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Synthesis and evaluation of starch-based polymers as potential dispersants in cement pastes and self leveling compounds

Lucie Crépy [a,b], Jean-Yves Petit [c,*], Eric Wirquin [a], Patrick Martin [a,b], Nicolas Joly [a,b]

[a] Univ Lille Nord de France, F-59000 Lille, France
[b] U Artois, IUT Béthune, Centre Technologique des Agroressources, F-62408 Béthune, France
[c] Momentive Speciality Chemicals, F-60170 Ribécourt, France

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ABSTRACT

In order to make concrete construction greener, new High Range Water Reducing Admixtures (HRWRAs) from natural origin-should be developed. Some natural polysaccharides and their derivates have interesting properties which explain their growing use in the field of materials. Their use is not only linked to the biodegradable and atoxic aspect but is also linked to the fact that they can confer new properties to cement-based materials.

In the presented study, starch has been chosen as main polysaccharide chain. Starch has first been used without any modification, and then with different grafted substituents like acetate, maleate, succinate, sulfonate to mimic the structure of petrochemical HRWRAs. Some tests have been done to evaluate the potential effect of these biobased derivatives as new HRWRAs. Some of the starch-based polymers were also evaluated in a commercial self-leveling compound.

Results show that a graft of sulfopropyle or sulfobutyle side chains on a starch polymer can lead to slump flows on grouts comparable with the ones obtained on PolyNaphtalene Sulfonate (PNS) based grouts, and also that starch-sulfobutyle or starch-maleate can potentially replace casein in self-leveling compounds.

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1. Introduction

The use of HRWRA can enhance flowability of cement paste by dispersing the cement particles into the interstitial solution, thus reducing the inter-particle friction among cement grains and decreasing the degree of water entrapment among flocculated particles. The benefit of using PolyNaphtalene Sulfonate (PNS), polymelamine sulfonate (PMS), and more recently polycarboxylate polymers (PC) as HRWRA is well established. However, depending on the characteristics of the binder system and the type of HRWRA, incompatibility problems can lead to high demand of admixture or excessive loss of fluidity with time [1]. Such cement-HRWRA incompatibility can involve an interaction between the sulfonate groups within the hydration reaction and the cementitious ionic matrix [2]. Long-chain polymers with significant molecular weights, such as PC, have been developed more recently to improve the dispersion of the cement particles through a more effective steric effect mechanism [3]. They are highly effective in enhancing concrete workability and its retention in time, given their superior dispersing ability compared to PNS- or PMS-based HRWRA that can exhibit sharper drops in fluidity with time [4]. Schematic view of PNS and PC are presented in Fig. 1.

However, the main admixtures used as HRWRAs for cement-based materials are extracted from oil derivates, a nonrenewable and polluting resource with a direct effect on the green house effect and, for some of them, toxic long term effects such as the creation of formaldehydes [5].

The cement industry is turning to sustainable development and to the elaboration of greener concrete [6]. Thus, new HRWRAs from natural origin should be developed [7,8] in order to achieve a greener concrete.

The proposed work aims at minimising the use of nonenvironmentally–friendly molecules presently used for concrete making and replacing them with biological polymers made with food wastes. The goals are:

- to decrease the part of chemically aggressive admixtures which has direct long term effects on public health releasing formaldehydes,
- at long term, not only to use eatable natural-based molecules but also to use sub-products or by-product of agro-industries,
- to have a ‘low cost admixture’ easy to synthesize, using the local food-plants and fisheries productions or wastes.

Lignin and derivate are known for long to have water reducing and fluidity enhancing effects in cementitious systems [9–11].

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* Corresponding author. Tel.: +33 344 75 86 47; fax: +33 344 75 86 41.
E-mail address: jeanyves.petit@momentive.com (J.-Y. Petit).

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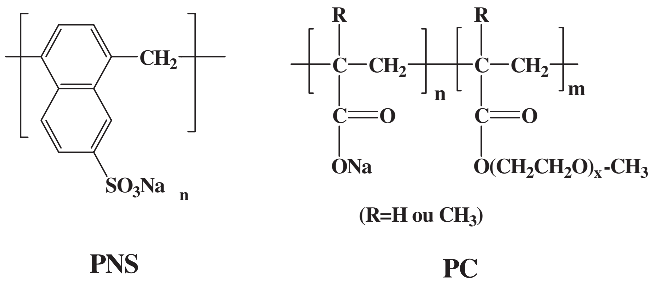


Fig. 1. Chemical structures of commonly used petrochemical-based superplacizers.

They were among the first plasticizers with a biobased backbone chain, and many investigations were conducted on this biopolymer used as HRWRA.

In the presented study, starch, one of the most abundant natural polymers in the world [12], has been chosen as the main polysaccharide chain. Acid derivatization of starch is a well-known technique to obtain lower viscosity products, which are dispersible at higher solids content than the ones made from native starch [13,14]. The introduction of acetic, succinic or maleic groups interrupts the ordered structure of native starch, leading to the inhibition of the starch gelatinization and increasing swelling and solubility [15–17].

In order to mimic petrochemical superplasticizers such as PC, whose efficiency is based on steric and electrostatic repulsions between cement particles [14,18,19], first it has been chosen to focus on the synthesis of carboxylate derivatives. Then, the synthesis of alkyl sulfonated starch was performed [20], whose chemical structure could mimic the PNS and thus should lead to an electrostatic repulsion between cement particles.

According to literature, starch succinate [5], sulfonate [21,22] and sulfoethylate [7] have already been tested as superplasticizers in concrete or mortar. Other starch-based HRWRAs, such as polycarboxymethyl-β-cyclodextrin were also proved to be efficient at dispersing cement particles in water [23–25]. These starch derivatives have shown a dispersing performance close to petrochemical ones. However, they are generally not tested in the same experimental conditions, and parameters such as the molecular weight of starch, the degree of substitution, the dosage superplasticizer/cement, the cement mixture, and so on, can differ. Thus, though not easily, they can be compared together or with a petrochemical reference like PNS, to determine the best potential bio-based HRWRA.

In order to continue the development of starch-based HRWRAs, hydrosoluble starch derivatives were synthesized with different grafted substituent like acetate, maleate, succinate, sulfopropylate and sulfobutylate to evaluate them as cement deflocculating agents using similar experimental tests. The aim of this work was to study and compare the influence of such lightly substituted starch derivatives on the rheological properties of cementitious materials, and to conclude on their potential application as new bio-based HRWRAs. At first, the starch-based derivatives were selected through tests conducted on cement pastes, and finally, some of the polymers that exhibit most promising results have been tested on a commercial Self Leveling Underlayment mix design.

2. Synthesis of starch derivatives

Hydrolyzed starch (~4000 g/mol, 96% amylopectine, Roquette Frères, France); acetic acid (99%, Aldrich), acetic anhydride (99%, Alfa Aesar); maleic anhydride (99%, Janssen Chimica); succinic anhydride (99%, Alfa Aesar); 1,3-propanesultone (99%, Alfa Aesar); 1,4-butanesultone (>99%, Molekula); sodium hydroxide (>99%, Acros); isopropanol (>99%, Prolabo); methanol (>99%, Prolabo); acetone (99%, Aldrich), Cement Portland (CEM I 52.5N, 97,2% of clinker, Holcim), PNS (Cimfluid 231™, Axim) were used without further purification. D_2O and $CDCl_3$ were purchased from Aldrich and stored at 4 °C.

