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Evaluation of the performance of sulfonated esparto grass lignin as a plasticizer–water reducer for cement

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Abstract

The objective of the work described in this first paper of a series is an investigation of the preparation of a sulfonated esparto grass lignin (SEL) and its behavior as a plasticizing–water-reducing agent for cement–water systems. SEL is prepared by extracting the lignin from the black liquor of a soda esparto grass pulping process and then sulfonating it with a mixture of sodium sulfite and formaldehyde.

Analyses and characterization of SEL carried out with high-performance size exclusion chromatography (HPSEC), reversed phase chromatography (RPC), infrared spectrometry and chemical methods show that both the molecular weight average and the combined sulfur content are relatively high. Moreover, HPSEC shows that SEL has a relatively more uniform molecular weight distribution (MWD) than the commercial products obtained from the sulfite wood pulping process. On the other hand, SEL could reduce the water content, improve the workability and compressive strength of mortars. SEL also permits a very low rate of slump loss of cements without excessive extension of the final set time.

Keywords: Esparto grass black liquor; Admixture; Water reducer; Workability; Mortar

1. Introduction

Many chemicals are used as plasticizers or superplasticizers for concrete [1–8]. This kind of concrete admixtures includes, among other things, sulfonated alkali salts of naphthalene or melamine formaldehyde polymers [3,4], sodium or calcium salts of lignosulfonic acids [5,6,8] as well as certain hydroxycarboxylic acids and their alkali salts [4]. The choice of which surfactant to employ depends on the performances needed as well as the cost and availability of the surfactant.

Among these admixtures, the lignosulfonates (LS) obtained in the pulping industry as a by-product of the sulfite process are useful as dispersing agent for concrete [5,6,8], drilling muds [9] and organic dyes [10] and also as anticaking agent for fertilizers [11] and emulsifier in animal feed.

Unlike the traditional sulfite pulping [12,13], the soda pulping process allows for the recovery of an unsulfonated form of lignin, which has not been possible to use for similar purposes due to the lack of any hydrophilic groups.

In Tunisia, a high quality of pulp is produced using the digestion of esparto grass (*Stipa tenacissima*) according to a soda process. At the end of the cooking, the noncellulosic fraction (essentially lignin) is dissolved in a dark alkaline solution with the chemicals that have not reacted. This black liquor is concentrated up to 36% of solids and then burned in a furnace to produce energy and recover soda to reuse in further cooking. The reader should note that under these conditions the recovery and recycling of soda is not a paying proposition but is environmentally essential; it would be most desirable from both an economic and ecological standpoint to convert this by-product into a commercially usable form.

The effectiveness of LS is believed to be strongly influenced by their structure and their molecular weight distribution (MWD) [14,15]. As lignin is a very complex natural polymer with many random couplings [14,16], its chemical structure, physical and chemical properties differ depending on its extraction origin (hard and soft wood, straw, corn stalks, bagasse and the like). Thus, we have assumed that lignin extracted from esparto grass can lead to sulfonated esparto grass lignin (SEL) that can be used as an effective plasticizer–water reducer for cement–water sys-

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tems or for other purposes such as dispersant for dyes or anticaking agent for NPK fertilizers. The reader should be reminded that in a previous study [17], we showed that a mixture of esparto lignin with polyformaldehyde naphthalene sulfonate can lead to a useful superplasticizer permitting a very low rate of slump loss of cements.

The main objective of this first paper of a series is to provide an SEL starting from black liquor as raw material. This product is then studied as a possible dispersant and water-reducing agent in cement–water systems to assess its properties in comparison with those of commercial products.

This paper studies the preparation and the analyses of a soluble sulfonated lignin from esparto lignin; this also includes the laboratory test program designed to determine the effect of the products on water reduction, set retardation, workability, flow–time relationship and mechanical properties of water–cement systems.

2. Experimental

2.1. Preparation procedure

Black liquor as obtained from the soda esparto pulping process contains substantial amounts of lignin and relatively small quantities of lignin degradation products (polyphenols), hemicellulose degradation products (carbohydrates), soda, small molecules of carboxylic acid salts, inorganic salts and some other materials. About half the solids in soda black liquor are lignins. The relative amounts of these materials present in a typical sample supplied by the Tunisian esparto grass pulping industry (SNCPA, Kasserine) and employed in this work are shown in Table 1. It should be noticed that contrary to the sulfite wood pulping process [12,13], only small quantities of free monosaccharides (arabinose, xylose, mannose, galactose and glucose) are found in the present soda process black liquor (about 1% of solids). The absence of larger quantities of free sugars can be explained by the severe conditions of the process such as elevated temperature and the high degree of alkalinity of the digesting mixture.

