Interactions between PCE and different polysaccharides and influences on the early hydration of cement

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Abstract

In order to observe the influence of stabilising agents (STA) based on starch and diutan gum, rheometric experiments and setting tests were conducted on cement pastes with and without PCE superplasticizers. The results show that with regard to yield stress both STAs show differing behaviours in systems without PCE. In presence of PCE, yield stress influences of the STAs retreat into the background. The Vicat results exhibit that STAs can reduce the retarding effect of PCE.

Introduction

Concrete systems with sophisticated rheological properties often incorporate superplasticizers based on polycarboxylates (PCE) and in combination with polymeric stabilising agents (STA) in order to avoid bleeding and segregation. Typically polysaccharides like celluloses, starches or sphingans are used. These can have a wide range of geometries with different effects on the rheology. Khayat distinguished between three modes of operation for cellulose and sphingan based STAs in dispersed systems: adsorption, association, and intertwining /1/. However, for starches the mode of stabilising can also be different. Starches consist of two types of macromolecules, the relatively small amylose (≈4.9×10^5 u) and the huge multi-branched amylopectin (≈3.2×10^7 u) /2/. The amylopectin molecules, which can have radii of gyration up to 0.5 µm, constitute approximately 80% of the starch’s mass, and therefore play an important role in the way, how starch affects dispersed particle systems. According to Simonides et al. /3/, the huge amylopectin molecules spread out between the particles, keeping them in distance. Hence, the stabilising mechanism of starch may be based on a buffering effect between the particles rather than on influences on the solution.
STAs like diutan directly adsorb on particles due to their anionic charges. Also other STAs are reported to adsorb in cementitious systems /4, 5/. Therefore STAs may behave differently in presence

and without PCE. This paper explains possible stabilising mechanisms of starch and diutan gum based STAs in cementitious systems.

Experimental Results and Discussion

Fig. 1 shows results of rheological measurement with a cylinder cell under assumption of Bingham behaviour. Starch and diutan gum were mixed in different dosages with water only and in water-cement-systems with a cement volume of 33%. At an addition of 20 g/l of starch and 1.0 g/l of diutan gum on water, the plastic viscosities of the water-STA mixtures were identically 8.02 mPa·s and 8.04 mPa·s, respectively. This is significantly higher plastic viscosity than the viscosity of water without STA (η_{Water}=1.002 at 20 °C). At the same time starch does not show a significant effect on the yield stress, while diutan gum generates a significant yield stress. At the same water to starch dosages, both systems show effects on yield stress and plastic viscosity, indicating that indeed as proposed in /3/ the stabilising mechanism of starch requires the presence of particles to become effective in terms of yield stress effects.

Fig. 2 shows the influence of different STA dosages. Yield stresses and plastic viscosities at dosages of 20 g/l for starch and 1.0 g/l of diutan gum were set as reference value (100%) for the water system, due to identical plastic viscosities (Fig. 1). For the cementitious system, dosages of 12.4 g/l and 2.0 g/l were found to yield identical plastic viscosities for starch and diutan gum, respectively. The respective rheological parameters were thus set as reference (100%).

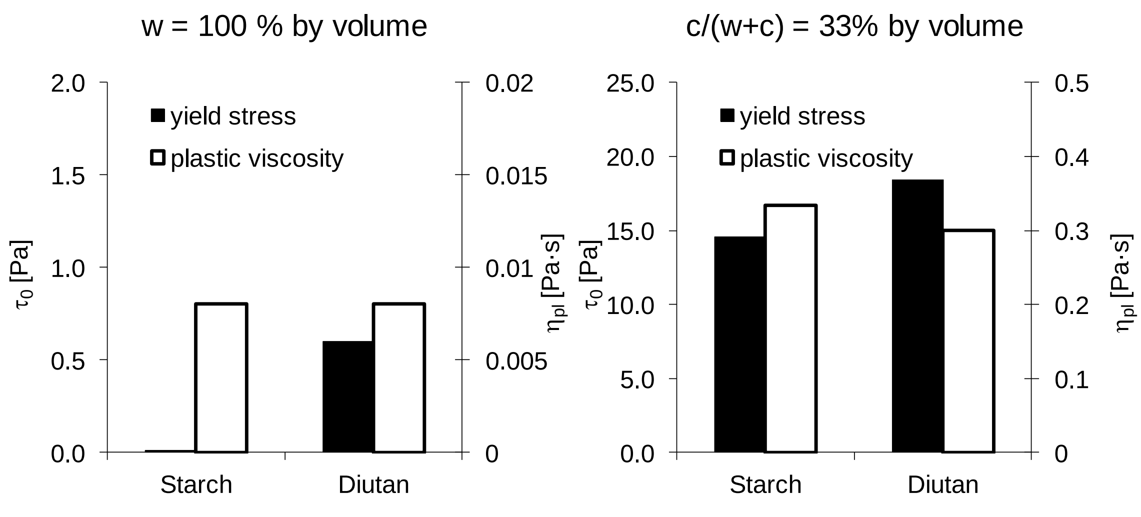

Fig. 1: Influence of starch and diutan gum on rheological parameters in water and water-cement systems.

