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PROSPECT OF SODIUM LIGNOSULFONATE DERIVED FROM HARDWOOD BLACK LIQUOR AS INGREDIENT IN MORTAR

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ABSTRACT

Lignosulfonate, derived from grasses and softwood lignins, are able to increase workability of concrete mixture. Based on the availability of hardwood as raw material in pulp and paper industry in Indonesia, the black liquor from this sector will be enormous. This experiment sought to prove that sodium lignosulfonate (NaLS) derived from hardwood would give mortar mixture better physical and mechanical properties as compared to commercial sodium lignosulfonate. Lignosulfonate was prepared and mixed at 0.1, 0.2, and 0.3% by weight of the mortar. Mortar made with fine aggregate consisting of portland cement, sand, water, and eucalypt sodium-lignosulfonate gave cement setting time up to 500 minutes with a flow diameter of up to 18 cm, indicating satisfactory water dispersion. The mechanical characteristics of the mortar, in terms of flexural and compressive strength meet the ASTM designation of C109, C185, C230, and JIS R5201. Therefore, lignosulfonate derived from hardwood has the potential as a dispersant as compared to commercial NaLS derived from softwood lignin.

Key word: hardwood, mortar, compressive strength, flexural strength

INTRODUCTION

Lignosulfonates are an anionic surfactants that can be used as a dispersant for binding other materials, as well as serve as an adhesive material in concrete and mortar mixture (Ouyang *et al.*, 2006; Barron, 2008). Experiments proved that lignosulfonate is able to increase workability of concrete mixture (Matsushita and Yasuda, 2004). Lignosulfonate used in these experiments are assumed to be derived from softwood lignin. Lignosulfonate, derived from esparto grass, improves plasticity of the mortar, reduces its water content, as well as inhibits the cement initial and post setting time. The mortar compressive strength increased after 28 days (Kamoun *et al.*, 2003). Sodium lignosulfonate (NaLS) derived from empty fruit bunch of oil palm tree as dispersant agent was evaluated by Ismiyati and co-workers (2009).

Hardwood is the major source of pulp and paper production in Indonesia and makes it one of the leading paper producers in the world. Annual production capacity of pulp and paper manufacture increased from 7.2 million tons to 11 million tons from 1997 to 2007 (The, 2008). From the hardwood used by paper manufacturers, there will be an enormous supply of black liquor, from which lignosulfonate is derived. Considering the difference in lignin precursors, being predominantly synapyl rather than coniferyl alcohol constituents, it is presumed that lignosulfonate from hardwood lignin will have better properties as dispersant in mortar mixtures.

This experiment sought to prove that NaLS, derived from black liquor originating from hardwood, would give mortar mixture better physical and mechanical properties as compared to commercial sodium lignosulfonate. Cement paste setting time, flow diameter, flexural strength, and compressive strength of the mortar, and water dispersion in the mixture were evaluated.

MATERIALS AND METHODS

Sodium lignosulfonate preparation

NaLS was synthesized as described by Kamoun *et al.* (2003). Black liquor was obtained from a local pulp manufacturer that used eucalyptus wood as the raw material in the kraft process. Commercial NaLS used as a control was supplied by PT Fosrocs.

Sand characterization

Sand used in this experiment was obtained from a local vendor; it has the following properties:

(1) Un-uniform particle size according to ASTM C136-2001, with the fineness modulus of 3.21. This value is out of the permitted range of 1.5–3.0;

(2) Relative granular specific gravity of sand of 2.22 g mL^{-1}, which is below the standard (2.50–2.65 g mL^{-1}) according to ASTM C128-2001;

(3) Absorption of water in the sand of 8.76%. This value is higher than that of the standard 1–5% according to ASTM C128-2001. The high water absorption capacity of the sand required a cement-sand ratio of 1:2.

Cement characterization

Portland cement used in this experiment had a specific gravity of 3.02 g mL^{-1} according to ASTM C188-95), which is somewhat lower than that reported by Kato (1990).

Mortar preparation

The mortar mixture consisted of commercial first-quality portland cement commonly sold in Indonesia, local sand from the area in Bogor vicinity, and tap water in the proportion of 1:2:0.65. These materials were mixed for 15 minutes to homogenize. Hardwood NaLS were added in concentrations from 0.1 to 0.5% by weight. The best property from these combinations was then compared to the commercial NaLS. The mixtures were molded at ambient condition (RH 70%, 25-28 °C) and was kept in a damp place during the test.