Table 1
Analysis of the major components present in the esparto black liquor

Characteristics	Results
Specific gravity (g/l)	1205
Dry solids (%)	33.6
pH 5% solution	≈ 13
% lignin	16
Ca (mg/kg)	240
Mg (mg/kg)	6
Na (g/kg)	80
K (g/kg)	4.52
Fe (mg/kg)	9.2
Pb (mg/kg)	4.6
Cr	trace
Ni (mg/kg)	0.6
Cl^- (mg/kg)	208.4
SO_4^{2-} (g/kg)	1.55
NaOH (%)	8
Molecular weight of lignin (g/mol)	9500–20,000
Pentosanes (reducing sugars, g/kg)	2.17
Color	Dark brown

The sulfonation of lignin is carried out by a conventional process, which involves the sulfonation of alkali lignin with sodium sulfite or sulfomethylation with a mixture of sulfite and formaldehyde. The process of obtaining the plasticizer consists of three steps: precipitation, filtration and sulfonation or sulfomethylation.

The first step is the removal of the major portion of inorganic salts, small molecules of organic salts and sugars from the soda black liquor. Thus, the soda black liquor (pH = 12–13) is acidified to a pH of approximately 3–4 with a 30% aqueous solution of sulfuric acid. The precipitated lignin is separated, in a second step, by filtration and washed to reduce its residual sulfuric acid content. The esparto lignin recovered according to this procedure is an aqueous slurry characterized by a lignin content of at least 17% by weight and by the absence of reducing sugars. Finally, the isolated lignin is sulfonated with sulfite or sulfomethylated with a mixture of sulfite and formaldehyde. The addition of formaldehyde and sulfite (molar ratio 0.6–0.8) to the lignin slurry increases the pH from about 4 to about 9. The reaction is carried out in an autoclave. The bomb and contents are heated at 140 °C for about 4 h under constant rotation. After cooking, the product is removed from the bomb, filtered to eliminate insoluble by-products, treated in order to reduce its sulfate content and then analyzed.

2.2. Analytical methods

SEL is examined using different chemical and physicochemical methods. The molecular weights of different samples are determined using high-performance size exclusion chromatography (HPSEC). They also are fractionated according to their polarity by reversed-phase liquid chromatography (RPLC). In addition, the products are analyzed for their chemical composition including the content of bonded sulfonate, free sulfate, chloride, alkalis, sugars and sulfite. Qualitative analysis is carried out by FTIR spectrometry.

2.2.1. Chemical analysis

Volumetric and spectrophotometric (atomic absorption) methods are performed to determine the amounts of sulfates, chlorides, sodium, sulfites and sulfur bonded to the lignin [18]. The sugar content of LS is determined using the traditional "reducing sugar test" (or Fehling test). This test takes into account the presence of residual $NaHSO_3$.

The consumption of sulfite (when the sulfonation is carried out without formol) is followed iodometrically [18]. The degree of sulfonation is determined by sulfite consumption and verified by the analysis of the total sulfur present in SEL before and after perchloric/nitric acid attack.

2.2.2. High-performance size exclusion chromatography

Aqueous size exclusion chromatography applied to SEL, unsulfonated lignin and commercial LS-based plasticizer (CP) is studied using an organic semirigid high-performance gel (TSK PW type).

The instrumentation used in these experiments is a Shimadzu solvent delivery system fitted with an SCL-6A system controller, a C-R 6A data module, a 20-μl injection loop and a UV detector ($\lambda = 280$ nm). The column used is a TSK PW (150×4.6 mm). The mobile phase consisted of filtered (0.45 μm) and degassed (0.1 M) phosphate buffer at pH = 7. A flow rate of 1 ml/min is used for the analysis. Chromatography is performed on sulfonated lignin samples dissolved in the buffer at a concentration of about 0.1% (w/v). Blue dextran (Pharmacia) is used to determine the superior limit of molecular exclusion (2×10^6 Da) of the TSK column. Standard proteins of molecular weight: 72,360 (Albumin), 46,440 (Ovalbumin) and 27,000 (Chymotrypsin) are used in order to obtain the calibration curve. Vanillin (168 Da) is used to determine the retention time of monomeric components.

2.2.3. Reversed-phase chromatography

SEL molecules are fractionated according to their polarities by high-performance RPLC. The apparatus used in these experiments are described above. Elution is carried out with a C_{18} column-Inertsil ODS 2 (150×4.6 mm) using a gradient produced from A [a phosphate buffer (KH_2PO_4 5×10^{-2} M, pH = 7)] and B [a water methanol mixture (70:30 v/v)]. The gradient consists in varying B from 0% to 100% in 90 min, maintaining 100% B for 30 min and then decreasing B from 100 to 0% in 30 min. RPC is performed on aqueous samples at a concentration of about 0.1% (w/v) with a flow rate of 0.6 ml/min at ambient temperature.

2.3. Testing program

Many tests are carried out on cement grouts and mortars containing SEL in order to ascertain the efficiency of the product and its conformity to international standards. The following conditions below are used.

2.3.1. Materials

The following materials are used in the laboratory tests:

- Cement: Tunisian Portland cement, CP Type I 32,5 (NT 47-01);
- Aggregate: silica sand graded as Tunisian standard sand (NT 47-30);
- Admixtures: a 40% aqueous solution of SEL (this work), a 40% aqueous solution of a premium commercial Ca-LS-based plasticizer and a commercial Ca-LS (powder of 85% purity).

