

Novel zwitterionic PCE superplasticizers for calcined clays and their application in calcined clay blended cements

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ABSTRACT

Calcined (thermally activated) clays are the most promising source for supplementary cementitious materials (SCMs) which can contribute to lower the environmental impact of cement and concrete. To make such substitution applicable, the interaction of calcined clays with superplasticizers must be known.

In this study, three different pure calcined clays – a meta illite, a meta kaolin and a meta muscovite – were prepared via flash calcination and in a laboratory-scale muffle furnace at temperatures ranging from 550 - 800 °C. Their mineralogical composition was assessed by Q-XRD.

A series of zwitterionic (amphoteric) polycarboxylate (PCE) superplasticizers was successfully synthesized and characterized. The dispersibility of the abovementioned pure calcined clays with these novel superplasticizers (PCEs) was proven both in pastes and mortars prepared from 80:20 wt./wt. blends of OPC and the calcined clays. Furthermore, heat flow calorimetry and strength tests evidenced that the amphoteric superplasticizers do not retard cement hydration, as is observed for most of the common PCE products.

The results suggest that depending on the different composition and surface charges of the calcined clays, novel zwitterionic terpolymers are a powerful and auspicious alternative to standard anionic polycarboxylate superplasticizers to combine both fluidity and a partially improved early strength of cements blended with calcined clays.

1. INTRODUCTION

Improving the sustainability of cement and concrete is one of the most challenging topics in the current research on construction materials. A promising way here is to blend Portland cement clinker with substitution materials which are often referred to as supplementary cementitious materials (SCMs) (Hollanders et al. 2016; Fernandez et al. 2011). However, supplies of common SCMs which include slag, silica fume and fly ash are limited in consideration of the fact that the worldwide production of cement is increasing. Calcined clays are seen as the source with the highest potential as new SCM which can make a substantial contribution to lower the environmental impact, e. g. by low carbon dioxide emission during the calcination process of clays (Beuntner & Thienel 2015; Lothenbach et al. 2011; Sabir et al. 2001).

Nevertheless, to overcome the known disadvantage of calcined clays of a considerably higher water demand (Thienel & Beuntner 2018), the use of superplasticizers is indispensable. Thus, to make substitution of cement clinker feasible, the interaction of calcined clays with superplasticizers must be studied (Plank et al. 2015).

The dispersing effectiveness of standard anionic polycarboxylate superplasticizers as well as that of zwitterionic polymers (containing negative and positive charges) on a calcined mixed layer clay has already been confirmed (Schmid et al. 2018). However, the influence of superplasticizers on specific calcined clay minerals is still unknown.

In this study, zwitterionic (amphoteric) polycarboxylate ether (PCE) superplasticizers containing two different cationic monomers, long side chains and different molar ratios of anionic/cationic monomer were synthesized and characterized *via* gel permeation chromatography (GPC) and measurement of their anionic charge amount. Their dispersing ability in paste and mortar based on blends of OPC and calcined clay samples was investigated *via* mini slump and spread flow tests. Moreover, their influence on cement hydration was tracked *via* heat flow calorimetry and their impact on strength development was made accessible by mortar tests.

2. EXPERIMENTAL

2.1 Raw materials

As clay samples, three phyllosilicates were calcined (thermally activated) at different temperatures to achieve complete elimination of OH-groups from the sheet structure (dehydroxylation) of the phyllosilicates. The calcined clay samples were

- a meta illite, calcined in a laboratory-scale muffle furnace at 770 °C
- a meta kaolin (industrial product), flash calcined at 550 °C and
- a meta muscovite, calcined in a laboratory-scale muffle furnace at 800 °C.

Table 1 summarizes their mineralogical compositions and gives the average particle diameter.

For the blends with calcined clays, an ordinary Portland cement (OPC) type CEM I 42.5 R obtained from Schwenk Zement KG (Allmendingen, Germany) was used. Its phase composition is shown in **Table 2**. The substitution rate for the cement clinker was set at 20 wt. % at a water-to-binder (w/b) ratio of 0.5.