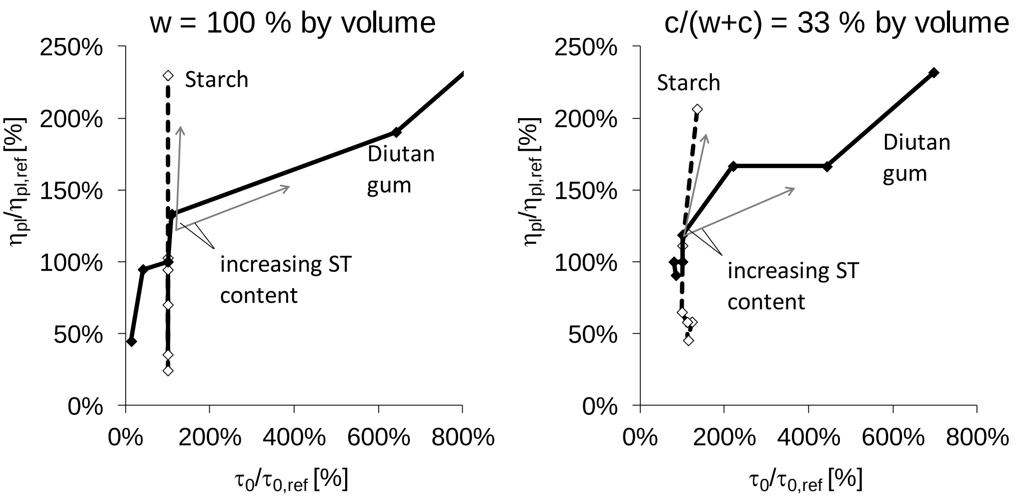

Fig. 2: The influence of the dosages of starch and diutan gum on τ_0 and η_{pl} when incorporated into water and into a water-cement suspension.

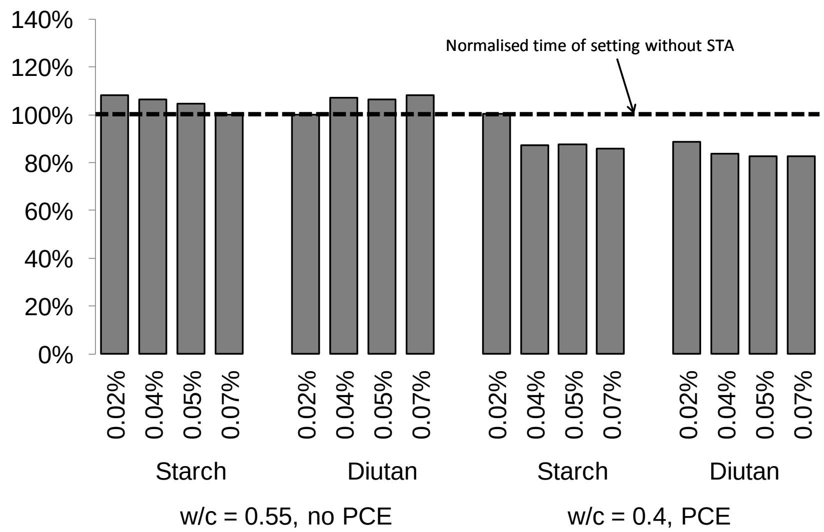

Fig. 3: Influence of the dosage of starch and Diutan gum on the setting without and in presence of PCE.

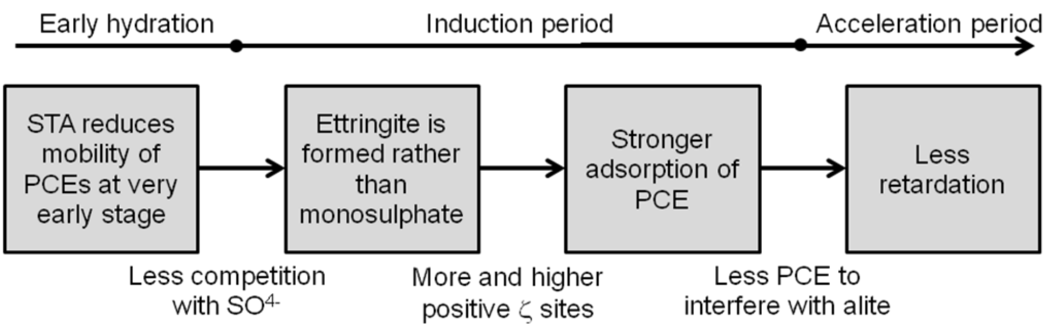

Fig. 4: Assumed mechanism of interaction of STA with PCE.

The figures confirm that also at high dosages starch affects the viscosity much stronger than the yield stress, while diutan gum affects both parameters.
However, it was also found that the influence of starch on yield stress increases with increasing solid content. Above a threshold solid fraction the yield stress is prominently affected by the presence of starch. Upon addition of already small amounts of PCE the influence of both STAs on yield stress diminishes /6/.
A strong interaction between STAs and PCE could also be observed with regard to the setting (Fig. 3). Without PCE, starch and diutan gum both caused a slight retardation without systematic effect of the dosage. In presence of PCE, both STAs showed earlier setting than systems with PCE only. Also in presence of PCE no systematic effect of the STA dosage could be found. This retarding effect might be attributed to the increase of the intrinsic viscosity or entanglement of polymers in the solution, which reduce the mobility of PCEs at early stage with the effects on the early hydration as proposed in Fig. 4.

Conclusions and Outlook

Starch and diutan gum have different dominating mechanisms of stabilising. While starch needs particles to effectively increase the yield stress, diutan gum directly affects yield stress if added to water. In presence of PCE, effects of STA on yield stress diminish.
Despite its retarding effect on cementitious systems, STA reduced the retarding effect of PCE, which can be justified by interactions between PCEs and STAs that modify the early cement hydration. The latter effect, however, needs further research.

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