Table 2
Mixture proportions

Mixtures	Portland cement (g)	Sand (g)	w/c	Admixture (based on dry solids)
Cement mortar (EN 480-1)	450	1350	0.40–0.50 (variable)	0.1–0.8 (variable)
Cement grout (for Marsh cone NF P18 357)	1000	–	0.365–0.450 (variable)	0–0.8 (variable)
Cement grout (for mini cone [17])	400	–	0.42	0–0.8 (variable)

2.3.2. Mixture proportions

Cement grouts and mortars are prepared according to the amounts indicated in Table 2. The whole admixture is added to the water, required for the test, before mixing. The dosage of each admixture is converted and expressed as the solid content by 100 g of cement.

2.3.3. Tests

The following effects on the properties of the cement–water systems are estimated:

2.3.3.1. Fluidifying effect. Fluidifying effect is determined on cement grouts using both Marsh cone (according to NF P18 358) and a mini cone which has been described previously [17]. The diameter spread of the paste is then measured.

The loss of workability (slump loss) of cement grouts with time is also evaluated.

2.3.3.2. Plasticizing effect. Plasticizing effect is determined on cement mortars using the standard flow table test in accordance with ASTM-109. The flow ω is defined by the formula:

$$\omega\% = 100\,(D_m - D_o)/D_o$$

where D_o is the diameter of the cone basis and D_m is the mean diameter of the pancake.

2.3.3.3. Setting time. This is achieved on cement mortars with a Vicat apparatus according to the EN 480-2 standard.

2.3.3.4. Compressive strength. Compressive strength is measured on hardened mortars with a calibrated hydraulic press (according to the EN 196-1 standard), using prismatic moulds $4 \times 4 \times 16$ cm.

3. Results and discussion

Sulfonation of esparto lignin is carried out using different experimental conditions. The chemical and physicochemical analyses focus on determining the degree of sulfonation and MWD. The product is then tested as possible plasticizing and water-reducing admixture for concrete.

3.1. Sulfonation reaction

The lignin must be made at least partially water-soluble in order to act as a surfactant; this is done by sulfonation or sulfomethylation. During sulfonation, the SO_3H groups enter the aliphatic side chain of the lignin molecule by replacement of hydroxyl or ether functions at the α-carbon of the phenyl propane unit [19,20]. The process of sulfomethylation of the lignin material with a mixture of sulfite and formaldehyde has been mentioned by Adler and Mauritz [21] and Dilling [10]. In this case, $-CH_2SO_3H$ groups (obtained by the reaction of sulfite with formaldehyde) are bonded to the aromatic nuclei of the lignin molecule. In addition, owing to the presence of an excess of sulfite, sulfonate groups ($-SO_3H$) are introduced into the aliphatic side chain of the lignin molecule. Depending on the sulfonation conditions used [22,23], the lignin can then be sulfonated to various degrees. Thus, several sulfonation runs are carried out to compare the solubility, the molar weight distribution and the hydrophilic character of the products obtained when using different experimental conditions. Favorable results are obtained when carrying out the reaction under the following conditions: pH of esparto lignin precipitation = 3–4, temperature: 130–160 °C, molar ratio of formaldehyde to sulfite: 0–0.8, pH = 7–9, time of reaction: 3–6 h, sulfite concentration: 20–50% of the lignin weight. Under these conditions, SEL produced are soluble in water, in glacial acetic acid and in diluted sulfuric acid (pH >1.5), and are precipitated from their aqueous solutions only at a comparatively high concentration of mineral acids.

In this study, the average of ranges of the factor levels given above are selected and applied to the preparation of testing samples.

3.2. Physicochemical analyses

The sulfonation reaction leads to water-soluble LS with molecular size ranging from small monomeric compounds up to high molecular weight polydisperse materials. The influence of molecular weight of different water-soluble polymers on their performance in cement–water systems has been tested [24] using methods such as gel permeation chromatography (GPC) or dynamic viscosity measurements for molecular weight determination.

It was demonstrated by Benko [25] that dispersing properties of LS increased with its molecular weight up to an optimum. Ultrafiltration can provide LS fraction of high purity and narrow range of MWD.

In the following paragraph, the analytical results of SEL, esparto lignin and commercial Ca-LS-based plasticizer are compared.

3.2.1. Chemical analyses

SEL has been analyzed for its chemical composition including the content of sulfonates (30%), sulfates (1.5%), chlorides (0.03%) and sugars (0.5%). The results obtained (based on dry solids) fall within the limits of those published for the commercial LS.

The sulfonated lignin product contains combined sulfonic sulfur of at least 2.6% relative to the dry sample. Dilling [10] considers as a highly sulfonated lignin, a product having above 1 mol of sulfonate group per 1000 g of lignin (3.2% of sulfonic sulfur).

