EFFECTIVENESS OF STARCH ETHERS AS RHEOLOGY MODIFYING ADMIXTURE FOR CEMENT BASED SYSTEMS

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Abstract

Polysaccharides are important rheology modifying admixtures in the building material sector. The use of starch is becoming increasingly important, due to many ecological and economic advantages. In the construction sector, starch ethers are being used as thickeners and as means to increase the yield stress. The starch ethers that are available on the market differ in their behaviour, which can vary greatly depending upon the binder system and mortar composition, e.g. solid volume content, binder type, additional admixtures. In view of the limited knowledge about the influence of molecular modifications associated with cement based systems, some fundamental rheological functional mechanisms were analysed in this study. The differently modified starch ethers used were derived from potatoes. They varied in their charges and degrees of hydroxypropylation. The setting and the flow behaviour of all examined variations of starch ethers were analysed in cement pastes. In order to illustrate the effects of the starch ethers that were used, the water-cement ratio (w/c) was held constant in all the mixtures [Schmidt 2012]. The results indicated significant differences in setting and flow behaviour.

Keywords:
Starch ether; Polysaccharides; Rheology; Cement based systems.

1 INTRODUCTION

Water-soluble polymers based on renewable raw materials, such as cellulose or starch based polysaccharides, are becoming increasingly important, due to their environmental friendliness. Native and modified starches are used for a wide range of applications in many industries, such as the paper, construction, and textile industries [Tegge 2004]. The starch is used, among others, as a "natural" binder or filler. It is used because of its' beneficial effects on the consistency of mixtures. Starch can be easily obtained from native plants, e.g. potatoes, wheat, rice, or maize. For most commercial applications, starch is chemically or physically modified to enhance the properties according to desired specifications. Starch ethers are chemical derivatives of native starch and they can be used in the construction sector as agent to modify the rheology of concrete, in particular, to control the flow behaviour and the viscosity [Khayat 1998].

2 MATERIALS AND SPECIMENS PREPARATION

Comparison with various other polysaccharides, which are composed of different monosaccharides (heteropolyssaccharides), starch contains only D-glucose units and is thus a homoglycan [Tegge 2004]. Starch consists mainly of two different D-glucose polymers, the amylose (10% to 30%) and the amylopectin (70% to 90%) [Brown 2005]. The starch products used in this study were obtained from potatoes. All starches were made soluble in cold water and hydroxypropylated (HP). Apart from these common properties, the starch ethers used varied in their specifications as shown in Tab. 1. The aim of the variations was to analyse the effects of the different types of starch derivates on the fresh concrete properties [Simonides 2007, Schmidt 2013].

Tab. 6: Overview of the starch products.

Name	Properties
Ref	Control mix without starch
St 1	HP + neutralising agent A
St 2	HP + neutralising agent B
St 3	HP + neutralising agent C + cross-linked structure
St 4	HP + mixed ether + anionic carboxymethylated
St 5	HP + mixed ether + cationic

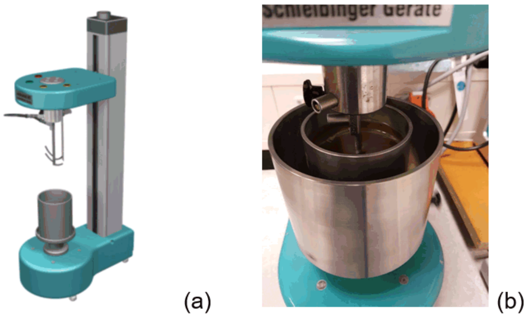
For the preparation of the samples ordinary Portland cement was used (CEM I 42.5 R). This cement shows a strength class 42.5 R and is produced by grinding Portland cement clinker and gypsum.