The syntheses of starch acetate and starch maleate were performed according to a method described elsewhere [8]. Starch (20 g; 1 eq. based on repetitive unit) was mixed with anhydride (acetic or maleic anhydride; 1–2 eq.). After 5 min stirring, 2 ml of 50% aqueous NaOH solution was added. The temperature was increased to 123 °C (starch acetate) or 80 °C (starch maleate) for 2 h. The reaction was finished by adding cold water until the filtrate was pH > 5. The resulting product was then freeze-dried.

Starch succinate was synthesized using the method described by Minkema [26]. Starch (20 g; 1 eq. based on repetitive unit) was mixed with water (30 ml) and NaOH pellets (1.2 g; 1 M). After stirring for 5 min at 80 °C, succinic anhydride (1–2 eq.) was added. The temperature was held to 80 °C for 4 h. The reaction mixture was purified by adding methanol, filtering and then freeze–drying.

The method developed by Knaus and Bauer-Heim [3] was used to synthesize both starch sulfopropylate and sulfobutylate. Caustic soda solution (30%, 2 eq. NaOH) was added dropwise under vigorous stirring to a suspension of starch (20 g; 1 eq. based on repetitive unit) in isopropanol (8 ml/g starch) and water (0.9 ml/g starch). The reaction mixture was stirred at 45 °C for 1 h, then sultone (1,3-propanesultone or 1,4-butanesultone; 2 or 4 eq.), dissolved in acetone (1 ml/g sultone), was added. The suspension was stirred for 6 h at 45 °C and allowed to stand at room temperature. After 12 h stirring, the reaction mixture was poured into methanol (15 ml/g starch), and neutralized with acetic acid. The product was filtered, washed with methanol and dried at room temperature.

Every product was characterized by FT-IR spectroscopy using a Bruker Vector 22 FT-IR apparatus equipped with a diamond reflection accessory. ^1H NMR spectroscopy was performed in D_2O using a Bruker DRX-300 Spectrometer (operating at 300 MHz) to determine the degree of substitution (DS) by an integration method described elsewhere for starch acetate, succinate and maleate [8,26], or by a titrimetric method for starch sulfoprolyte and sulfobutylate. The DS is defined as the number of substituents grafted per anhydroglucose unit (maximum value of 3).

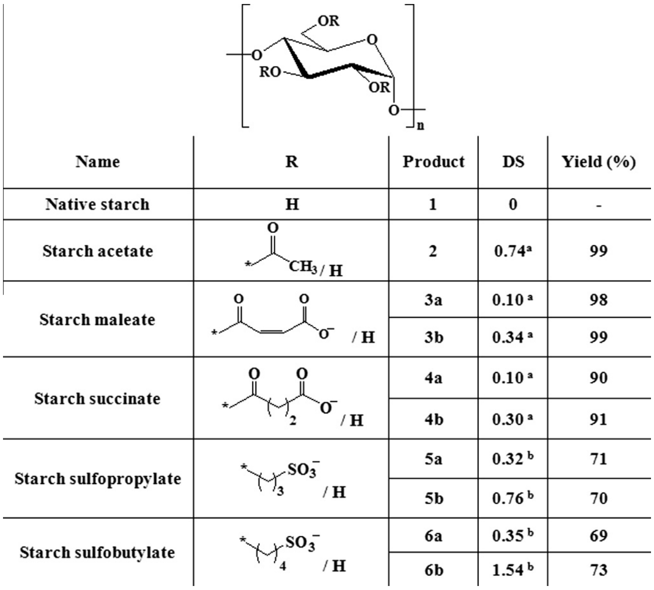
The general structure of the synthesized starch derivatives and the chemical representation of the grafted substituent are represented in Fig. 2. The efficiency of the reactions and the purity of the synthesized products are confirmed by the FT-IR and ^1H NMR analyses (Table 1).

Most of synthesized starch derivatives are hydrosoluble, easing their use in cementitious suspensions. Only native starch is not hydro soluble and has to be introduced in the cement paste as a powdered solid form.

3. materials and mixture proportioning for physical tests for starch derivatives characterization in cement paste

Physical tests were then performed in order to determine the impact of starch derivatives on the physical and rheological properties of the cement pastes. This study was undertaken on 0.33 w/c cements pastes prepared using a CEMI I 52.5N cement, complying with EN 196-1 standard, and starch derivatives as HRWRAs. Physical and chemical characteristics of the cement and the mix design for the preparation of the cement paste are summarized in Table 2.

All synthesized polymers used as HRWRA in this investigation were prepared in aqueous solution at 30% solid content, except native starch that was introduced as a solid in cement paste A refer-



Name	R	Product	DS	Yield (%)
Native starch	H	1	0	-
Starch acetate	CH_3 / H	2	0.74[a]	99
Starch maleate	O⁻ / H	3a	0.10[a]	98
		3b	0.34[a]	99
Starch succinate	O⁻ / H	4a	0.10[a]	90
		4b	0.30[a]	91
Starch sulfopropylate	SO_3^- / H	5a	0.32[b]	71
		5b	0.76[b]	70
Starch sulfobutylate	SO_3^- / H	6a	0.35[b]	69
		6b	1.54[b]	73

Fig. 2. Chemical characteristics of starch derivative syntheses; (a) determined by ^1H NMR spectroscopy (standard deviation: 5%) and (b): determined by volumetric method (standard deviation: 10%).

Table 1
FT-IR wavenumbers and ^1H NMR chemical shifts of starch derivatives.

Product	ν (cm^{-1})	δ (ppm)
2	3400 (O—H) 2800–2900 (C—H) 1740 (O—C═O)	3.50–5.30 (7H, br.m., H_{sugar}) 1.9–2.1 (3H, s, -CH_3)
3a and 3b	3400 (O—H) 3010 (=C-H) 2800–2900 (C—H) 1630 (C═C) 1740 (O—C═O)	3.50–5.30 (7H, br.m., Hsugar) 5.90 (1H, d, —CO—CH═) 6.50 (1H, d, ═CH—COOH)
4a and 4b	3400 (O—H) 2800–2900 (C—H) 1740 (O—C═O)	3.50–5.30 (7H, br.m., Hsugar) 2.50 (4H, t, CH_2—COOH) 2.60 (2H, t, -CO—CH_2-)
5a and 5b	3400 (O—H) 2800–2900 (C—H) 1380–1347 (—S═O) 1193–1170, 1040 (SO_3H/SO_3-)	3.50–5.30 (7H, br.m., Hsugar) 1.90 (2H, m, O—C—CH_2—C—S) 2.86 (2H, m, CH_2—S) 4.33 (2H, m, CH_2—O).
6a and 6b	3400 (O-H) 2800–2900 (C—H) 1380–1347 (—S═O) 1193–1170, 1040 (SO_3H/SO_3-) 720 ((CH_2)$_4$)	3.50–5.30 (7H, br.m., Hsugar) 1.90 (2H, m, CH_2—C—O) 2.86 (2H, m, CH_2—C—S) 3.33 (2H, m, CH_2—S) 4.34 (2H, m, CH_2—O)

ence sample proportioned with widely used 32% solid content PNS at a dosage of 1.6%, by mass of cement (on a dry basis) was prepared and all tests were performed to have a comparison point.

