

Why nonionic starch ethers act as anionic flocculants in cementitious systems

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Abstract

Starch ethers are added to mortars in order to modify the rheology of the fresh mortar by bridging flocculation. The proper function as flocculant for cement requires that the starch ether molecules possess anionic charged functional groups. With this in mind, the different types of commercially available starch ethers are evaluated. Two types of starch ethers can be distinguished, which differ in the dependence of the effect on dosage. All starch ethers are anionic charged at pH values above 11. At neutral pH, CM-HP-starches are more efficient flocculants than HP-starch.

1 Introduction

In modern dry-mix mortars a wide variety of additives are used to adjust the rheological properties. Mortar formulations quite often comprise more than ten different ingredients and the development of such formulations requires great efforts. To minimize this experimental effort, targeted selection of the components is necessary, the knowledge about mode of actions and possible interactions is crucial. Behind cellulose ethers, starch ethers are of major importance as additives, even though their addition rate is very low (usually 0.01 to 0.05%). Nearly all starch ethers available for use in mortars are hydroxypropyl starches (HP-starch). However, at least one product is a mixed ether containing additionally carboxymethyl groups (CM-HP starch).

The only purpose of a starch ether in a mortar is to change the consistency in such a way that wall plasters do not sag, and ceramic tiles do not slip if applied on vertical walls. Starch ethers distinctly increase the mortar viscosity at low shear rates and are responsible for generating yield stress in the fresh mortar. They act as flocculants, binding fine particles through particle bridging, resulting in the desired rheological effect. When nearly all starch ethers are nonionic HP-starches,

how can they adsorb on mineral phases like cement clinker? As we know, adsorption on cement clinker needs anionic charged functional groups on the polymer chain. All superplasticizers are anionic for this reason.

2 Structure and working mechanism

Starch can be considered as a condensation polymer of glucose, consisting of anhydroglucose units. Main component of starch is amylopectin, one of the largest molecules in nature with an average degree of polymerization of about 2 million (corresponding with an average molar mass of about 400 million). It has a highly-branched structure, consisting of short linear chains with a DP ranging from 10 to 60 glucose units. In solution, it spreads out into a treetop-like structure. A starch ether molecule, dissolved in cement pore solution, has a typical diameter of about 0.3 microns. Unfortunately, there are very few published data on the hydrodynamic radius of starch ethers, and those published were determined in water and at neutral pH [1].

In general, starch ethers are referred to as nonionic polymers. The product data sheets promise “universally applicable and suitable for use in both neutral and alkaline mortars”. However, practice has shown that this is just half the truth. It is not wrong, but it does not take into account that, at high pH, some of the hydroxy groups get deprotonated. Therefore, starch ethers are anionic polymers at pH values of 11 and higher [2]. Commercially available HP-starches have a DS of 0.4 to 0.6. The DS is defined as the number of substitutions made per monomer unit. Starch has three hydroxyl groups per monomer. In an etherification reaction with propylenoxide all three may be hydroxypropylated, and the maximum DS would be 3. In starch the hydroxyl group at C-2 is more acidic than the others due to the neighboring acetal group. So, a DS of about 0.5 means that only half of the most acidic hydroxyl group is protected by hydroxypropylation.

In cement pore solution, every starch ether is anionic because of the mentioned deprotonation. The same is true for hydrated lime containing gypsum systems. But at neutral pH, e.g. in pure gypsum mortars, HP-starch does not work efficiently. In this case the starch ether has to be anionic by nature like CM-HP-starches. HP-starch based on potato starch is suitable in neutral systems, but not very efficient, because its molecules contain only few negatively charged phosphate ester groups. Products based on other botanical starch sources do not show efficient flocculation effects at neutral pH.