Determination of cement setting time

Cement begins to stiffen after contact with water. Mixed concrete is usually transported in a mixing truck to the site where mortar structures are installed which could lead to degradation of fresh concrete caused by heat such as high ambient temperature. It was very important to know when fresh concrete begins to harden. Starting time of stiffening is described as initial setting time. Measurement of the time when the concrete finished stiffening to provide some data to control the concrete work, and ending time is called final setting time (JIS R5201, ASTM C187, C19, BS 1881 part 105).

Mortar flow diameter test (ASTM equivalent C348)

Prior to pouring the mortar in the mould, the mortar flow was checked at the standard table. The upper surface of the cone was finished by grinding and the vertical spindle was finished by polishing.

Determination of flexural and compressive strength (BS 1881 part 116; ASTM C109)

Flexural strength was determined using Mihaelis as a simple device, at the age of 3, 7, and 28 days. The specimen used for from flexural strength measurement was also subjected to compressive strength determination. In the preliminary test, mortar flexural test was carried out with commercial NaLS in five different levels (0.1, 0.2, 0.3, 0.4, and 0.5%). Further analysis was carried out with seven different levels of additive in the mortar, i.e. 0% NaLS as control, 0.1, 0.2, and 0.3% synthesized NaLS, and 0.1, 0.2, and 0.3 commercial NaLS, at 3, 7, and 28 days.

The Shimadzu testing machine was run with additional load at a rate of 5 kg sec^{-1} automatically (Kato, 1990). The flexural load was converted to compressive load of the standard machine, i.e. load $\times$ 50 $\times$ 0.234 kg cm^{-2}.

Cement hydration after 3-days

Fifty grams of cement was mixed with some NaLS as additive, which was dissolved in 25 mL deionized water, and stirred. The hydration process was terminated after 3 days, the sample was crushed and soaked in acetone. The sample was analyzed using a Shimadzu X-ray defractometer at 40kV and 20 mA. This analysis was also carried out on cement mixture without additive as a control. (Grierson *et al.*, 2004)

Observation on interaction between cement and water

The interaction between mortar and water was observed using a scanning electron microscope (SEM) with 1000× magnification, which produces largely magnified image by using electrons instead of light to form an image.

Statistical analysis

The experiment used a complete random experiment (RAL) one factor in time with two replications.

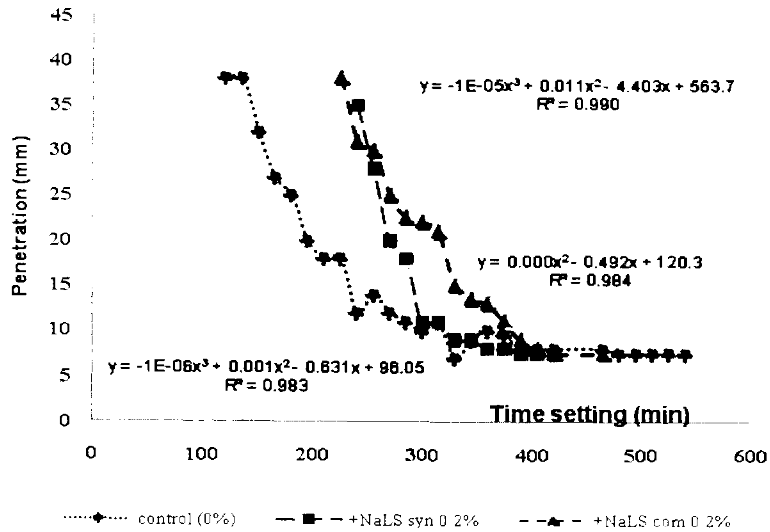
RESULTS AND DISCUSSION

Cement paste setting time (ASTM C403/C403M)

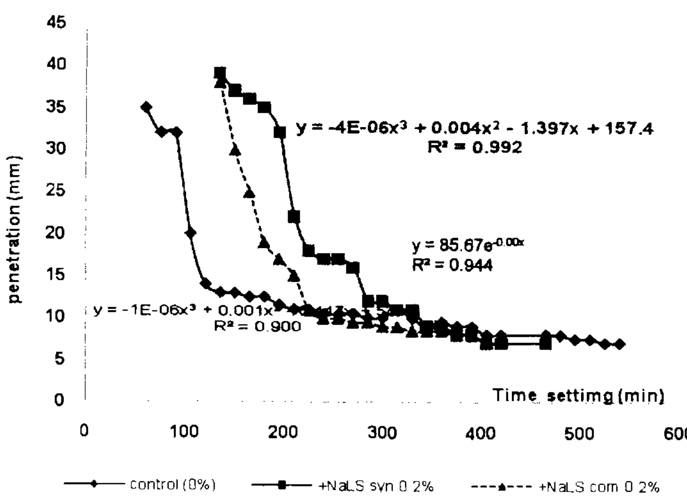
Setting time aspect was considered from the initial and the terminal setting times. Setting time of the mortar containing hardwood NaLS was approximately 500 minutes, which is longer than that of the control (240 to 300 minutes) and the mortar containing commercial NaLS (Fig. 1). The prolonged setting time would be very beneficial for transportation to distant areas.