As cement paste rheology can be affected by the mixing procedure and equipment, and in order to have comparable results, the same mixer and the same mixing sequence were used for each set of pastes. The pastes were prepared in batches of 1 L using a helicoidal mixer rotating at successive speeds ranging between 140 and 285 rpm.

The mixing procedure consisted of adding the cement, the water and HRWRA into the mixer. The paste was then mixed during 90 s at 140 rpm. After a rest period of 60 s, the mixing was resumed for an additional 90 s at 285 rpm, as recommended in EN 196.

The raw materials were conditioned to adhere to the targeted test temperature of 20 °C (±2 °C). In order to avoid heat loss or gain during mixing, all apparatuses used for mixing and testing were maintained at the targeted temperature. At the end of mixing, samples were taken to perform rheological tests at 10 and 60 min after batching, including a mini slump test, and viscosimetry.

The mini slump test was done in accordance with EN 13 395-2 standard. It consists in pouring the cement paste into a 38 mm base diameter cone, opened in upper and lower sides, then lifting the cone and measuring the diameter of the spread to have an idea on the workability and fluidity of the mixture. As this test is mainly informative, rheological measurements at 10 min were performed to get the yield stress (τ_0) and plastic viscosity (μ) of the cement paste. A co-axial cylinder rheometer (Haake VT550, MV rotor and cup) was employed to evaluate the rheological properties of mortars. A 60 cm^3 sample was used for measurements. The surfaces of the inner and outer cylinder of the viscometer were not roughened since the materials tested in this investigation were highly flowable. The apparent viscosity was determined, after a stabilization time of 20 s., at five shear rates of 5.1, 170, 340, 510 and 1020 s^{-1}. The apparent viscosity is calculated as the ratio between the shear stress (τ) and shear rate (γ°). The yield stress refers to the resistance of the material to undergo initial flow, and the plastic viscosity (μ) refers to the slope of the shear stress–shear rate relationship. As the up and down curves coincided, τ_0 and μ values are derived by regression analysis using the shear stress–shear rate data assuming a polynomial response. The second order value is considered as insignificant and is suppressed. The resulting expression can be expressed as $\tau = \tau_0 + \mu . \gamma^\circ$ representing the behavior of a Bingham fluid. When using a Bingham model for flow modelization, τ_0 refers to the resistance of the material to undergo initial flow, and μ describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. Repeatability experiments showed little dispersion of the results. The maximal

Table 2
Characteristics of the CEM I 52.5N cement.

Chemical composition (%) (Bogue)		Physical characteristics	
SiO_2	20.5	Blaine fineness, m^2/kg:	410
Al_2O_3	4.4	Specific gravity:	3.13
Fe_2O_3	2.3	Setting time (Vicat), min:	
CaO	63.3	· Initial :	209
MgO	2.1	· Final:	247
NaO_2 Eq.	0.66	Compressive strength, MPa:	
Clinker	97	2 d:	37
Limestone filler	3	7 d:	52
		28d:	63

Raw materials	Mass of raw materials for the preparation of the sample (g)	Volume of raw materials for the preparation of the sample (mL)
Cement paste mix design		
CEM I 52.5N cement	1533	494.5
Water	505.9	505.9
Dry polymer	Variable	Variable

relative deviation was of 6% for both yield stress and plastic viscosity for the mixtures tested on data presented herein.

In order to ensure homogeneity before each rheological test, the mortar was remixed at 140 rpm during 60 s. After each rheological test, the sample was discarded in order to ensure confidence in test results.

Setting time was monitored using a Vicat test. The Vicat setting time is the determination of the beginning of setting of cementitious materials due to the acceleration of the hydration process consequent to precipitation of calcium hydroxyde in the pore solution, taking into account the time needed by the specimen to penetrate to a depth of 4 mm by a 300 grams loaded flat-ended needle with a 1 square mm circular section. This test was performed in accordance with EN 196-3 standard.

The compressive strength of the tested pastes at 7 days was then evaluated on 4 × 4 × 4 cm cubic samples. Tests were performed according to the EN 196 standard.

Rheometric measurements at 60 min, setting time and compressive test at 298 days were performed only if the initial rheological test gave measurable data.

4. results and discussion

4.1. Chemical characterization

The general structure of the synthesized starch derivatives and the chemical representation of the linked substituent are represented in Fig. 2.

These starch derivatives can be listed into families: starch ester (starch acetate), starch carboxylates (starch maleate and succinate) and starch sulfoaklylates (starch sulfopropyle and sulfobutyle), whose structure mimics the petrochemical superplasticizers one (PC and PNS respectively). Moreover, their syntheses lead to high yields from 69% to 99%, which is an important industrial aspect for their potential use.

Spectroscopic characterization by FT-IR and ^{1}H NMR have confirmed the efficiency of the reactions. IR-TF analysis allowed us to identify chemical functions with the specific vibration bands of functionnal groupments. ^{1}H NMR spectra informed us about the protons' chemical shifts, and allowed us to determine the structure of the synthesized products. Characteristic wave numbers ν (cm^{-1}) and chemical shifts δ (ppm) are reported in Table 1, and are correlated to the proposed starch derivative structures. These analyses also confirm the purity of the synthesized products, since no trace of reagents or solvents are observed.

^{1}H NMR spectroscopy informs us about the degree of substitution (DS), defined as the number of substituents linked per anhydroglucose unit (maximum value of 3). It is determined with an integration method described elsewhere [8,27] for starch esters and carboxylates, or by a volumetric method adapted from previous work [28] for starch alkylsulfonates (Table 3).

DS values are reported in Fig. 2. Their variations are due to the quantity of reactive (anhydride or alkylsultone) introduced during the synthesis (from 2 to 4 equivalents based on starch repetitive unit). Starch derivatives with low DS values (from 0.1 to 1.54) have specifically been synthesized, in order to observe the effect of the grafted substituant, and also to get hydrosoluble starch derivatives.

