

# Performance of Starch Ethers in Drymix Mortars

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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. The interactions of starch ethers with calcium ions are discussed and recommendations are given for the targeted selection of the appropriate product.

**Keywords:** mortar additive, starch ether, hydroxypropyl starch, working mechanism

## I. 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 (HPS).

## II. WHAT ARE STARCH ETHERS USED FOR?

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.

## III. 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 (Fig. 1). 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. That is not wrong, but it does not take into account that – at high pH – some of the hydroxy groups get deprotonated and the starch ether is effectively an anionic polymer.

The starch ether molecules have to simultaneously adsorb on two particles, bridging them together. For doing this in an efficient way, the molecule needs to be anionic in charge. Superplasticizers are anionic for the same reason. High-performance adsorption on particle surfaces in a wide range of mortar types seems to require anionic polymers. 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, HPS does not work efficiently. In this case the starch ether has to be anionic by nature. Therefore, especially suitable starch ethers for neutral pH gypsum mortars are carboxymethyl hydroxypropyl starches (CM-HPS). Carboxymethylation is boosting the thickening effect of the starch ether not only in neutral systems, but also at high pH. HPS based on potato starch is suitable in neutral systems, but not very efficient. Products based on other botanical starch sources do not show flocculation effects at neutral pH. The reason for the different behavior of potato starch is, that its molecules contain a few negatively charged phosphate ester groups.

Two different starch ether types exist among the commercially available products. This was discovered in 2003 and published in 2005 [2]. They differ in the dependence of the thickening effect on dosage (Fig. 2).

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 (Fig. 3). In the authors experience, the peak is found at dosages between 0.08 and 0.3%, depending on formulation, water/binder factor, and last, but not least, the individual starch ether. The dosage of saturated adsorption is reached when the thickening effect approaches its minimum. Type 2 starch ethers work by a slightly different mechanism and they show no dispersing ability. This may be due to their much higher molecular weight. The author is not able to determine molecular weight distributions, so this is just an educated guess.

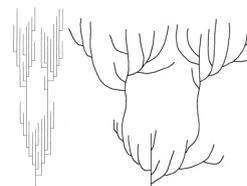


Fig. 1. Model of amylopectin molecule (left), and its extended structure in solution

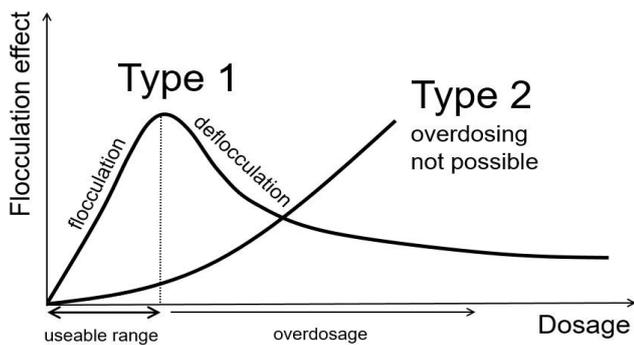


Fig. 2. Simplified diagram of flocculation effect vs. dosage for the two types

The two types are just the extremes, there are products which show a behavior somewhere in-between. However, most commercially available starch ethers belong to type 1.

There is one main side-effect of starch ethers: Most of them retard cement hydration quite intensive. They do not only have an effect on the rheological properties, they also influence setting and strength development, just as superplasticizers do, too. Table 1 lists data on some well-known commercially available starch ethers.

#### IV. INTERACTIONS WITH OTHER COMPONENTS

In Europe, there are three big starch ether producers, namely (in alphabetic order): Agrana, Avebe, and the Emsland Group. In product data sheets, they usually state no product details that would clarify how they differ among themselves, often not even the ether type is disclosed (e.g. HP, CM-HP), much less details on possible interactions with other formulation ingredients. Any individual user is left alone and the product information reads like *universally applicable* and *suitable for use in both neutral and alkaline mortars*. However, practice has shown that this is just half the truth.

In the authors experience, the individual effects of the different starch ethers depend on the: a) composition of the cement, b) composition of the aqueous phase, especially the calcium concentration, and c) structure of the starch ether, especially the distribution of substituents within the glucose unit, and along the polymer chain.

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, calcium chloride, or calcium nitrite.

Table I. Comparison of application properties and side-effects for type 1 and type 2 starch ethers; lists some well-known products in alphabetic order

Type 1	Type 2
Over-dosage leads to rapidly decreasing sag resistance	Over-dosing not possible, very high level of sag resistance may be realized
Retards cement hydration strongly	Only little retardation effect on cement hydration
Stickiness of mortars decreases	Stickiness and wet-adhesion of mortars drops strongly
Amitrolit 8850, Amylotex 8100, Amylotex ST 2000 and ST 2100, Casucol 301, Opagel CMT, Opagel FP 6, Tylovise SE 7	Solvitose FC 50, Solvitose H 2060, Eloset 542, Casucol Fix-1 * * in-between type 1 & 2

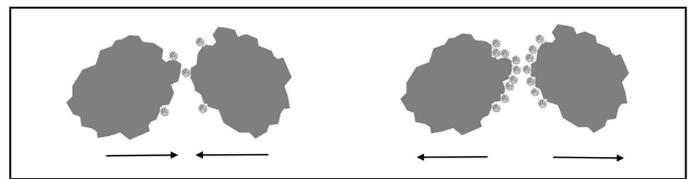


Fig. 3. As long as only few starch ether molecules are present, the desired flocculation takes place (left), as soon as a certain critical dosage is exceeded, deflocculation is achieved (right).

In German mortar formulations, calcium formate is preferred and 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 [2]. 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.

#### V. COMPLEMENTARY AND ALTERNATIVE ADDITIVES

There are two possible alternatives to starch ethers – clay minerals and polyacrylamides.

Clay minerals are broadly used as thickeners and thixotropic agents: Bentonite, attapulgite, and sepiolite. They do not interfere with cement hydration and increase the thixotropic behavior of cement-based mortars significantly. In the authors experience, these clay minerals should be seen as complementary to, and not as replacements for starch ethers. See

Polyacrylamides (PAA) are synthetic polymers, actually they are copolymers of acrylamide with other monomers, and they are used as flocculants in various applications. The anionic PAA are suitable flocculants for dry-mix mortars, but their effect is very sensitive to shear history because they are susceptible to mechanical degradation. For further reading start at [3].

#### VI. FUTURE DEVELOPMENTS

In short, there is room for improvement. The first starch ethers were optimized for alkaline mortars and got marketed in the 1970s. Since then, moderate progress has been achieved. Compared to superplasticizers, which have improved from lignosulphonates (1930) via naphthalene formaldehyde sulfonate and melamine formaldehyde sulfonate (1960) and the first generation of PCE (2000) to current state with the third generation of PCE, starch ethers did not undergo fundamental improvements.

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