Flow diameter

Without NaLS (control), the inner and outer diameters of mortar flow is slower as compared to that with NaLS as dispersant (Fig. 2, left-hand side). The flow diameter increased and reached 18 cm for the mortar containing 0.2% NaLS, but decreased with addition of more dispersant. On the other hand, the maximum flow diameter of mortar containing commercial NaLS is only 16 cm (Fig. 2, right-hand side). Reported in terms of dimension (cm), the behavior is depicted in Fig. 3.



(a). Initial setting time



(b). Terminal setting time

Fig. 1. Setting times of mortar as control and mortars containing hardwood NaLS (synthetic) and commercial NaLS (com). Initial setting time (a) and terminal setting time (b).

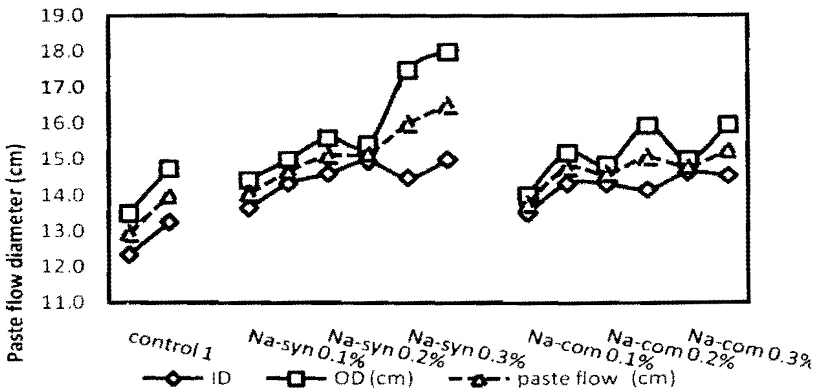


Fig. 2. Paste flow diameter versus additive concentration of NaLS.

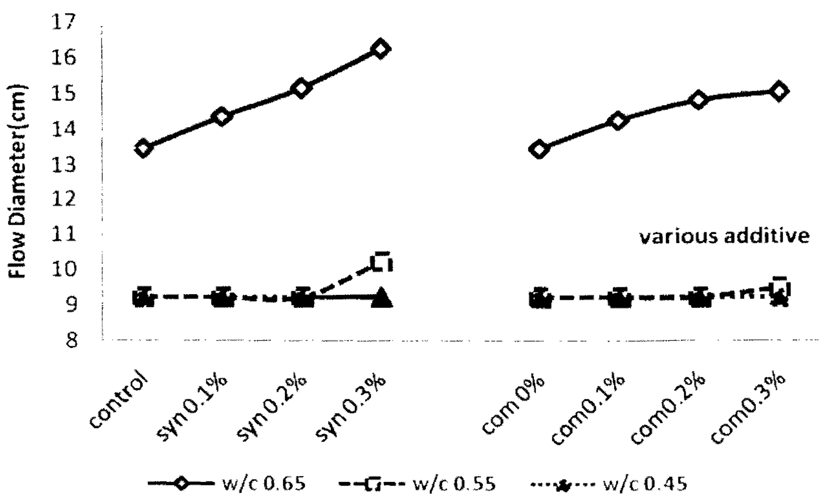


Fig. 3 Flow diameter properties of specimens containing hardwood NaLS (left-hand side) and commercial NaLS (right-hand side) at different water:cement (w/c) ratios and levels of hardwood NaLS (control, NaLS commercial (com) and NaLS synthetic (syn), respectively)

Figure 4 shows a significant change on flow diameter properties due to different type and concentration of dispersant. At a water cement ratio of 0.55, there is significant change of flow diameter of hardwood NaLS up to 0.10% as compared to commercial NaLS at the the same concentration, which is only 0.02% (indicated by corresponding arrows).

From the flow test using a manual device, there is a consistent indication of the flow between the group of treatment using hardwood NaLS and commercial NaLS. One distinct property is observed from water dispersion at water:cement ratio of 0.65:1.