Table 1. Mineralogical compositions, as determined *via* Q-XRD using *Rietveld* refinement, and average particle size of the calcined clay samples

Mineral phase [wt. %]	Meta illite	Meta kaolin	Meta muscovite
Quartz	-	5.0	-
Anatase	-	0.6	-
Muscovite	-	1.4	80.8
Calcite	4.9	-	-
Illite	38.2	-	-
Portlandite	0.2	-	-
Carbonate (calcite)	0.2	-	-
X-ray amorphous content	56.4	93.0	19.2
Total	99.9	100.0	100.0
Average particle size (d_{50} value) [μm]	6.8	14.8	19.2

Table 2. Phase composition of the CEM I 42.5 R sample as determined by Q-XRD using *Rietveld* refinement and thermogravimetry

Phase	wt. %
C ₃ S	52.4
C ₂ S	19.9
C ₃ A, c	3.3
C ₃ A, o	3.2
C ₄ AF	11.8
CaO	0.7
MgO	0.7
Anhydrite	1.4
Hemihydrate*	1.9
Dihydrate*	1.3
Calcite	1.6
Quartz	0.4
Dolomite	1.4
Total	100.0

* determined by thermogravimetry

2.2 Experimental procedures

2.2.1 Synthesis of zwitterionic superplasticizers

The zwitterionic superplasticizers were synthesized *via* aqueous free radical copolymerization from the monomers methacrylic acid (MAA), MPEG-methacrylate macromonomer (ω -methoxy poly(ethylene glycol) methacrylate ester with a chain length (n_{EO}) of 113) and 3-trimethylammonium propyl methacrylamide chloride (MAPTAC) or diallyl dimethylammonium chloride (DADMAC). In synthesis, two solutions were prepared, one containing MAA, the MPEG-methacrylate, the cationic monomer MAPTAC or DADMAC and 3-mercaptopropionic acid as chain transfer agent (solution I). The second solution

contained the radical initiator ammonium peroxodisulfate (3.3 mol. % relative to the monomers, dissolved in 30 mL DI water, solution II). The reactor was equipped with a stirrer, a nitrogen inlet and a thermometer and charged with 30 mL of DI water. The vessel was then heated to 80 °C and both solutions were fed continuously into the reactor using two peristaltic pumps. Solution I was added within four hours and solution II within five hours. After complete addition, the mixture was stirred for one more hour, cooled to ambient temperature and neutralized with 30 wt. % sodium hydroxide (NaOH) solution yielding yellowish, viscous polymer solutions of ~ 35 wt. % solid content. For reference, a standard anionic PCE copolymer MAA-113MPEG (6:1) was synthesized following the same procedure. The chemical structures of all polymers are shown in **Figure 1**. All polymer samples were used as is without further purification at a dosage of 0.3 % by weight of binder (% bwob).