Only very small quantities of free monosaccharides were detected in the SEL samples (0.5%). This can be explained by the fact that the starting material obtained by acidification and filtration does not contain free sugars. In addition, the relatively moderate conditions of the preparation process (pH = 7–9, temperature 140 °C and duration 4–5 h) may

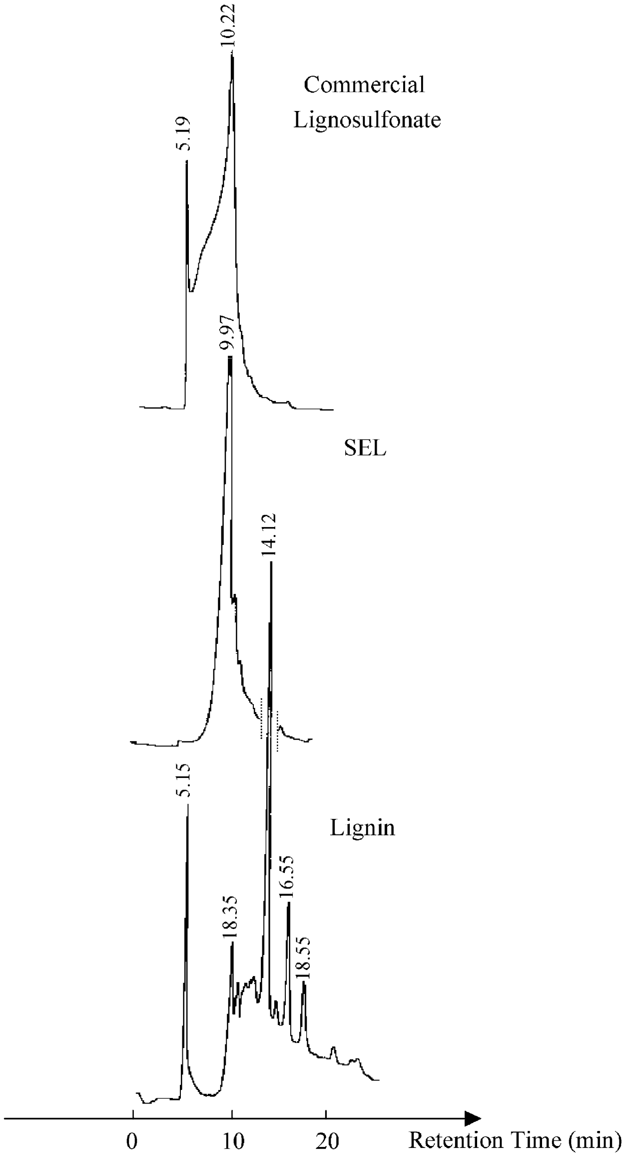

Fig. 1. Molecular weight distribution of SEL.

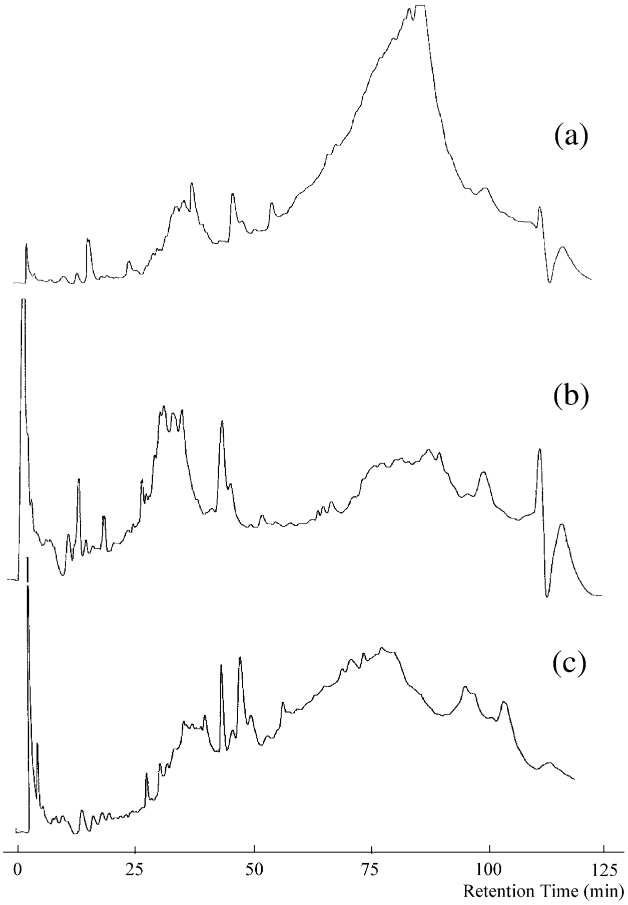

Fig. 2. Reversed-phase analysis of (a) lignin, (b) SEL, (c) commercial LS.

avoid the degradation of the hemilignin structure and the release of sugars.

It should be noted that the LS obtained from the sulfite wood pulping almost always contain sugars or small-molecule polymers of sugars, which have detrimental retarding effects on the stiffening and hardening of concrete [26]. To address this problem, expensive methods such as ultrafiltration, fermentation and ion exchange can be applied to eliminate the major part of sugars.