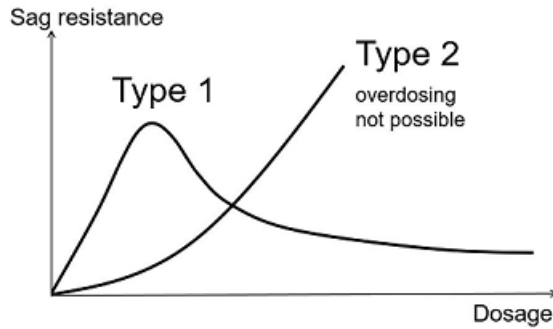


Fig. 1: Dosage dependency of flocculation efficiency of the two different starch ether types. Type 1 starch ethers may be overdosed. The maximum effect is often found at dosages between 0.08 and 0.3% based on cement content.

Two different starch ether types exist among the commercially available products. This has been discovered in 2003 and published in 2005 [3,4]. They differ in the dependence of the thickening effect on dosage (Fig. 1). The so-called type 1 starch ethers show a maximum in their flocculation efficiency, while the efficiency of type 2 products increases steadily with dosage. The peak in the graph of type 1 starch ethers marks the dosage at which deflocculation and stabilization starts to turn up. In the authors experience, the peak is found at dosages between 0.08 and 0.3%, depending on formulation, water/binder factor, and the individual starch ether. Some starch ethers are so good dispersing agents, that they work as a plasticizer when they are heavily overdosed. Type 2 starch ethers show no dispersing ability. This may be due to their much higher molecular weight. (The author has not the possibility to determine molecular weight distributions, so this is just an educated guess based on viscosities measured in aqueous solution.) They act not only as flocculants, but also by water absorption. In Fig. 2 three starch ethers are tested a) in cement paste, and b) in a tile adhesive formulation where the starch competes with the cellulose ether for the water. Solvitose H 2060 belongs to type 2, Solvitose FC 50 is somewhere in-between type 1 and 2, and Casucol 301 is a typical type 1 starch ether. In cement paste Casucol 301 the yield stress peaks at 0.08%, while the other two starch ethers have nearly no effect at this dosage. Solvitose FC 50 starts working at 0.1%, and Solvitose H 2060 has to be dosed with at least 0.3%. In the tile adhesive, where a cellulose ether occupies much of the water, the ranking at a dosage of 0.08% is completely different – Solvitose FC 50 works best, followed by Solvitose H 2060, and Casucol 301 gives the lowest yield stress.

Component	Cement paste	Tile adhesive
Portland cement CEM I 42.5 R	100 g	40 g
Quartz sand 0.1-0.4 mm	-	59.6 g
Walocel MKX 6000 PF 01	-	0.40 g
Starch ether	0.02 to 0.32	0.02 to 0.12
Water	50 g	25 g

Tab. 1: Formulations used for comparing three starch ethers in two different systems

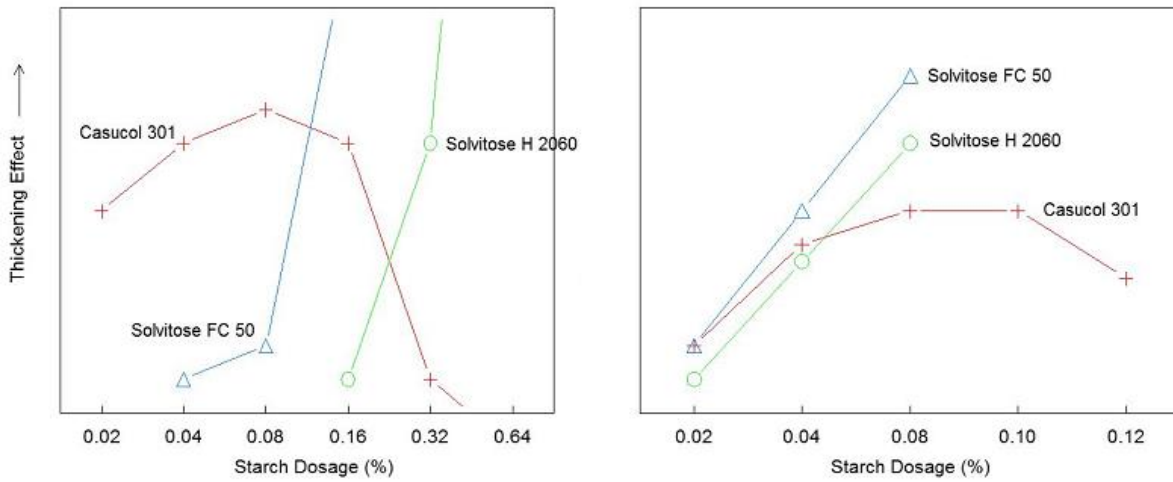


Fig.2: Yield stress vs. dosage in cement paste (left) and tile adhesive formulation