3 EXPERIMENTAL PROGRAMME

The rheological tests were carried out on cement paste samples at a solid volume fraction of 0.39 (water cement ratio = 0.5). In order to exclude influences of the water, deionized water at a temperature of 20 ± 2 °C was used. For the purpose of obtaining reproducible results, the mixing and testing procedure was the same for all samples. For the preparation of cement paste a mortar mixer was used (Fig. 6). Firstly, cement and water were mixed for 60 sec at 140 ± 5 rpm. Then the cement paste was removed from the bowl wall, so the resting time was 30 sec. Further the cement paste was mixed additionally 60 sec at 285 ± 10 rpm.

Fig. 6: Testing mortar mixer.

The measurements were conducted using a mortar rheometer (Viskomat NT, Fig. *8* (a)) with a wing stirrer system for cementitious pastes. The wing stirrer called cement paste probe V0013 [Schleibinger 2017] is made of stainless steel (Fig. 7). This device is used for cement paste and mortar with a maximum particle size of 0.5 mm. It used for relative measurements of Bingham fluids [Schleibinger 2017]. The stirrer ensures a good homogenization of the mixture under high shear.



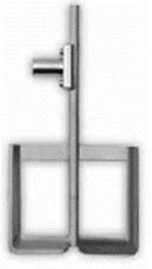
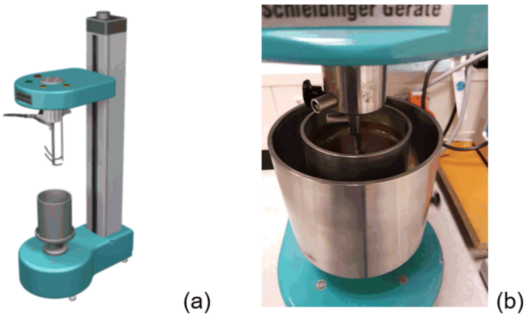


Fig. 7: Wing stirrer called cement paste probe V0013.

This machine includes two vessels of different sizes. A small one for cement specimens (specimen vessel) and a big one to control the specimen temperature (outer vessel). In this case, only the small vessel was used. This vessel was filled with 375 ml of cement paste. Then the specimen vessel was put into the outer vessel. The measurements started when the wing stirrer (Fig. *8* (b)) was immersed slowly in the cement paste.



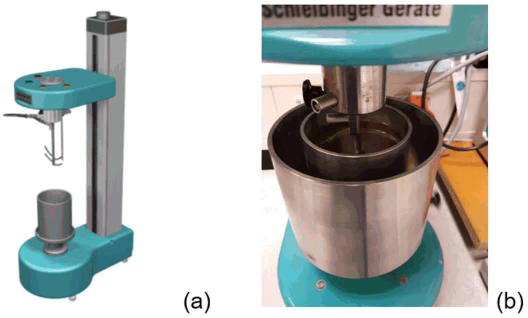


Fig. 8: (a): Scheiblinger Viskomat NT. (b): Wing stirrer in the cement paste.

3.1 Measuring profile

The applied profile is shown in Fig. 9. The observation of the influence of different admixtures was made at a constant rotational speed of 240 rpm. The stirring time for each admixture dosage was 4 minutes, of which only the last 10 values were chosen for the evaluation (Fig. 10). This guaranteed a good distribution and homogenization of the admixtures before the measurement data were taken [Schmidt 2017].

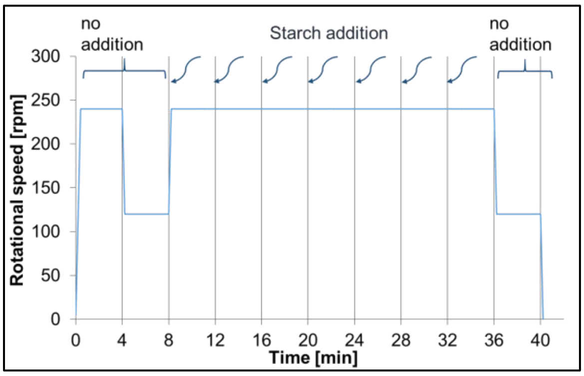


Fig. 9: Speed profil.

