



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



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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 derivatives 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 derivatives, 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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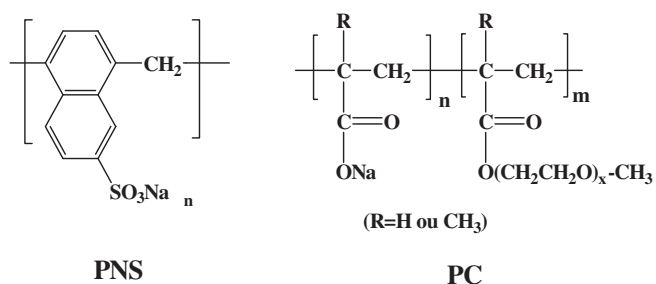


Fig. 1. Chemical structures of commonly used petrochemical-based superplasticizers.

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- $\beta$ -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 ( $\sim 4000$  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-butanedisultone (>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<sub>2</sub>O and CDCl<sub>3</sub> 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-propanedisultone or 1,4-butanedisultone; 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. <sup>1</sup>H NMR spectroscopy was performed in D<sub>2</sub>O 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 sulfopropylate 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 <sup>1</sup>H 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-

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