3.2.2. HPSEC analysis

GPC has previously been used by Forss et al. [27] and Hachey et al. [28] for analysis of LS and Kraft lignin on Sephadex G gel.

HPSEC has been used by Pellinen and Salonen [29] and Lewis and Yean [30]. It provides a rapid and convenient way to obtain information on the MWD and molecular weight average of lignin and LS.

In this work, GPC is performed on three samples: the crude lignin, the SEL and the commercial LS-based plasticizer (Fig. 1). The graphs show two peaks for the commercial plasticizer (CP), one peak for the laboratory sample and several peaks for the crude lignin.

The first peak of the commercial LS corresponding to the exclusion limit (of about 100,000 Da) suggests that a low concentration of high molecular weight LS or sulfonated lignocarbohydrate complexes is present only in the commercial sample. The second peak is large, having a maximum corresponding to a molecular weight of about 10,000 Da according to the calibration curve established with proteins as standards. The MWD is spread over a range of 60,000–8500 Da.

In the case of SEL, the product has a relatively more uniform molecular weight than the commercial sample. The distribution curve is symmetrical and narrow with an average molecular weight of about 10,000 and a range of about 8000–11,000. These values are different from those of LS obtained as by-products of the sulfite process [10] which are in the range 2000–20,000 and from those of sulfonated lignin obtained by sulfonation of Kraft lignin which are in the range 1000–3000. It is noteworthy that SEC of lignin-related material can suffer from artifacts due to adsorption on the gel or ionic interactions. The extent of adsorption depends on the combination of the gel and solvent. The adsorption can be hydrophilic or hydrophobic and leads to an underestimation of the molecular weight.

The chromatogram of crude lignin corresponds to a fraction isolated at pH ranging from 7 to 3 to avoid precipitation of lignin on the gel when using the phosphate buffer as a mobile phase. This explains the absence in the chromatogram of large peaks corresponding to high molecular weights.

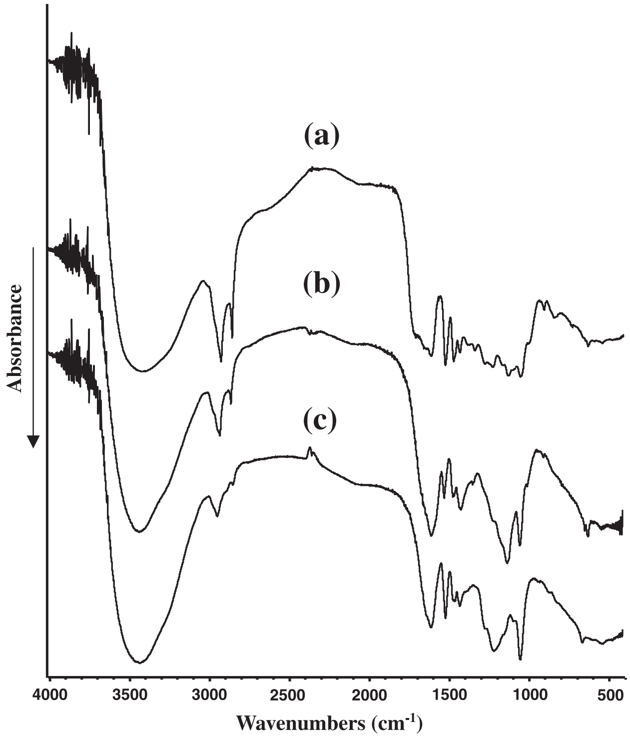

Fig. 3. FTIR analysis of (a) lignin, (b) SEL, (c) commercial LS.

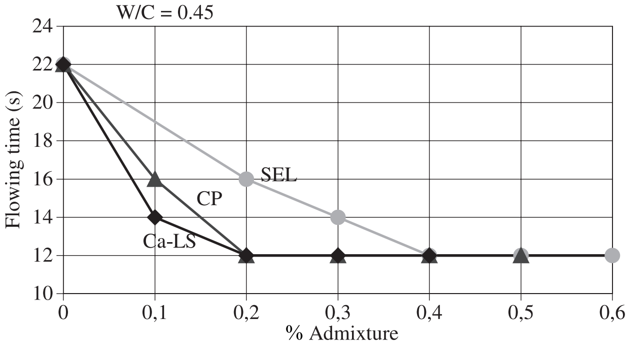

Fig. 4. Fluidifying effect of SEL in cement grouts (Marsh cone).

3.2.3. RPC analysis

Reversed-phase HPLC offers potential advantages over other chromatographic methods for the analysis of samples containing mixtures of sulfonated lignins and crude lignin [31]. In this study, this technique is applied to follow the progress of the sulfonation reaction using an Inertsil ODS column.

Sulfonated lignins are fractionated according to their polarities by RPLC. Hydrophilic compounds elute before hydrophobic ones.