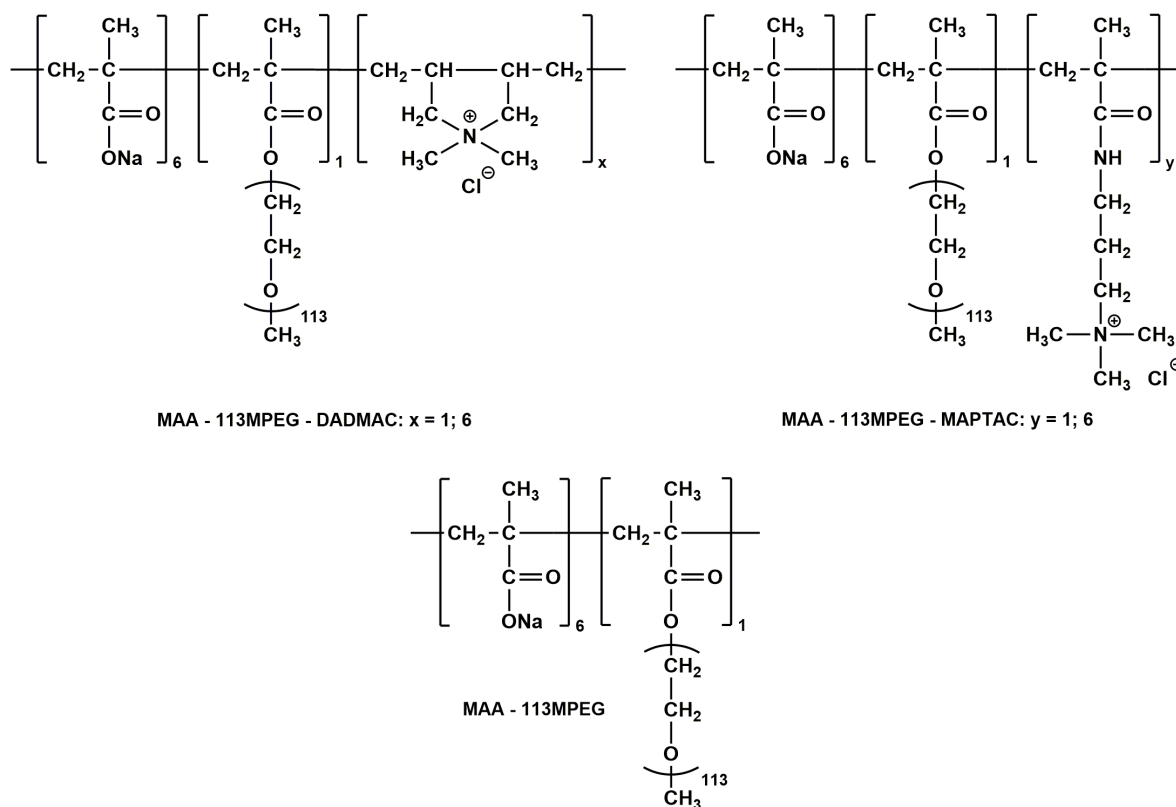


Figure 1. Chemical composition of the synthesized amphoteric and anionic PCE samples

2.2.2 Characterization of the synthesized superplasticizers

Molecular properties of the amphoteric terpolymers and the anionic PCE copolymer MAA-113MPEG (6:1) (M_w , M_n , PDI) were determined *via* gel permeation chromatography (GPC) using a Waters 2695 separation module (Waters, Eschborn, Germany) equipped with a differential refractive index detector (Waters, Eschborn, Germany) and a three angle static light scattering detector (“mini Dawn” from Wyatt Technology Corp., Santa Barbara, CA, USA). Separation of the polymer fractions was achieved by using three Ultrahydrogel™ (120, 250 and 500) columns and an Ultrahydrogel™ guard column (Waters, Eschborn, Germany). The eluent was composed of 0.1 M NaNO₃ and 0.1 g/L NaN₃ adjusted to pH = 12. The value of d_n/d_c applied to calculate the molar masses of the PCEs was 0.135 mL/g (value for polyethylene oxide) (Kawaguchi et al. 1998). The analytical results are shown in **Table 3**.

Table 3. Molecular properties and macromonomer conversion of the synthesized polymers

Polymer sample	M_w [g/mol]	M_n [g/mol]	PDI	Conversion [%]
MAA-113MPEG-DADMAC (6:1:6)	26,700	14,000	1.9	88.2
MAA-113MPEG-DADMAC (6:1:1)	40,400	19,000	2.1	93.9
MAA-113MPEG-MAPTAC (6:1:6)	21,100	11,800	1.8	87.7
MAA-113MPEG-MAPTAC (6:1:1)	33,400	15,400	2.2	92.7
MAA-113MPEG (6:1)	34,200	15,900	2.2	95.0

The charge amounts of all synthesized superplasticizers were determined in DI water and synthetic cement pore solution (SCPS) by polyelectrolyte titration using cationic polydiallyl dimethylammonium chloride (polyDADMAC) as a titrator. The tests were performed utilizing a PCD 03 pH particle charge detector (Mütek Analytic, Herrsching, Germany).

The composition of the SCPS used in this work was based on the characteristic ion concentrations found in the pore solutions of a common Portland cement (CEM I) (Kelzenberg et al. 1998; Rechenberg & Sprung 1983). It contained 0.4 g/L Ca^{2+} , 7.1 g/L K^+ , 2.25 g/L Na^+ and 8.29 g/L SO_4^{2-} . The pH value of the SCPS was 13.2. The values for the specific anionic charge amounts of the polymer samples are shown in **Table 4**.

Table 4. Specific anionic charge amounts of the polymer samples in DI water and SCPS.