4.2. Initial slump spread

As shown in Fig. 3, only starch sulfopropylate (5) and starch sulfobutylate (6) can compete with PNS with a slump spread around or over 130 mm, except for the former at 0.32 DS and at a dosage of 1% that exhibits a 50 mm diameter slump flow (paste made with 5a). On the contrary, starch maleate (pastes made with 3a and 3b) and starch succinate with a 0.3 DS (4b) display poor dispersing efficiency exhibiting flows inferior to product proportioned with native starch. Starch acetate (polymer 2) and starch succinate with a 0.1 DS (4a) behaved as a viscosant, stiffening the tested paste, resulting in the absence of flow (the spread is equal to the 38 mm down diameter of the cone initially poured with modified cement paste). This can be explained by the superior ability of the sulfate and O^- groups, compared to methyl, to adsorb on the cement grains, groups usually used on commercially available HRWRAs [29]. Furthermore, an increase in the degree of substitution resulted in enhancing the flow spread (Fig. 2 Figs. 3–5a–b at a dosage of 1%). It is assumed that a larger number of side chains augment the number of anionic sites leading electrostatic repulsion, resulting in improving the flowability of the paste. It is noteworthy that, even if starch succinate has already been successfully tested as HRWRA [5], it proved to be disappointing in this investigation, due to the low DS of the grafted polymers. Starch succinate at 2 eq. only (4b) showed a light ability to deflocculate paste suspension, and further investigations should be done using this polymer to enhance its dispersing performances.

The best results were obtained with starch sulfobutylate (6a and 6b) and sulfopropylate (5a and 5b). Although the molecular weight values of these two polymers are low compared to PNS (about 4200 g/mol for starch derivatives and about 100,000 g/mol for PNS), their ability to enhance workability of cementitious pastes was proved, with slump spread matching the one obtained with the reference mixture proportioned with PNS. It is noteworthy that the lower the DS, the higher the HRWRA demand to get the targeted 130 mm flow spread. The introduction of the propyl or butyl group between the trunk chain and the sulfate ending of the side chain lengthen the latter, and a steric hindrance may appear, enhancing the dispersing effect. When the DS is augmented (5a–5b at the same dosage of 1%), less polymer quantity was necessary to get the same slump spread due to the rise of anionic ending, thus improving electrostatic repulsion.

From this point, only mixes that showed sufficient flow spread were investigated in terms of rheology and rheology retention with time, and initial setting time.

Table 3
Equations for the determination of starch derivatives DS.

Product	Equation	Significance
Starch acetate	$\mathrm{DS} = \frac{I_{\mathrm{CH_3}/3}}{I_{\mathrm{sugar}}/7}$	DS: degree of substitution I_{sugar}: ^{1}H NMR peak's integration of all protons in anhydroglucose unit
Starch maleate	$\mathrm{DS} = \frac{I_{\mathrm{CH=CH}}/2}{I_{\mathrm{sugar}}/7}$	$I_{\mathrm{CH_3}}$: ^{1}H NMR peak's integration of terminal methyl protons
Starch succinate	$\mathrm{DS} = \frac{I_{(\mathrm{CH_2})_2}/4}{I_{\mathrm{sugar}}/7}$	$I_{\mathrm{CH=CH}}$: ^{1}H NMR peak' integration of methylene protons
Starch sulfonate derivatives	$\mathrm{DS} = \frac{\mathrm{M_{UG}}}{\mathrm{m/n_{RSO_3-}} - \mathrm{M_{RSO_3-}}}$	$I_{(\mathrm{CH_2})_2}$: ^{1}H NMR peak's integration of methyl protons
		M_{UG}: molar mass of anhydroglucose unit (g/mol) m: sample mass (g) $\mathrm{n_{RSO_3-}}$: moles of sulfonate functions (moles) $M_{\mathrm{RSO_3}}-$: molar mass of sulfonate chain (g/mol)

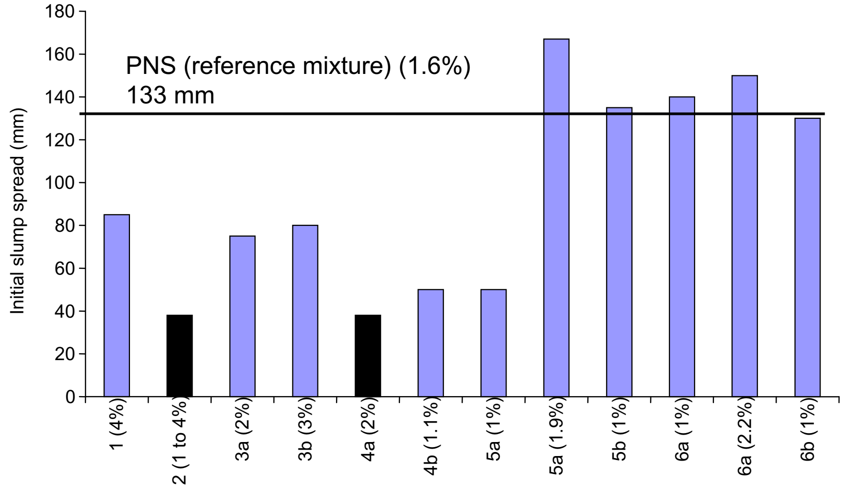
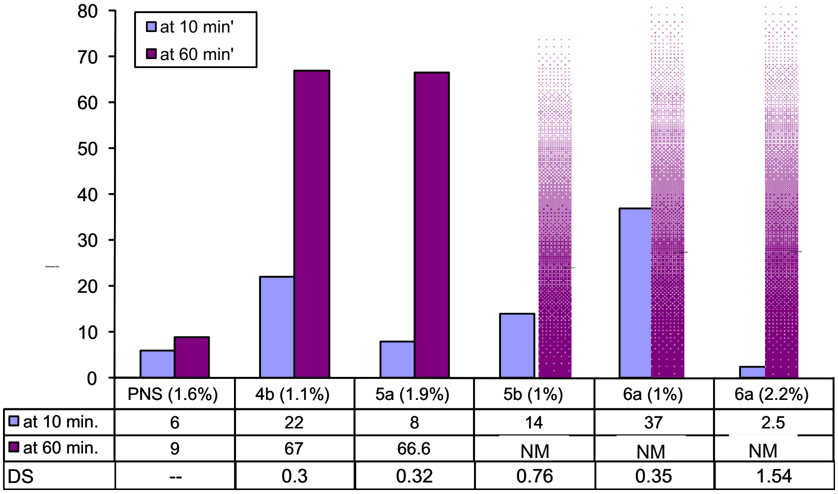


Fig. 3. Initial slump spread on cement pastes made with starch derivatives (38 mm for products 2 and 4a means that no spread was observed).



	PNS (1.6%)	4b (1.1%)	5a (1.9%)	5b (1%)	6a (1%)	6a (2.2%)
▢ at 10 min.	6	22	8	14	37	2.5
■ at 60 min.	9	67	66.6	NM	NM	NM
DS	--	0.3	0.32	0.76	0.35	1.54

Fig. 4. Yield stress at 10 and 60 min on cement pastes made with PNS and starch derivatives (N.M means non-measurable).

4.3. Yield stress monitoring at 10 and 60 min

The first rheological test was done 10 min after the water – cement contact, and results are presented in Fig. 4 for yield stress evaluation at 10 and 60 min. The *yield stress* relates with the distance between the particles in the paste matrix and governs the mix deformability [30]. Self-Leveling Underlayment will have a low Yield Point meaning not much energy (gravity) is needed for the material to flow and level.