In Fig. 2 are compared RPC chromatograms of esparto lignin, SEL and a commercial Ca-LS. Lignins and LS eluted in the retention time range of 0–50 min are strongly polar, whereas those eluted in the range of 60–120 min behave as less polar compounds with polarity decreasing with increasing retention time. Comparison of the three chromatograms shows that:

- crude lignin is essentially composed of nonpolar compounds. This is illustrated by the presence of a large and intense peak centered at 95 min;
- SEL seems to be composed of LS and a small part of unsulfonated lignin;
- commercial LS is composed of a great range of LS with different polar characters. This result is in accordance with that of GPC, which shows a large and continuous peak corresponding to high MWD of the polymers.

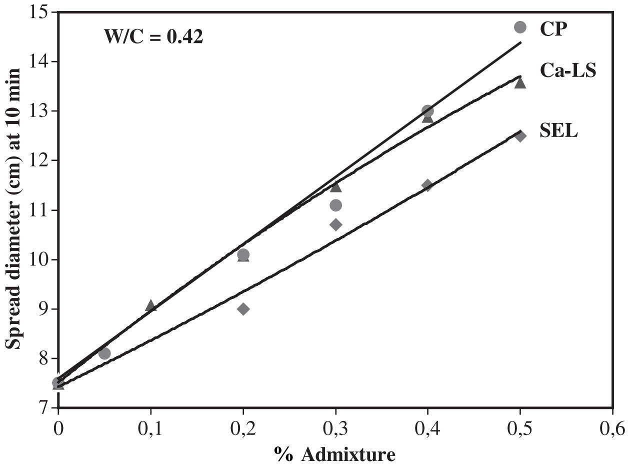

Fig. 5. Fluidifying effect of SEL in cement grouts (mini cone).

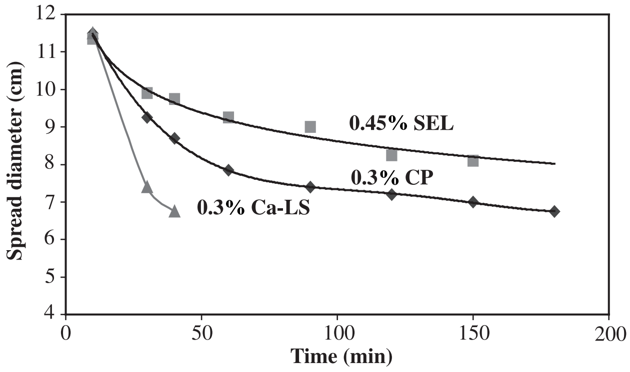

Fig. 6. Slump loss of cement grout (mini cone).

3.2.4. FTIR analysis

The infrared spectra of SEL and commercial LS are compared with each other and with unsulfonated lignins (Fig. 3). Although no major differences in wavelengths of the absorption bands are observed, differences in the relative intensities of the bands are apparent especially in the 1000–1250 cm^{-1} region. The adsorption bands in the SEL spectrum are similar to those of commercial LS and are less well-defined than those of lignin.

Characteristic infrared frequencies of functional groups occurring in the lignin and LS molecules such as carbonyl groups, ethylenic double bonds, aromatic rings and hydroxyl groups have been discussed and reported in Refs. [32,33].

The absorption bands for sulfonic acids and salts are 1260–1150 cm^{-1} for antisymmetric stretching, 1080–1010 cm^{-1} for symmetric stretching and 700–600 cm^{-1} for deformation.

Both the 1210 and 1040 cm^{-1} bands (C−O stretching of phenol and C−O deformation of methoxyl group) are present in both unsulfonated and sulfonated lignin molecules; thus, they are not particularly valuable for diagnostic

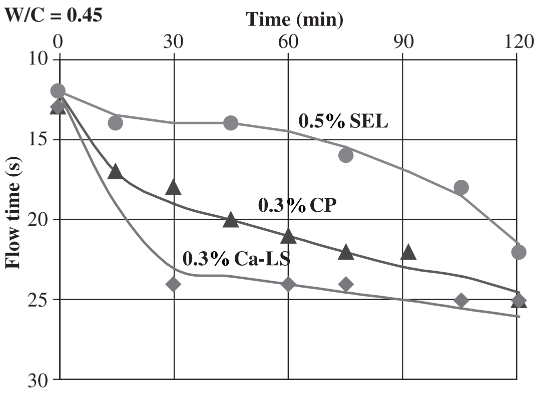

Fig. 7. Effect of time on flow behavior of cement grout.

Table 3
Results of setting time of mortars at 20 °C

Samples	w/c	Consistency	Admixture (%)	Initial setting time	Final setting time
Unmodified mortar	0.485	plastic	0	5 h 05 min	6 h 30 min
Mortar + CP	0.45	plastic	0.25	8 h 00 min	9 h 50 min
Mortar + SEL	0.45	plastic	0.40	8 h 15 min	11 h 15 min

study. On the contrary, the relatively weak band at 650 cm^{-1}, which is assigned to the deformation frequency of the sulfonated group, does not occur in unsulfonated lignin, so it can be used for qualitatively analyzing the sulfonation product.