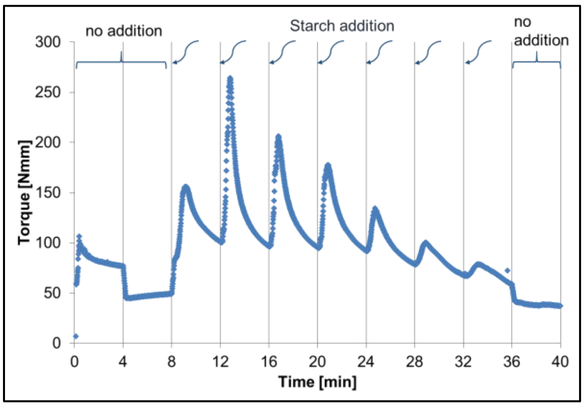


Fig. 10: Shear moment profile with addition of starch.

In addition, for the initial measurement without admixtures as well as for the highest dosage of added admixtures (0.07% by mass of cement) the rotational speed was changed between 240 rpm and 120 rpm, respectively, with 4 minutes for each step. This choice allows to obtain stress values at two different shear velocities. Under the simplified assumption of Bingham-behaviour for the fluids, the data allow to derive qualitative flow curves, which can indicate yield stress and plastic viscosity variations by changes in the ordinate intercept and the slope, respectively [Schmidt 2017].

The applied profile does not qualify for detailed rheological analyses, since the shear rates are extremely high, the assumption of Bingham-behaviour does not hold true for the observed systems, and time effects of hydrating cement are ignored. Still, it is a good and rapid method to distinguish between the effects of various admixtures and dosages. A reference mixture of pure cement paste observed over 40 minutes pointed out that no significant change in the torque can be observed over the course of the measurement time (Fig. 11).

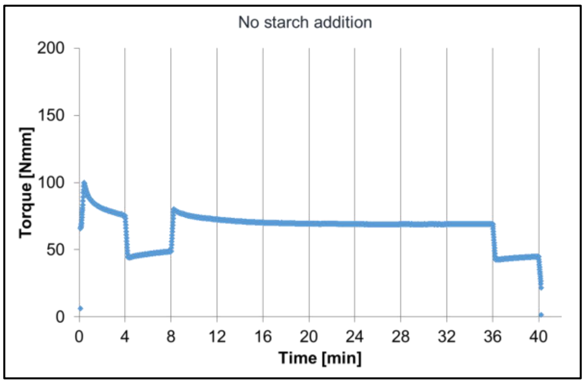


Fig. 11: Shear moment profile without admixtures.

3.2 Flow curves

The flow behaviour of cementitious suspensions is often simplified described as Bingham-like [Bingham 1922]. In this model shear rate and shear stress are directly proportional to each other [Bingham 1924, 1929]. Such behaviour cannot always adequately describe the flow of cementitious pastes, which often exhibits shear rate dependent changes of the viscosity depending upon the solid volume fraction and the admixtures added. Nevertheless, the Bingham approximation allows the easiest and quickest assessment of performance changes since the relevant observed parameters yield stress and plastic viscosity are constant over all shear rates. The flow curve of for the Bingham model can be be described by these two parameters as follows:

$$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad (1)$$

where: τ = shear stress [Pa]; τ_0 = yield stress [Pa]; η_{pl} = plastic viscosity [Pa·s]; γ;˙ = shear rate [1/s].

With the employed equipment, only torque and rotational velocity can be determined. Due to the unknown shear field, the measured torque values cannot be converted to shear stresses and the rotational speeds cannot be used to derive shear rate values. In order to still assess qualitatively the influence of the starches on the relative flow behavior of the samples, the Bingham model was applied in this study without conversion of rotational velocity to shear rate and torque to shear stress, respectively. To determine the flow curve, the last two values from each sample were used for the evaluation. The generated shear moments after 32 minutes at 240 rpm and after 36 minutes at 120 rpm were linearly connected. Hence, the results are expressed as torque versus rotational velocity, which only allow qualitative assessments of viscosity and yield stress changes by changes of the slope and the ordinate intercept, respectively.