Polymer sample	DI water [$\mu eq/g$]	SCPS [$\mu eq/g$]
MAA-113MPEG-DADMAC (6:1:6)	781	199
MAA-113MPEG-DADMAC (6:1:1)	1,110	421
MAA-113MPEG-MAPTAC (6:1:6)	190	140
MAA-113MPEG-MAPTAC (6:1:1)	833	685
MAA-113MPEG (6:1)	1,276	617

2.2.3 Dispersing performance in cement paste

In order to determine the fluidity of cement pastes admixed with the polymers, mini slump tests adapted from and modified after DIN EN 1015-3 were carried out. In this test, the mixing water and the polymer solution were placed in a porcelain cup. Next, 300 g of the calcined clay blended cement were added within one minute to the cup. After one minute soaking time, the cement paste was stirred manually for two minutes, then a *Vicat* cone (bottom diameter: 8.0 cm, top diameter: 7.0 cm, height: 4.0 cm) was filled with the paste to the brim and the spread diameter was recorded after removing the cone. The average value of two spread diameters in a 90° angle was reported as the test result.

2.2.4 Dispersing performance in mortar

The spread flow of mortars holding OPC blended with calcined phyllosilicates was determined according to DIN EN 1015-3. A *Hägermann* cone (bottom diameter: 10.0 cm, top diameter: 7.0 cm, height: 6.0 cm) was placed on a wet metal plate and the mortar was poured in two layers in the cone. Each layer was compacted ten times with a tamp. Subsequently, the cone was removed vertically and the flow table was lifted and dropped 15 times, causing the mortar to flow. The resulting spread flow was measured twice, the second measurement being perpendicular to the first and averaged to give the spread value. Additionally, to prevent air entrainment caused by the superplasticizers, 0.03 g of defoamer (Surfynol® MD-20, Air Products, Hattingen) was added.

2.2.5 Isothermal heat flow calorimetry

Hydration kinetics were investigated by isothermal heat flow calorimetry. All neat and blended (OPC:calcined clay 80:20 wt./wt.) cement pastes were prepared from 4.0 g of binder and 2.0 g of DI water ($w/b = 0.5$) in a glass ampule, shaken in a wobblers (VWR International, Darmstadt, Germany) for two minutes at 2400 rpm and placed into the calorimeter (TAM AIR, Thermometric, Järfälla, Sweden) at 20 °C.

2.2.6 Mortar tests

Selected synthesized zwitterionic polycarboxylate superplasticizers were measured according to DIN EN 196-1 for their efficiency as strength enhancer in a mortar. The spread flows of the blended mortars were determined according to DIN EN 1015-3. Three mortar prisms (dimensions: 40 x 40 x 160 mm) were prepared from each mixture and stored in a climate chamber at 20 ± 1 °C and 90 % relative humidity. Compressive and tensile strengths were measured according to DIN EN 196 on a test apparatus provided by Toni Technik (Berlin, Germany) after curing for 24 hours.

3. RESULTS AND DISCUSSION

3.1 Dispersing performance of zwitterionic superplasticizers in paste of calcined clay blended cement

Generally, the cement blended with meta illite always produced the lowest fluidity with all polymers (**Figure 2**). This result correlates only poorly with the water demand determined for the three calcined clays (Sposito et al. 2018). Normally, meta muscovite exhibits the highest water demand, implicating that in the presence of this clay the lowest slump flow should result. Opposite to this, meta muscovite achieved extremely high fluidity with all superplasticizers.

It should be noted here that the paste prepared from OPC and meta muscovite exhibits a very unusual rheological behavior, namely a shear-thickening rheology which is completely different to that from the other calcined clays. Most interestingly, such behavior was not observed in pure meta muscovite pastes admixed with superplasticizers and prepared with SCPS. Thus, the spread flow values shown for meta muscovite in **Figure 2** are random and not really comparable with those from the other meta clays.

Furthermore, the kind of cationic monomer has a huge impact on the performance of the amphoteric superplasticizers. DADMAC outperforms MAPTAC at both monomer ratios in all blended cement systems. Moreover, among the zwitterionic polymer samples, polymer MAA-113MPEG-DADMAC (6:1:1) performs best, implying that a low content of cationic monomer seems to be more advantageous in all systems. **Figure 3** also reveals that this best amphoteric polymer (MAA-113MPEG-DADMAC (6:1:1)) only slightly outperforms the conventional anionic PCE copolymer MAA-113MPEG (6:1) in cement blended with meta illite.