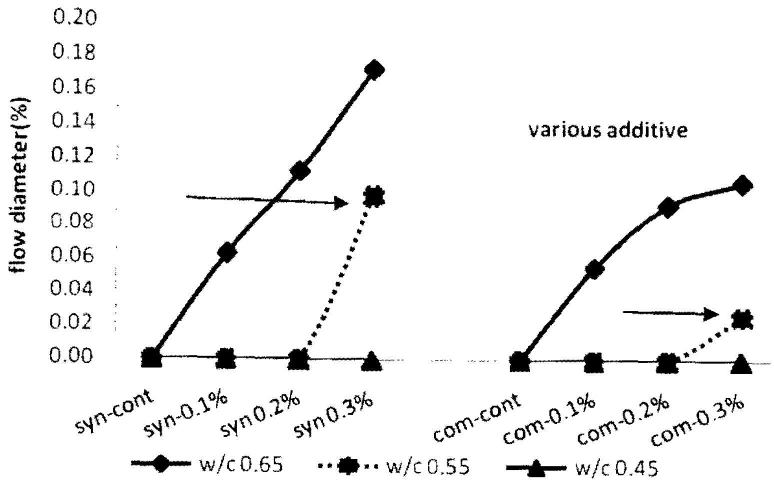


Fig. 4. Percentage change of NaLS flow diameter by water cement ratio containing hardwood NaLS (left-hand side) and commercial NaLS (right-hand side) at different additive ratios.

Flexural strength

Flexural strength was also compared as the result of different level of NaLS in the mortar. The optimum flexural strength was obtained when 0.2% NaLS was added to the mortar for samples taken 3, 7 and 28 days after mixing (Fig. 5).

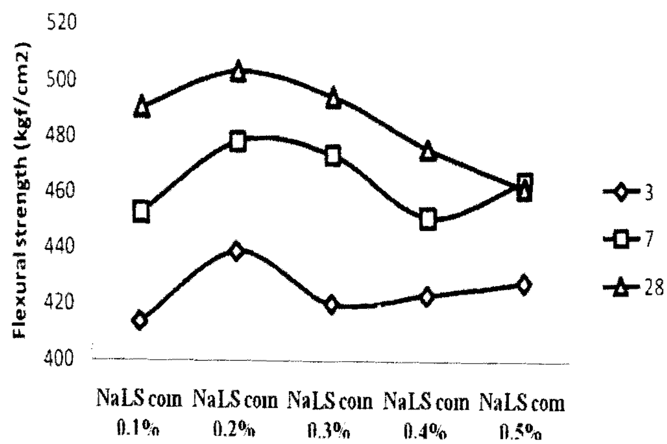


Fig. 5. Preliminary flexural strength evaluation at various NaLS concentrations.

The rate of mortar curing to reach high strength value was faster for mortar containing 0.2% hardwood NaLS as indicated by the steep slope in the curve. The behavior of mortars at 3, 7, and 28 days were similar (Fig. 6). Statistically, there is no significant difference in the F_{test} (Table 1).

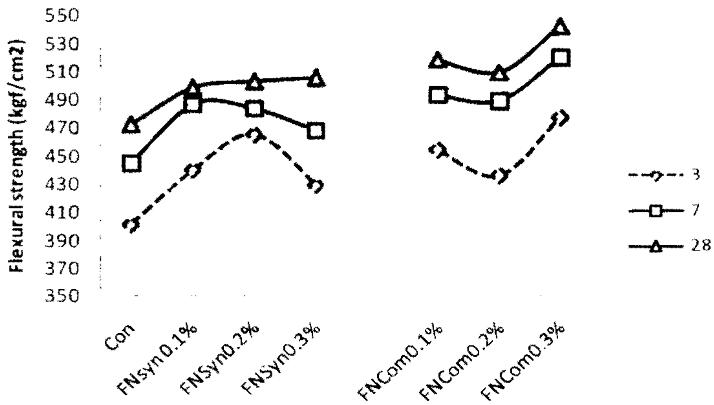


Fig. 6. Flexural strength of mortars containing different levels of hardwood NaLS (left hand side) and commercial NaLS (right-hand side) tested at 3, 7, and 28 days.

Table 1. Relationship between flexural strength and time of measurement at 3, 7, and 28 days.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	511.583[a]	20	25.579	69.877	.000
Intercept	93481.509	1	93481.509	255372.426	.000
Treatment	190.378	6	31.730	86.679	.000
Time	306.034	2	153.017	418.011	.000
Time treatment	15.172	12	1.264	3.454	.006
Error	7.687	21	.366		
Total	94000.779	42			
Corrected Total	519.271	41			

[a] R Squared = 0.985 (Adjusted R Squared = 0.971)

Compressive strength

The compression strength characterized using a manual device and a more sophisticated device showed different results even though the trend is similar (Fig. 7). Flexural strength results are better measurements and distinguishable when a more sensitive sensor is used at 3, 7, and 28 days. Compressive strength properties are similar to the flexural strength as previously discussed.