It is shown in Fig. 4 that, for pastes tested at 10 min, a DS ranging from 0.30 to 0.35 and a HRWRA dosage around 1% (products 4b and 6a) resulted in yield stress over 22 Pa, far over the 6 Pa obtained with the reference mixture at 10 min. For product 5a displaying a 0.32 DS but proportioned with 1.9% of starch sulfopropylate, the yield stress at 10 min lowers to 8 Pa, a value similar to the PNS mix. When DS is augmented to 0.76 (product 5b), and even if starch sulfopropylate is incorporated only at 1%, the yield stress is diminished to an acceptable value. Pastes are tested with 2.2% starch sulfobutylate at 1.54 DS exhibited an impressively low yield stress of 2.5 Pa (Table 4).

The decrease in yield stress with increasing HRWRA dosage is a well known phenomenon [31], explaining the better results obtained on pastes proportioned with 5a and 6a, independently of the DS of the tested starch derivative. Moreover, as previously explained, a rise in the degree of substitution resulted in increasing the number of side chains, augmenting the number of anionic sites leading electrostatic repulsion, and resulting in decreasing the yield stress.

Yield stress retention over time is also important as workability of concrete should be sufficient to permit casting on sites, without being altered by delivery delays due to traffic. Changes in rheological properties with time can be due to physical factors (coagulation and restructuring of the microstructure) and chemical factors (cement hydration and reduction in free water content). Key factors affecting changes in rheological properties with time include temperature, mixture composition, the grinding history of the binder, and the interaction between the binder and HRWRA in use [1,32–37].

To evaluate workability retention with time of the pastes made with starch derivatives, a rheological test was held 60 min after water – cement contact. All held natural-based HRWRAs proved to be disappointing concerning their ability to keep their efficiency over time, and this point will be analyzed later while discussing on the effect of the tested starch derivatives on initial setting time of cement pastes.

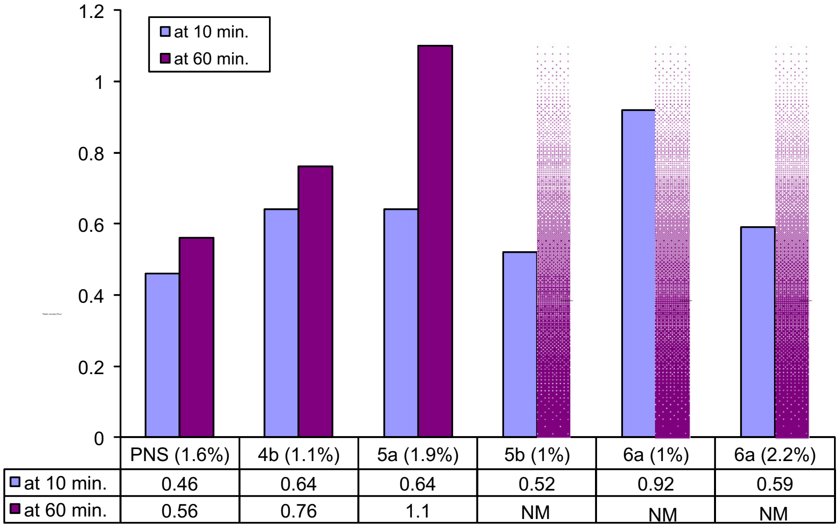


Fig. 5. Plastic viscosity at 10 and 60 min on cement pastes made with PNS and starch derivative (N.M means non-measurable).

Table 4
Physical tests results obtained with addition of PNS or starch derivatives in cement paste.

HRWRA	% (w/w cement)	Initial slump spread (mm)	Rheology				Vicat initial setting time (h)
			At 10 min.		at 60 min.		
			τ_0 (Pa)	μ (Pa s)	τ_0 (Pa)	μ (Pa s)	
PNS	1.6	133	6	0.46	9	0.56	8
1	4	85	–	–	–	–	–
2	1.0–4.0	NM	–	–	–	–	–
3a	2	75	–	–	–	–	–
3b	3	80	–	–	–	–	–
4a	2	NM	–	–	–	–	–
4b	1.1	50	22	0.64	67	0.76	7
5a	1	50	–	–	–	–	–
	1.9	167	8	0.64	66.6	1.1	3.25
5b	1	135	14	0.52	–	–	>10
6a	1	140	37	0.92	–	–	1.25
	2.2	150	2.5	0.59	–	–	0.75
6b	1	130	–	–	–	–	–

NM: non measurable.

4.4. Plastic viscosity monitoring at 10 and 60 min

Plastic Viscosity is a material resistance to increase flow rate with an increase in force, mainly guided by interparticle friction during the motion of the paste. A minimum Plastic Viscosity is needed to prevent segregation in Self-Leveling Underlayment application. Leemann and Winnefeld found that, on mortars made with PCP-HRWRA and various Viscosity modifying agents (siliceous, ethylenoxy derivate, Natural polysaccharide, and Starch derivate), that the addition of VMA can be combined with the addition of an appropriate amount of HRWRA keeping the water over cement ratio constant. In this case the yield stress will be unchanged, while the plastic viscosity is increased [38].

The results obtained in this investigation are presented in Fig. 5.

Except for product 6a, all measured plastic viscosities at 10 min on starch derivatives mixes are 13–39% higher than the one obtained on PNS paste, which is acceptable. This may be due to the inhibition of the starch gelatinization attributable to the draft of side chains. This neutralization of the gelatinization depends on the chosen component of the lateral chain and the DS. For low DS products (from 0.3 to 0.35), succinate and sulfopropylate exhibited the same 0.64 Pa s plastic viscosities. The increase in DS from 0.32 to 0.76 for product 5, or from 0.53 to 1.54 for product 6, resulted in lowering the μ values from 19% to 36%, depending on the tested starch derivative.

When monitoring plastic viscosity at 60 min, pastes proportioned with starch sulfobutylate displayed a quick heat release 15 min after water – cement contact, stiffening the paste, disabling to measure rheological parameters. While no heat release was observed on the other mixes, only product 4b showed a loss in fluidity comparable to the one monitored with the reference sample. As for yield stress measurements at 60 min, the results on setting time may explain the obtained results on μ.

4.5. Initial setting time

The low DS starch sulfopropylate (5a) exhibited an initial setting time of about 3 h, inferior to the one monitored with the reference sample (8 h). When the DS is augmented, and even if the dosage is lowered (5b), a delay is observed and the setting time measured was of 10 h approximately, as shown in Fig. 6. These noticeable differences of setting times can be explained by an excess of sulfonate functions. When reaching a threshold concentration in the cementitious solution, the SO_3^{2-} can strongly delay the hydration reaction.