4 RESULTS

The ordinate intersection point of the reference sample without the addition of starch is at 20 Nmm (Fig. 12).The flow curves with starch were derived at starch dosages of 0.07 % by mass per weight cement. The starches St 3 and St 1 have a low influence on the yield stress but have a stronger effect on the plastic viscosity. The starches St 4 and St 2 have a viscosity-reducing effect. The behaviour of the carboxymethylated starch (St 4) was prominent. It caused a lowering of the yield stress (Fig. 12) confirmed by the parallel displacement of the flow curve.

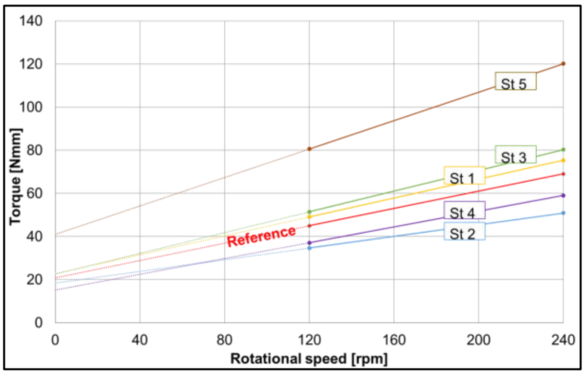


Fig. 12: Influences of different starches of the flow properties.

The reason might be found in the anionic charges that provide better adsorption properties on particle surfaces creating a superplasticizing effect. The St 2 with neutralizing agent B shows little influence with regard to the yield stress but it reduces the viscosity. The cationic starch showed an overproportional increase in yield stress and viscosity.

Comparing the shear moments (as absolute values) after the addition of 0.07% starch by mass of cement with the reference sample (Fig. 13) the shear moment in the presence of the carboxymethylated starch (St 4) is 15% lower than the reference. A reduction of the shear moment equal to 26% was achieved with the neutralising agent B (St 2).

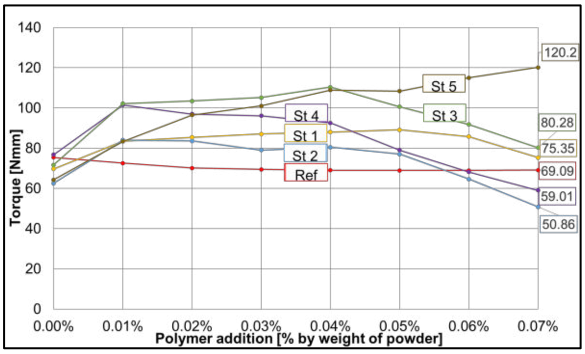


Fig. 13: Influences of different starches after 0.07% by mass (per weight cement) of the shear moment.

The use of starch St 1 with neutralising agent A shows a very limited influence on flow properties. The shear moment was increased by 16% compared to the reference after 0.07% by mass starch addition from starch St 3. The starch St 5 significantly increased the total shear moment (74%) compared to the reference. This difference is 65% more than St 1 and 58% more than St 3.

The results (Fig. 13) show that the shear moment increase when the addition of starch is within 0.03% by mass. Over this limit of 0.03% by mass of cement, a decrease of the shear moment was noticed. Only in the case of cationic mixed ether (St 5) an increase of shear moment after the aforementioned limit was observed.