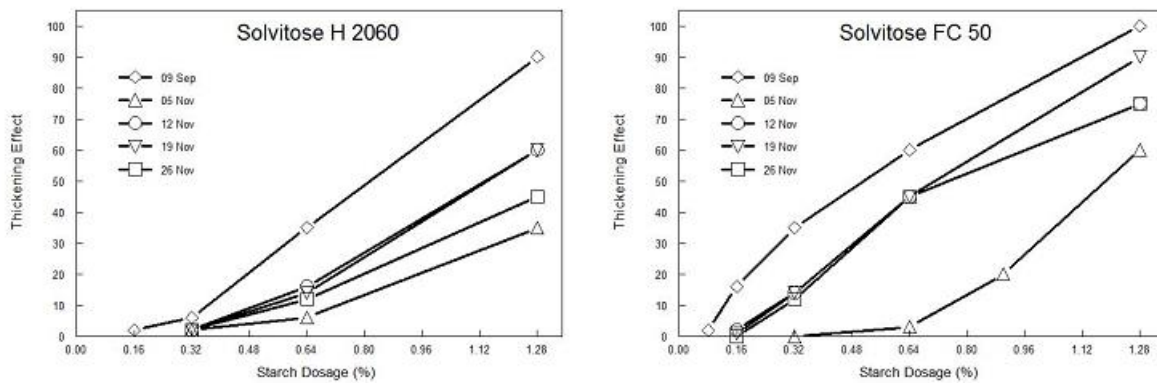


Fig. 3: Yield stresses of cement pastes with five different cement deliveries. Yield stress at dosage of 1.28% has been set to 100%.

Fig. 3 shows the sensitivity of type 2 starch ethers to changes in cement composition. That means, there are interactions with the cement particles. These findings show, that type 2 starch ethers (like Solvitose H 2060) have only little capability for flocculation and work mainly by water binding mechanism, whereas type 1 starch ethers (Casucol 301) are very efficient flocculants and do not bind a lot of water.

There is one main side-effect of starch ethers: Most of them retard cement hydration quite intensively. They do not only have an effect on the rheological properties, they also influence setting and strength development, just as superplasticizers do, too. It seems logical that the retarding effect is linked to the working mechanism as flocculant. Type 1 starch ethers retard the cement hydration very strongly, while type 2 starch ethers retard less than hydroxyethyl methyl celluloses do.

3 Interactions with other components

Because of the set retarding effect, often starch ethers are combined with accelerators. The most common cement accelerators are calcium salts, e.g. calcium formate. The author studied the calcium sensitivity of 20 different starch ethers by adding 1% of calcium formate to Portland cement and different dosages of starch ether [3,4]. All tested starch ethers were limited effective if additional calcium ions were present in solution. The impact differed for the individual products between 20 and 90% loss in thickening effect. It was not known then that starch at high pH is an anionic polymer and therefore, the reason for this behavior was not understood. Today, we can interpret the differences in calcium sensitivity as an indicator for structural differences resulting in different anionic charge density. Sowoidnich et al. [5] studied the calcium complexation of superplasticizers and could show that they complex calcium ions in solution as well as calcium on particle surfaces. It is very likely, that starch ethers complex calcium as well. In food chemistry, it is well-known that amylose and amylopectin react with calcium ions in alkaline conditions. Lobato-Calleros et al. studied what happens when starch is gelatinized while calcium hydroxide is present. They found strong changes in various properties at $\text{Ca}(\text{OH})_2$ concentrations of about 0.2%, indicating inter- and intra-molecular crosslinking via calcium ions [6]. And Vargas et al. found that up to 1.5% of calcium can be chemically bound by pregelatinized corn starch at a pH of 12.4 [7].

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