3.3. Properties evaluation of SEL in cement

SEL is tested as possible water-reducing admixture and plasticizer for cement–water systems. In particular, the influence of SEL in varying dosages is studied with respect to fluidity, flow–time relationship, plasticity, water reduction capacity, setting time and compressive strength.

3.3.1. Testing on cement grouts

3.3.1.1. Fluidifying effect. Figs. 4 and 5 show the results of experiments carried out with Marsh cone [34,35] and mini cone [17,36], respectively, to compare the fluidity of cement grouts containing SEL, a conventional plasticizer and a pure Ca-LS.

Measurements with Marsh cone (Fig. 4) indicate that, when the water-to-binder ratio is 0.45, SEL needs slightly more dosage (0.4%) than the conventional plasticizer and the Ca-LS (0.2%) to reach the optimal dosage (saturation point).

Measurements with mini cone (Fig. 5) at w/c = 0.42, indicate that the demand of SEL is slightly higher than that of the other two admixtures.

3.3.1.2. Flow–time relationship. The loss of workability of cement grouts as a function of time is measured using the mini cone (Fig. 6) and the Marsh cone (Fig. 7). The behavior of SEL is compared to that of Ca-LS and to an LS-based CP. All mixes made with the different admixtures have the same initial fluidity; this fluidity is obtained by adjusting the plasticizer content at a constant w/c ratio.

The fluidity of the cement grout decreases with time due to the hydration phenomenon of the cement constituents [1–3]; hence, the spread of the grout decreases and the flow time increases with time.

Slump loss characteristics of cement grout prepared with SEL, Ca-LS and an LS-based CP are shown in Fig. 6. Obviously, the rate of slump loss for a mixture containing SEL is slightly lower than that of a mixture containing an LS-based CP. The rate of slump loss for these two mixtures is far lower than that of the Ca-LS mixture.

The results of the effect of time on flow behavior of cement grouts for the various admixture studied (SEL, Ca-LS and CP) are plotted in Fig. 7. These results confirm those obtained with the mini cone.

3.3.2. Testing on cement mortars

3.3.2.1. Setting time. Table 3 shows results of the effect of the prepared SEL on the setting time of cement mortars, using 0.4% of SEL. The results for the commercial LS are also listed for comparison.

As for all LS-based plasticizers [1–3], SEL delays initial and final setting times of cement mortars. At a dosage of 0.4% of SEL (by weight of cement), delays of the initial and

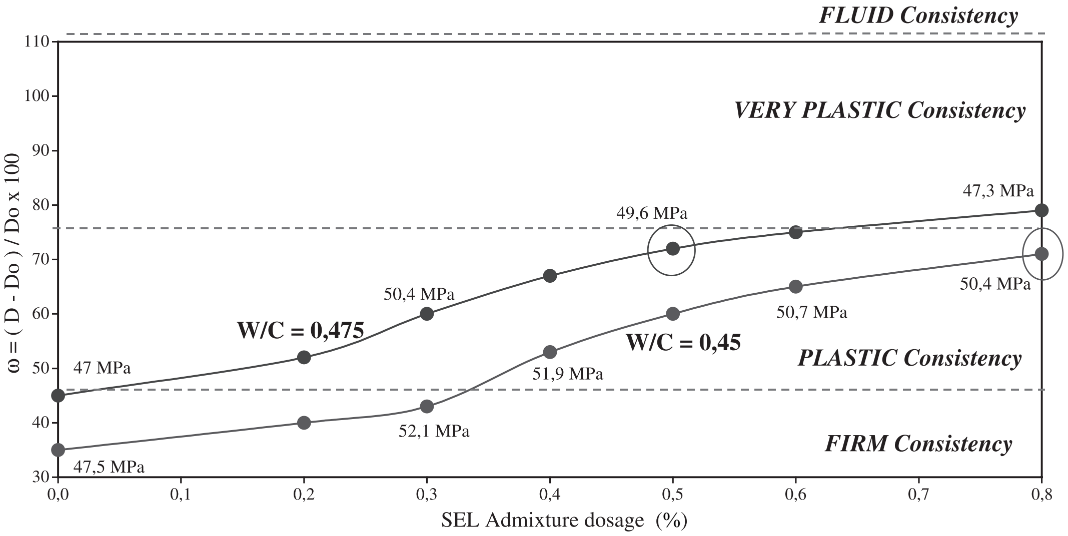

Fig. 8. Plasticizing effect of SEL.

final sets are 3 and 4 h, respectively, compared to those of the unmodified mix. These values are similar to those obtained with the commercial LS-based plasticizer and are in accordance with the EN 480-2 standard relative to set retarding admixtures which requires the following two conditions:

- Initial setting time of the modified mortar greater than or equal to 1 h 30 min + initial setting time of the reference mortar prepared at the same consistency.
- Final setting time of the modified mortar smaller than or equal to 6 h 00 min + final setting time of the reference mortar prepared at the same consistency.