5 DISCUSSION OF RESULTS

The results show that the addition of starch has a significant influence on the shear moment of the cement paste. A summary of the results is given in Tab. 7. Depending on the starch modification, the starch affects the cement paste system differently. Although only the neutralising agents differed in starches St 1 and St 2, they had the exact opposite effect. Neutralisation agent A leads to a slight yield stress and viscosity increase, while neutralisation agent B achieves a much higher reduction in yield stress and viscosity. Starches 1 and 3 have similar effect on the yield stress ($\tau_0 = 22.5$ Nmm), although they have different neutralising agents and different structures. Starch St 3 has a 7% steeper slope of the torque vs. rotational speed curve indicating viscosity higher than starch St 1. Based on the current findings, the reason for this difference may be found in its cross-linked structure. To examine the effect of the cross-linked structure on the viscosity it is necessary to test if a cross-linked structure for starch St 1 could increase the torque at the same level as in St 3.

Starch St 4 and St 5 produced very strong variations. Both are mixed ethers. Starch St 4 decreased the intercept torque value by 29% and caused a slope reduction of 15%. This “liquefying” behaviour of starch 4 is presumably due to the presence of carboxy methylation.

The addition of cationic mixed ether starch caused an increase of yield stress and viscosity to the cement paste. The yield stress of the tested cement paste was 95% higher than the values found in the reference. According to the results of this study it is required to study the influence of this modification further. The aim of this additional study would be to examine the effect of these two modifications and, thus, understand their function on the rheological behaviour.

Tab. 7: Influences of different starches.

Name	Properties	Yield stress [Nmm]	Comparison yield stress with the reference as absolut yield values [%]	Yield stress ⇧ Yield stress ⇩	Torque after starch addition of 0.07% by mass [Nmm]	Comparison torque with the reference as absolut yield values [%]	Viscosity ⇧ Viscosity ⇩
Ref	Control mix without starch	21.0	100%		69.1	100%	
St 1	HP + neutralising agent A	22.5	107%	⇧	75.4	109%	⇧
St 2	HP + neutralising agent B	18.5	88%	⇩	50.9	74%	⇩

St 3	HP + neutralising agent C + cross-linked structure	22.5	107%	⬆	80.3	116%	⬆
St 4	HP + mixed ether + anionic carboxymethylated	15.0	71%	⬇	59.0	85%	⬇
St 5	HP + mixed ether + cationic	41.0	195%	⬆	120.2	174%	⬆

A similar behaviour is described by author [Glatthor 2005] where twenty three commercial starch ethers were categorised in two and a half types. The starch ethers of type 1 increase the viscosity to an amount of 0.01% by mass untill a maximum after which the system redispersed (degraded). The starch ethers of type 2 required greater amounts of material to react and showed a constantly increasing viscosity. Type 1½ exhibits a saturation level. The starch ethers which were used in [Glatthor 2005] were sometimes additionally carboxymethylated and varied in their molecular weight.

6 CONCLUSION

The present study focused on differently modified starch samples to compare their effects on the cement paste with the aim of analysing the relation between the modifications and the setting and flow behaviour. Results show that even a low quantity of 0.01% by mass of starch ethers increases the shear moment from approx. 15% (St 1, St 2 and St 5) to 40% (St 3 and St 4). The addition of more starch ether in the cement paste showed a decrease of the shear moment. Only the cationic mixed ether (St 5) exhibited steadily increasing shear moments.

Furthermore, in the current study it could be shown that the carboxymethylated starch (St 4) has a viscosity-reducing effect. But it could also be presented that a cationic mixed ether has influences also in low quantities in contrast to the starch type 2 as they are described in [Glatthor 2005]. However, the model of two and a half types of starch ethers, like the one used in [Glatthor 2005], is too simplified especially because modified starches can show a much greater variety of performances in a cementitious system.

A supplementary study will be carried out with different starches and different modifications in order to clarify the interaction between the starch modification and flow behaviour.

7 ACKNOWLEDGMENTS

The authors would like to thank the PhD programme of Bundesanstalt für Materialforschung und –prüfung (BAM) for financial support.

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