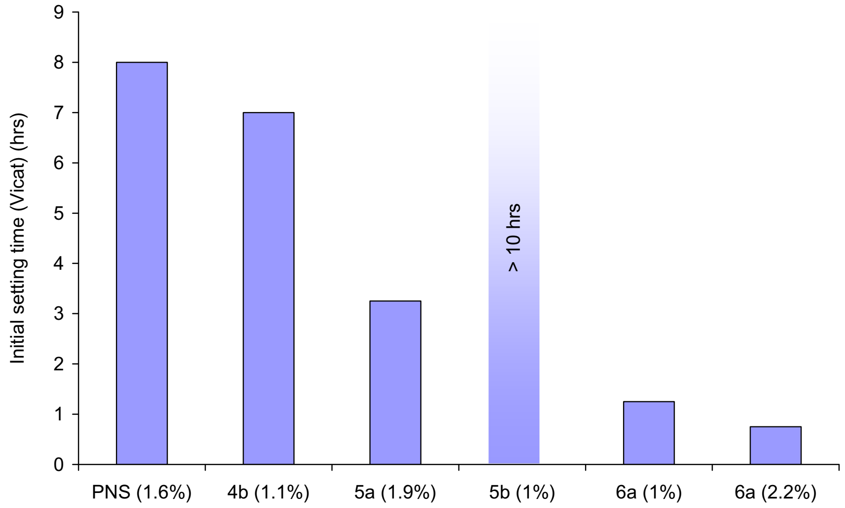


Fig. 6. Initial setting time (Vicat) on cement pastes made with PNS and starch derivatives.

Switching from sulfopropylate to sulfobutylate side chains induces an unexpected reduction in setting time, with even a gelatinization of the mixture proportioned with the highest DS (6b). The HRWRA made with starch sulfobutylate showed two effects:

- a superplasticizing effect at very short term,
- a set accelerator effect few minutes after casting.

4.6. compressive strength at 7 days

As shown in Table 5, only starch alkylsulfonate mixtures gave good 7 days compressive strength, except for the mixture proportioned with 6a at a dosage of 2.2%, by mass of cement, which exhibits a low resistance to compression. This latter phenomenon may be due to an excessive dosage in HRWRA that can significantly influence the cement hydration, and thus, the compressive strength of the tested sample. On the contrary, sample proportioned at a dosage of 1% showed better compressive performances than the reference mix.

Only product 4b was tested as carboxylated modified starch-based polymers, and compressive test results proved to be disappointing.

At this stage of the investigation, further investigations are needed to highlight the effects of these tested starch derivatives on cementitious materials, focusing on the determination of the best starch derivatives to substitute petrochemical HRWRA, according to their molecular weight and DS. It was shown that the introduction of a small amount of polysaccharide (0.5% by weight of cement) induces a strong modification of cement hydration [39].

Table 5
Compressive strength results at 7 days obtained with addition of PNS or starch derivatives in cement paste.

HRWRA	% (w/w cement)	Initial slump spread (mm)	Compressive strength at 7 days (Mpa)
PNS	1.6	133	72.2
1	4	85	–
2	1.0–4.0	NM	–
3a	2	75	–
3b	3	80	–
4a	2	NM	–
4b	1.1	50	5.0
5a	1	50	–
	1.9	167	66.5
5b	1	135	69.1
6a	1	140	80.9
	2.2	150	6.9
6b	1	130	–

The retardation in hydration could be linked to an adsorption of polysaccharide admixtures on the hydrates forming a less permeable coating, delaying the formation of both CSH and portlandite. The retarding effect of polysaccharide depends also on the chemical structure of the admixtures. A higher soluble fraction of starch derivative is more effective to retard cement hydration [39]. Consequently, the lower the hydration kinetic due to starch derivates coating onto cement grains is, the lower the compressive strength is.

5. Evaluation of starch-based polymers in commercial self leveling compounds mix design as alternative to casein

Self leveling compounds (SLC) are very fluid cement based mixtures, usually containing High aluminous cement and an alkaline accelerator for fast setting purpose. But the very role of this cementitious material is to ease screed casting by a high fluidity. To enhance the flow, HRWRAs are added in the dry mix as powder, and the most commonly used is casein. Unfortunately, the cost of this raw material has increased these last years, and alternative HRWRAs are tested for cost control of the final product. Regrettably, these alternative HRWRAs are mainly PC or PNS, hence, it was quite natural to test bio-based cement dispersant as alternative to bio-based casein.

While products 5a, 5b, 6a and 6b gave good performances in cement pastes, it has been chosen to test starch maleate (3b), starch

Table 6
Mix design of the SLU used for starch-based SP evaluation.

Materials	Quantity (%wt)
Lime	3
Ordinary Portland cement CEM I 52,5 R	25
High aluminous cement	8
Calcium CARBONATE	20
0/1 Quartz sand	41.1
Cellulose ether	0.1
Casein	0.5
Trisodium citrate	0.2
Lithium Carbonate	0.1
Defoamer	0.1
Latex redispersible powder	2
Water/powder ratio	0.24

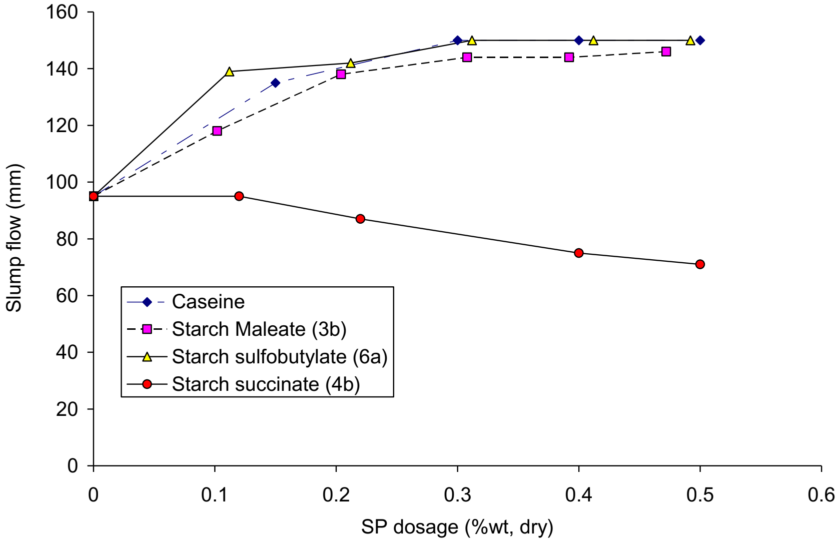


Fig. 7. Slump flow as a function of the SP dosage on the tested SLUs.

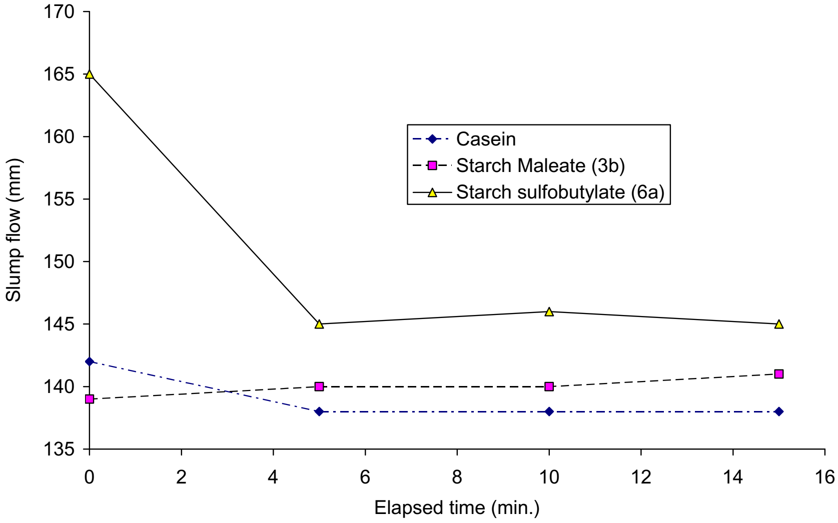


Fig. 8. Slump retention over time for the tested SLUs (all HRWRAs were dosed at 0.5%wt. of the total dry mix).