3.3.2.2. Plasticizing effect. The tests on plastic mortars shown in Fig. 8 indicate that there is a minimum dosage (0.2%) below which SEL do not influence substantially the consistency and the mechanical properties of the mortars. At a dosage of 0.2–0.4%, an increase of flow and a slight increase of mechanical strength at 28 days can be observed. Also, the use of 0.5% to 0.8% of SEL by weight of cement in mortars, with w/c ratios ranging from 0.45 to 0.475, leads to a change from a firm to a very plastic consistency of the mortars, which is in accordance with the EN 934-2 standard fixing plasticizer features. It should be noticed that the incorporation of SEL does not adversely affect the mechanical properties of the mortars.

3.3.2.3. Water reduction capacity. Fig. 9 shows the effect of the prepared sulfonated lignin on the percentage of water reduction required to maintain the plastic consistency. These results indicate that the incorporation of SEL (0.4–0.6%) leads to a significant reduction of water (7–12%) and consequently an increase of the compressive strength as shown below.

3.3.2.4. Compressive strength. The hardened mortar was tested for compressive strength. Figs. 8 and 9 show the compressive strength of cement mortars containing different doses of SEL.

Fig. 9 shows that, for a plastic consistency of the mortar, the use of 0.4% of SEL leads to a water reduction of 7.2% accompanied by an increase of compressive strength at 28 days of 12.8%. The use of 0.8% of SEL permits a water reduction of 12.3% and an increase of the 28-day compressive strength of 21.3%. This can be explained by the decrease of w/c ratio and the high dispersing effect of SEL in the cement mortar, which permits better hydration [4]; this leads to an improvement of the compressive strengths at 28 days.

These results allow us to term SEL as a water-reducing admixture according to the EN 934-2 standard. This standard requires a water reduction greater than 5% in the case of plastic consistency and an increase of the compressive strength of more than 10% at 28 days.

4. Conclusion

As a conclusion, we consider that the major significant findings of this research devoted to the preparation of a cement plasticizer are:

- Under the selected experimental conditions, the product has a relatively high degree of sulfonation, high molar weight and narrow molar weight distribution. These physicochemical characteristics depend upon the levels of the factors of the sulfonation reaction.
- The optimal dosage of SEL, determined on cement grout, is around 0.4% by weight of cement. In this case, SEL

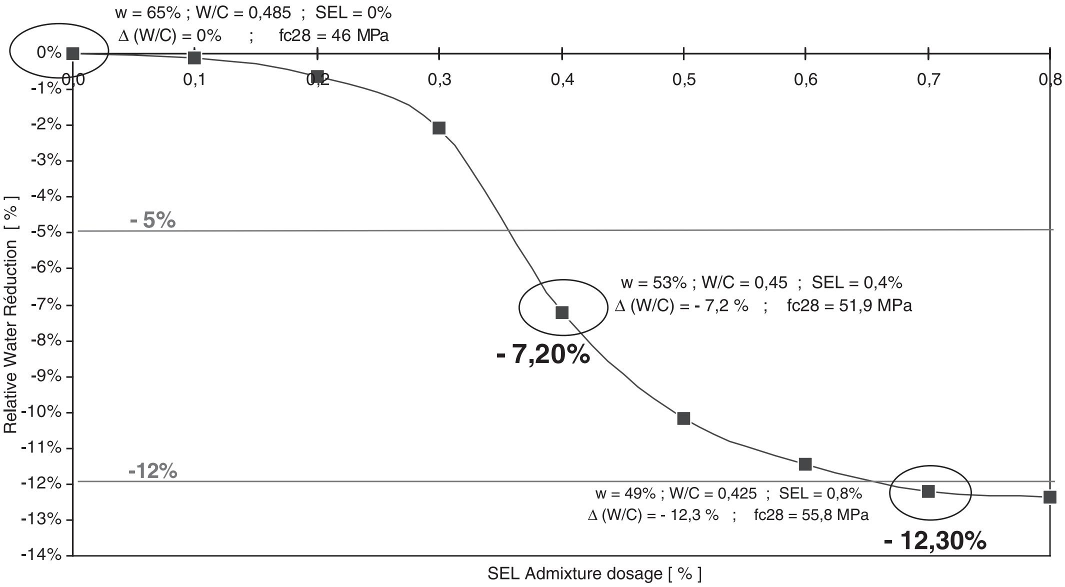

Fig. 9. Percentage of water reduction vs. SEL dosage for plastic consistency of mortars.

reduces the rate of slump loss more than Ca-LS and a premium LS-based CP.

- SEL has a good plasticizing effect on mortars. It also permits a reduction of the water content in a given mortar mix without affecting the workability. SEL, as all LS-based plasticizers, leads to a moderate delay of the initial and final times of set. In addition, SEL allows an increase of the compressive strength after 28 days of age.

In conclusion, all of these results confirm that the effectiveness of the product are comparable to those of a commercial LS-based plasticizer and, thus, confirm the possibility of utilizing this low-cost product as dispersant. It should be noted that better properties could be obtained from the viewpoint of the plasticizing effect and the water-reduction capacity by further reducing the amount of sulfates and residual sulfite.

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