The neat OPC paste (no calcined clay present) was tested with the same dosage of 0.3 % bwob of all polymers and always showed strong bleeding and segregation, due to its significant lower water demand. For this reason it was not mentioned anymore here.

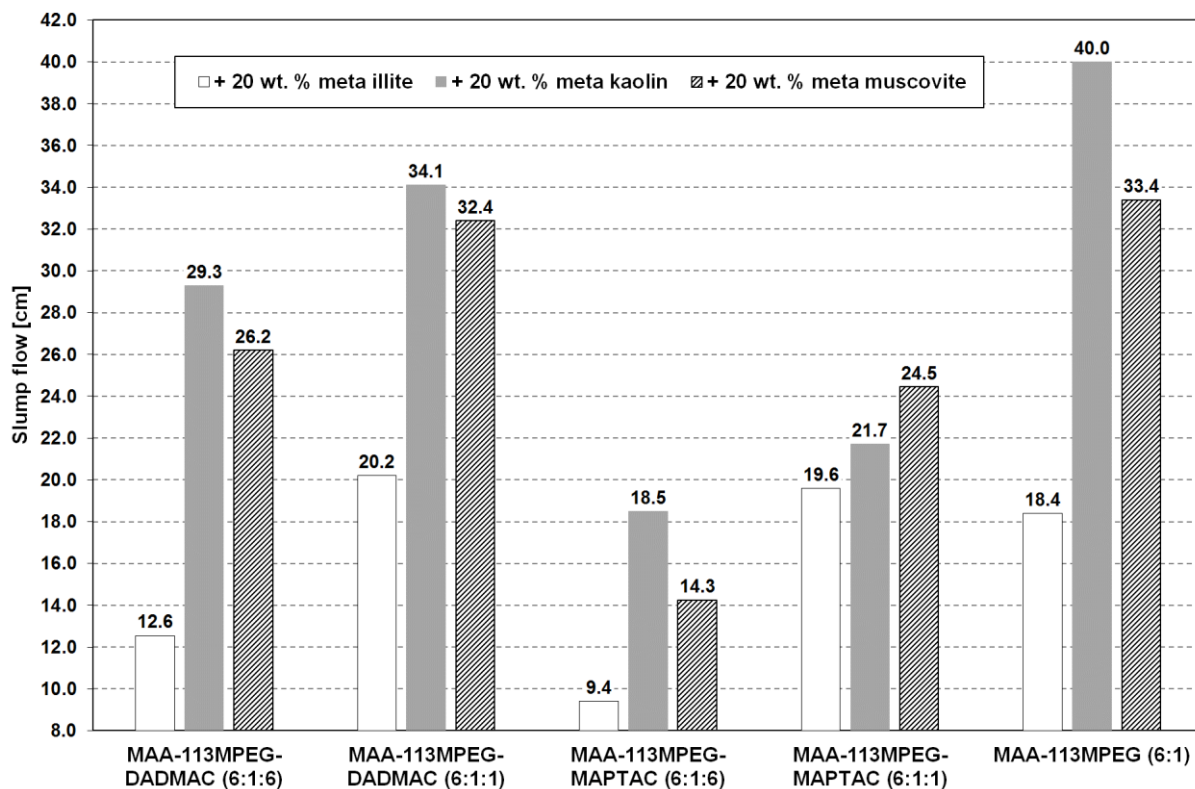


Figure 2. Slump flow of 80:20 blends of cement and different calcined clay samples admixed with 0.3 % bwob of synthesized polymers

3.2 Dispersing performance of zwitterionic superplasticizers in calcined clay blended mortar

As was reported before, the cement paste containing meta muscovite shows a shear-thickening flow behavior. In order to study the influence of aggregates like sand on the flow behavior, the polymers were tested in mortar (Figure 3). Similar as in the paste tests, none of the mortars without superplasticizer was fluid at the selected w/b value of 0.5, meaning the spread flow of the non-treated mortar was the bottom diameter of the *Hägermann* cone (10.0 cm).

