasing until -44 mV. It indicated an overdosing of the dispersant. Most probably, this behaviour is connected with the molecular weight of LigniOx-HL, it has the highest Mw (9670 Da) in comparison with

other LigniOx samples (4950 and 5210 Da). Though, the molecular weight of the polymeric dispersant should be sufficient to provide polymer chains of optimum length to overcome the Van der Waals forces of attraction between pigment particles. If the chains are too short, polymer could not provide a sufficiently thick barrier to prevent flocculation. However, if molecular weight is too high, long polymer chains can “fold back” on themselves and consequently dispersant performance will be reduced. The best performance could be reached when polymer chain of dispersant is free to move in the dispersing medium and the surface of the particles are covered with sufficient density of chains to minimize particle to particle interaction.<sup>7</sup>

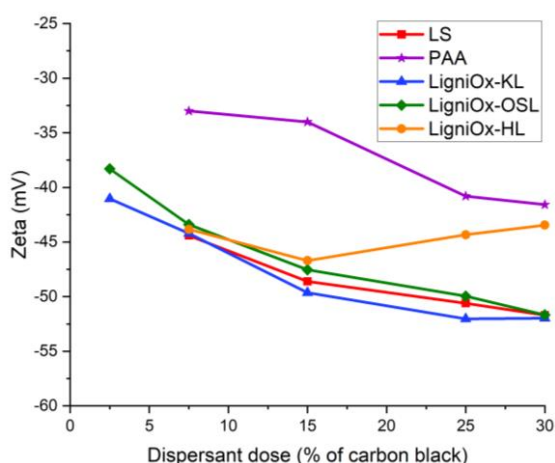


Figure 1. Zeta potential as a function of dispersant dosage at 15 wt% dosage of special CB.

The viscosity of dispersion was measured as function of shear rate, shear stress and dispersant dose. The lower the shear stress at a given shear rate, the better the dispersing of the pigment particles. In Figure 2, the performance of LigniOx lignins and reference dispersant is illustrated. The LigniOx-KL, LigniOx-OSL, and LigniOx-HL showed lower optimum dosing than the reference dispersants, PAA and LS. LigniOx-KL and LigniOx-OSL demonstrated the same or lower viscosity values (~0.003-

0.0035 Pa s) at 15 % dosages as the PAA reference at 25 % dosage (0.0036 Pa s). LigniOx-HL demonstrated the same viscosity values (0.0056 Pa s) at 15 % dosage as the LS reference at 30 % dosage (0.0053 Pa s). However, with increasing LigniOx-HL dosage (25-30 %), the viscosity was increasing that indicated a dispersant overdosing. The other samples demonstrated either an insignificant increase or the same viscosity values with increasing dispersant dosage. Zeta potential measurements also indicated the LigniOx-HL overdosing as it was discussed earlier. Therefore, the lowest viscosity and the most stable dispersion of special CB with LigniOx-HL was obtained only at 15 % dose of dispersant.

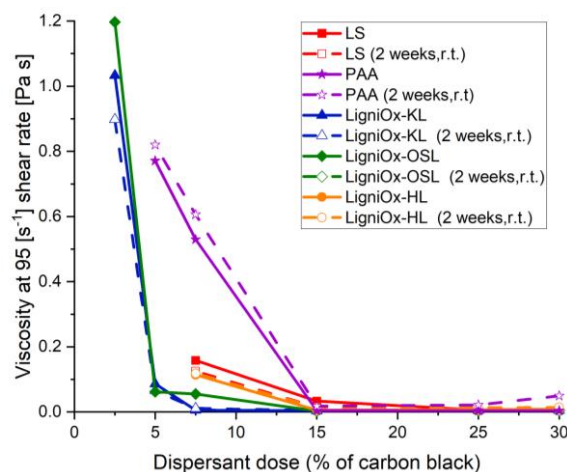


Figure 2. Viscosity at 95 s<sup>-1</sup> shear rate as a function of dispersant dosage at 15 wt% dosage of special CB.

The long-term stability of the special CB dispersions was evaluated after storing the samples for two weeks, both, at room temperature and elevated temperatures (50°C). There was no significant change in viscosity of special CB dispersion with LigniOx-KL, LigniOx-OSL, and LS at room temperature. While LigniOx-HL had the highest increase in viscosity at room temperature, the values were still comparable with the increasing viscosity of reference dispersants PAA. The viscosity values after storage for two weeks at room temperature

(r.t.) are illustrated in Figure 2 by dash lines. Viscosity of special CB dispersions at elevated temperatures has increased with all dispersants, however, LigniOx-OSL and LigniOx-KL demonstrated good stability. LigniOx-HL showed lower stability at 50°C after two weeks storage time compared to the reference PAA or LS.