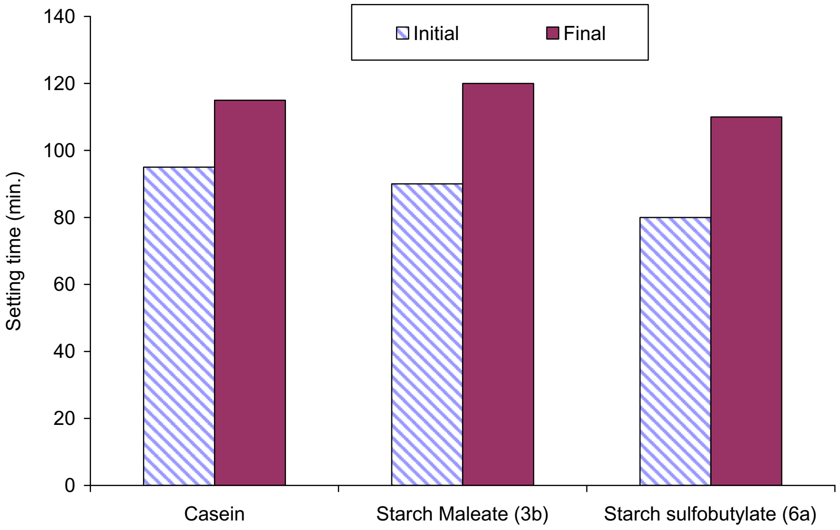


Fig. 9. Initial and final setting time for the tested SLUs (all HRWRAs were dosed at 0.5%wt. of the total dry mix).

Table 7
Flexural and Compressive strength results at 1 and 28 days obtained with addition of casein or starch derivatives in SLU mix design.

Mechanical properties (Mpa)		Casein	Starch Maleate (3b)	Starch sulfobutylate (6a)
At 1 day	Flexural stress	2.11	1.90	1.75
	Compressive stress	7.7	6.0	9.8
At 28 days	Compressive stress	29.3	26.6	32.6

succinate (4b) and starch sulfobutylate (6a) in a commercial SLC, whose mix design is given in Table 6. This self leveling compound is composed of 37% of binder by mass (ordinary Portland cement, high alumina cement and lime), 41.1% by mass of siliceous sand as aggregate, 20% by mass of fine calcium carbonate used to control fluidity and act as secondary nucleation sites for cementitious hydrates. The alkaline accelerator for alumina phases is lithium carbonate, used at 0.1% by mass, and the chosen set retarder was trisodium citrate. Cellulose ether is used as water retaining admixture to avoid bleeding and segregation, and a defoamer is added in order to release the air entrapped by the cellulose ether. The organic binder was a vinyl acetate- vinyl versatate – based latex in redispersible powdered form and used at 2% by mass. All these components are premixed in dry form, and have to be mixed with water at a 24% rate, by mass.

Fig. 7 presents the variation of the slump flow on SLCs with the increase of HRWRA. It is seen that, except for product 4b that induces a stiffening of the mixture, the tested products proved to be as efficient as casein in fluidifying the SLC, with equivalent saturation dosage of around 0.3% of the total dry mix. Consequently, product 4b was excluded for further investigation.

The next step consisted in evaluating the flow retention with time over 15 min, which is the usual open time for fast setting SLC. The results are presented in Fig. 8, and show that, at a 0.5% dosage, by weight of the total dry mix, product 3b and 6a proved to have a slump retention over time as good as casein.

While setting time seemed to be affected by the switch from PNS to bio-based HRWRA on cement pastes, no effect of the two selected bio-HRWRA are visible compared to casein-based mix design, with initial set around 90 min Fig. 9. Hydration kinetics is slightly faster for casein-based SLC, with a difference of time between initial and final set of 20 min compared to 30 min for mixtures proportioned with 3b and 6a. This had no influence on early age mechanical resistance, as 1 day flexural stress ranged from 1.75 to 2.11 MPa, and 1 day compressive strength ranged from 6.0 to 9.8 MPa, as shown in Table 7. It can be concluded that the two starch-based superplasticizers can be a good bio-based alternative to casein in SLC mix designing.

6. Conclusions

Starch derivate with short maleate, succinate, sulfopropylate and sulfobutylate side chains was synthesized, and their use of as HRWRA was investigated and compared to a reference sample proportioned with PNS. Based on the data presented in this investigation, the following conclusions appeared to be warranted:

1. Caboxylated-modified starch proved to be disappointing as dispersing agents for pure cement matrices, while more promising results were obtained with alkylsulfonated starch.
2. Sulfate and O^- ionic groups as side chains ending can permit a better adsorption of the grafted starch-based polymer used as HRWRA on cement grains, enabling a better retention in fluidity.
3. A larger number of side chains, i.e. a more important DS, augment the number of anionic site leading electrostatic repulsion between cement grains, and resulting in larger slump spreads of cement pastes using starch derivates as HRWRAs.
4. The use of sulfonated starch derivates (starch sulfobutylate and sulfopropylate) as HRWRAs seems to be very promising. At dosages comparable to the one in use in the reference PNS-based sample, these derivates can achieve similar slump spreads, initial yield stress and plastic viscosity as the ones measured on the reference sample. However, rheological tests performed at 60 min showed a more rapid gelatinization of the pastes containing starch derivates.
5. The setting time of the tested pastes showed great differences linked to the length of the grafted sulfonated side chains. The sulfopropyl group exhibited an important delay effect when having a DS close to 1, while the sulfobutyl group showed a remarkable set accelerator effect, independent of the DS.
6. 7 days compressive strength values of al ylsufonated starch-based mixtures are comparable to results obtained with PNS, when used at appropriate dosages. An over dosage can lead to a rapid decrease in compressive strength.
7. Starch maleate or starch sulfobutylate were proved to be good alternative to casein in self-leveling compounds.