At 0.2% NaLS, there is an indication that bonding with water is higher than at 0.1 and 0.3% (Fig. 7) indicating that 0.2% NaLS in the mortar was the optimum additive level. The results of this particular determination again showed that NaLS derived from hardwood is better than the commercial NaLS. United States patent (Willy, 1981) shown that ASTM C270 mortars in the laboratory using cement type I, 35 % and flow 107% flow, had compressive strength of 82.3 kg cm^{-2} for 7 days and 131.1 kg cm^{-2} at 28 days. In building constructions, the same cement needed 53.4 kg cm^{-2} in 7 days, and 69.6 kg cm^{-2} at 28 days.

Thirteen samples composed of cementitious mortar, grout and concrete had a density of 90 to 161 pcf and a compressive strength of around 640 to 1400 kgf cm^{-2} (Charles et al. 1982). According to Rixom and Mailvaganam (1999), the relationship between the slump and the water-cement ratio for mixes, reached a maximum value of compression strength of 283 kgf cm^{-2} with water reducing mixture at 28 days and 224 kgf cm^{-2} without admixture.

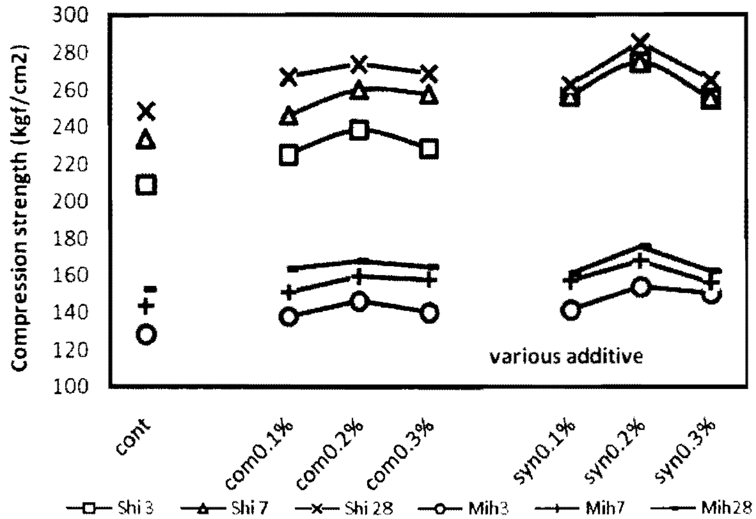
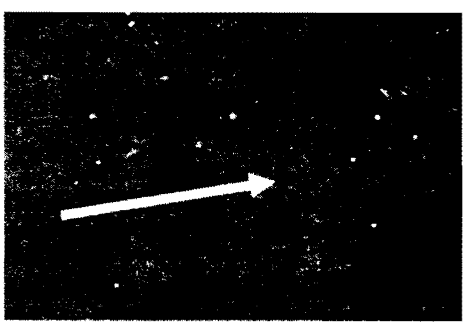


Fig. 7. Compression strength of mortar containing various levels of hardwood NaLS (right hand) and commercial NaLS (left hand) while using a Shimadzu X-ray defractometer (above) and Mihaelis apparatus (bottom) at 3, 7, and 28 days.

Water dispersion

Mechanical properties of the mortars (flexural and compression strengths) as discussed previously were further verified with a visual method. The results of scanning electron microscopy (SEM) on after-heated specimen clearly show that, the mortar without NaLS as additive, has a rough surface due to flocculation and void spaces left by evaporated water (Figure 8a). Figure 8b definitely shows a smooth and homogeneous surface of mortars containing hardwood NaLS. Water dispersion in the mortar is aided by a proper dispersant. This property is consistent with all mechanical properties tested in this experiment.



a) without hardwood additive

b) with NaLS

Fig. 8. Surface of mortar without hardwood additive (a) and smooth surface, with NaLS (b).

CONCLUSION

Mortar made with fine aggregate consisting of portland cement, sand, water, and eucalypt sodium-lignosulfonate has the potential as a dispersant. It is comparable to commercial NaLS derived from softwood lignin. Hardwood-NaLS is promising considering the abundance and continuous supply of black liquor as a by-product of the pulp and paper manufacturing industry in Indonesia. The mechanical characteristics of the mortar, flexural and compressive strength, meet the ASTM designation of C109, C185, C230, and JIS R5201.

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