The dispersing performance could be properly determined by measuring particle size distribution of the pigment suspensions. LigniOx increased negative charge around the special CB particles and it enlarged the electrostatic repulsion between the particles and therefore provided electrostatic stabilization. Particle size values obtained from experiments are illustrated in Figure 3

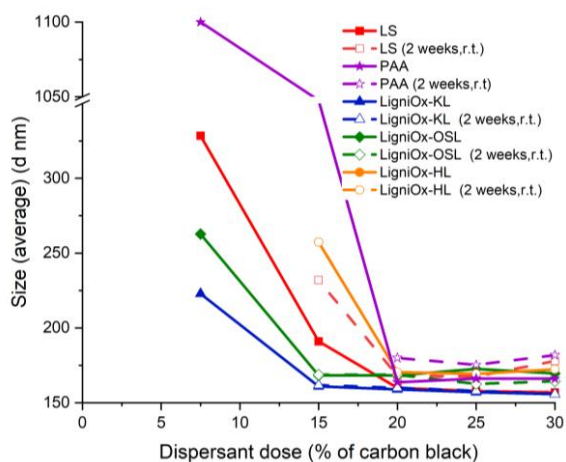


Figure 3. Average particle size as a function of dispersant dosage at 15 wt% dosage of CB.

The lowest particle size of special CB dispersion (~ 155-163 nm) was demonstrated by LigniOx-KL and LigniOx-OSL at 15-30 % dosage and those values are comparable with values obtained by reference PAA at 20-30 % (163-167 nm) and reference LS (158-160 nm) at 25-30 % dose. The LigniOx-HL demonstrated slightly higher particle size values (~180-185 nm) at 15-30% dosage.

Particle size distribution correlates with viscosity data. From Figure 2 and Figure 3 it is clear that LigniOx-KL and LigniOx-OSL

demonstrated the lowest particle sizes as well as lowest viscosity at 15% dose. Additionally, zeta potential values from Figure 1 demonstrated that dispersions are stable, because no significant variation in  $|\zeta|$ -values to place in the range from 15 to 30 % dosage. Stability of dispersion was also proved by two weeks storage time. It is also depicted on the Figure 2 and Figure 3 – no changes or slight variation were determined in viscosity and particle size distribution measurements after two weeks storage at room temperature. In Figure 4, the correlation between zeta potential and particle size demonstrated that in LigniOx-KL dispersion there are no changes in particle size or zeta potential above 15 % dosing, which indicates a stable special CB dispersion.

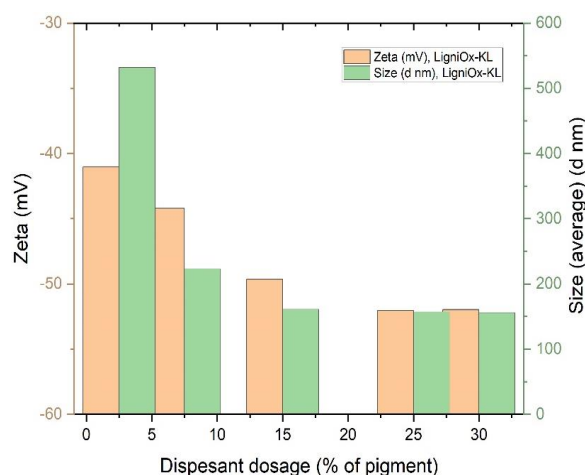


Figure 4. Correlation between zeta potential and particle size of special CB dispersion with LigniOx-KL.

LigniOx-HL performance is sensitive to the dose of the dispersant, which is most probably connected with the higher Mw of the sample.

## CONCLUSION

Based on all the results, it can be concluded that all the studied LigniOx lignins demonstrated very good dispersing ability of studied special CB grade. These novel dispersants, especially LigniOx-KL and

LigniOx-OSL, even outperformed the commercial LS and PAA based references, which are sold especially for special CB dispersing. The LigniOx lignins demonstrated the same performance at significantly lower dosage than the commercial references, which can provide significant cost-reduction for the end-user. Additionally, special CB dispersions with LigniOx lignins demonstrated very good stability at room and at elevated temperatures after storing for two weeks. LigniOx-HL has high charge density and most probably, LigniOx-HL produced with Mw in the range 4900-6000 Da can demonstrate the same good performance as LigniOx-KL and LigniOx-OSL in special CB dispersion. Based on the present results it can be concluded that the molecular weight of oxidized lignins has significant role in the dispersant properties of special CB.

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