References

[1] Flatt RJ, Martys N, Bergström L. The rheology of cementitious materials. Mat Res Soc 2004;29(5):314–8.
[2] Jolicoeur C, Sharman J, Otis N, Lebel A, Simard MA, Page M, The influence of temperature on the rheological properties of superplasticized cement pastes. In: Proceedings 5th CANMET/ACI International Conference. ACI SP 173, ACI, Rome; 1997. p. 379–415.
[3] Knaus S, Bauer-Heim B. Synthesis and properties of anionic cellulose ethers: influence of functional groups and molecular weight on flowability of concrete. Carbohydr Polym 2003;53:383–94.
[4] Sakai E, Kazuo Y, Ohta A. Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan. Adv Concr Tech 2003;1(1):16–26.
[5] Zhang DF, Ju BZ, Zhang SF, Yang JZ. The study on the synthesis and action mechanism of starch succinate half ester as water-reducing agent with super retarding performance. Carbohydr Polym 2008;71:80–4.
[6] 6. Müller F, Wallevik OH. Benfits of filler material on rheology in Eco-SCC. In: Shah SP, editor. In: Proceedings of the 3rd North America Conference on Self-Compacting Concrete. Chicago, USA; 2008. p. 6.
[7] Vieira MC, Klemm D, Einfeldt L, Albrecht G. Dispersing agents for cement based on modified polysaccharides. Cem Concr Res 2005;35(5):883–90.
[8] Xu Y, Miladinov V, Hanna MA. Starch acetate-maleate mixed ester synthesis and characterization. Cereal Chem 2005;82(3):336–40.
[9] Chatterjee AK. Lignosulphonate is a valuable by-product from the black liquor. Indian Pulp Paper Tech Assoc 2012;24(4):147–50.
[10] Qiu XG, Wang B, Lou HM, Yang DJ. Graft sulfonation and water reducing-performance strengthening effect of acid precipitation lignin. J South China Univ Tech (Natural Science Edition) 2007;4:7p.
[11] Stráněl O, Sebök T. Relationships between the properties of ligninsulphonates and parameters of modified samples with cement binders: Part I Characterizing ligninsulphonates and studying their sorption propertie. Cem Conc Res 1997;27(2):185–91.
[12] Xing GX, Zhang SF, Ju BZ, Yang JZ. Microwave-assisted synthesis of starch maleate by dry method. Starch/Stärke 2006;58:464–7.
[13] Miladinov VD, Hanna MA. Ind Crops Prod 2000;11:51.
[14] Raquez JM, Nabar Y, Srinivasan M, Shin BY, Narayan R, Dubois P. Maleated thermoplastic starch by reactive extrusion. Carbohydr Polym 2008;74:159–69.
[15] Biswas A, Shogren RL, Selling G, Salch J, Willett JL, Buchanan CM. Rapid and environmentally friendly preparation of starch esters. Carbohydr Polym 2008;74:137–41.
[16] Alomaa M, Asplund T, Soininen P, Laatikainen R, Peltonen S, Hyvärinen S, et al. Determination of the degree of substitution of acetylated starch by hydrolysis, ^{1}H NMR and TGA/IR. Carbohydr Polym 2004;57:261–7.
[17] Biswas A, Shogren RL, Kim S, Willett JL. Rapid preparation of starch maleate half-esters. Carbohydr Polym 2006;64:484–7.

[18] Uchikawa H, Hanehara S, Sawaki D. The role of steric repulsive force in the dispersion of cement particules in fresh paste prepared with organic admixture. Cem Concr Res 1997;27:37–50.

[19] Patural L, Machal P, Govin A, Grosseau P, Ruot B, Devès O. Cellulose ethers influence on water retention and consistency in cement-based mortars. Cem Concr Res 2011;41:46–55.

[20] Tegiacchi F, Casu B. Alkylsulfonated polysaccharides and mortar and concrete mixes containing them. GB Patent 2138014; 1987.

[21] Abd El-Rehim HA, El-Sayed A, Hegazy A, Diaa DA. Radiation synthesis of eco-friendly water reducing sulfonated starch/acrylic acid hydrogel designed for cement industry. Radiat. Phys. Chem. 2013;85:139–46.

[22] Zhang DF, Ju BZ, Zhang SF, Yang JZ. The study on the dispersing mechanism of starch sulfonate as a water-reducing agent for cement. Carbohydr Polym 2007;70:363–8.

[23] Lv SH, Gao RJ, Cao Q, Li D, Duan JP. Preparation and characterization of poly-carboxymethyl-β-cyclodextrin superplasticizer. Cem Concr Res 2012;42(10):1356–61.

[24] Zhao D, Zhao L, Zhu CS, Tian ZB, Shen XY. Synthesis and properties of water-insoluble β-cyclodextrin polymer crosslinked by citric acid with PEG-400 as modifier. Carbohydr Polym 2009;78(1):125–30.

[25] Lv SH, Gao RJ, Duan JP, Li D, Cao Q. The effects of β-cyclodextrin side chains on the dispersing and retarding properties of polycarboxylate superplasticizers. J Appl Polym Sci 2012;125(1):396–404.

[26] Minkema WH. Preparation of starch esters. US Patent 2868780; 1959.

[27] Crépy L, Chaveriat L, Banoub J, Martin P, Joly N. Synthesis of cellulose fatty esters as plastics – Influence of the degree of substitution and the fatty chain length on mechanical properties. ChemSusChem 2009;2:165–70.

[28] Joly N, Granet R, Krausz P. Crosslinking of cellulose by olefin metathesis. J Carbohydr Chem 2003;22:47–55.

[29] Ramachadran VS, Malhotra VM, Jolicoeur C, Spiratos N. Superplasticizers: properties and application in concrete. Ottawa, Canada: CANMET Publications; 1998. p. 404.

[30] Shah SP, Konsta-Gdoutos MS. Measuring, monitoring and modeling concrete properties. In: Konsta-Gdoutos S, editor. Dordrecht, The Netherlands: Springer; 2006. p. 785.

[31] Artel C, Garcia E. Impact of superplasticizer concentration and of ultra-fine particles on the rheological behaviour of dense mortar suspensions. Cem Concr Res 2008;38(5):633–42.

[32] Jolicoeur C, Sharman J, Otis N, Lebel A, Simard MA, Page M. The influence of temperature on the rheological properties of superplasticized cement pastes. In: Malhotra VM, editor. Proceedings fifth CANMET/ACI international conference on superplasticizers and other chemical admixtures in concrete. Rome, 1997. p. 379–415.

[33] Flatt RJ, Houst YF. A simplified view on chemical effects perturbing the action of superplasticizers. Cem Concr Res 2001;31(8):1169–76.

[34] Hanehara S, Yamada K. Interaction between cement and chemical admixtures from the points of cement hydration, admixture adsorption and paste rheology. Cem Concr Res 1999;29(8):1158–65.

[35] Golaszewki J, Szwabowski J. Influence of superplasticizer on rheological behaviour of fresh cement mortars. Cem Concr Res 2003;34(2):235–48.

[36] Petit JY, Wirquin E, Duthoit B. Influence of temperature on the yield value of highly flowable micromortars made with sulfonate-based superplasticizer. Cem Concr Res 2005;35(2):256–66.

[37] Petit JY, Khayat KH, Wirquin E. Methodology to evaluate the coupled influence of time and temperature on rheological properties of cement-based materials. ACI Mater J 2008;105(4):342–9.

[38] Leemann A, Winnefeld F. The effect of viscosity modifying agents on mortar and concrete. Cem Concr Res 2007;29(5):341–9.

[39] Peschard A, Govin A, Grosseau P, Guilhot B, Guyonnet R. Effect of polysaccharides on the hydration of cement paste at early ages. Cem Concr Res 2004;34(11):2153–8.