Surprisingly, in the mortar holding meta muscovite the superior dispersing effect observed for all superplasticizers in the paste tests disappeared completely. In mortar, meta kaolin which exhibits the lowest water demand of all calcined clay samples studied achieved the highest workability with all superplasticizers. Nevertheless, the trend regarding the content of cationic monomer could be approved - the lower the cationic amount, the higher is the spread flow.

A comparison with mortar prepared from neat cement revealed that here all polymers achieved the highest workability, mainly because of the low water demand of the OPC. Also here in mortar, the conventional anionic PCE (MAA-113MPEG (6:1)) performed at least comparably as the best amphoteric polymer.

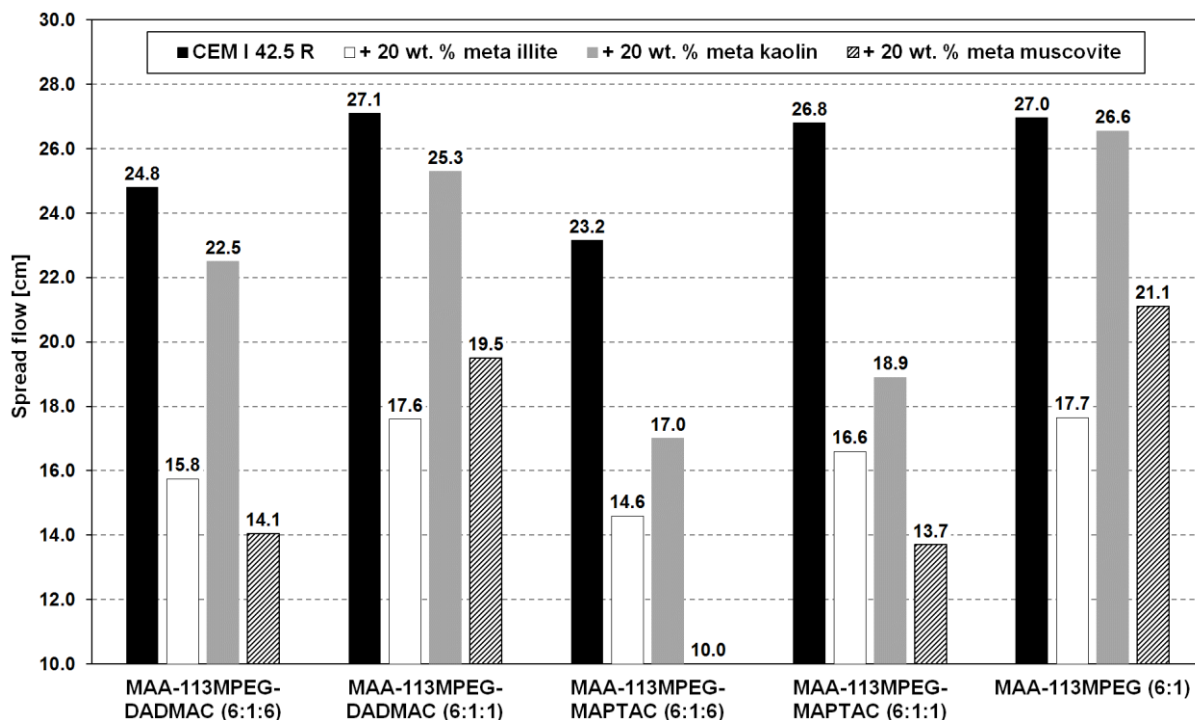


Figure 3. Spread flow of mortars prepared from 80:20 blends of cement and different calcined clays admixed with 0.3 % bwob of synthesized polymers

3.3 Effect on cement hydration

The effect of the synthesized amphoteric terpolymers on the hydration of cements blended with different calcined clays was studied *via* isothermal heat flow calorimetry. For all systems, an identical shift of the heat flow to delayed hydration was observed. **Figure 4** shows the trend exemplary for the cement blended with 20 wt. % meta kaolin.

Addition of the amphoteric comb polymers delays the induction period only slightly (~ 1 hour to 2.5 hours) for MAA-113MPEG-MAPTAC (6:1:6) and MAA-113MPEG-DADMAC (6:1:6), indicating less retardation of the silicate hydration as compared to the conventional anionic PCE superplasticizer. Nevertheless, at the selected dosage, the DADMAC-modified polymer behaves quite similar to the anionic one which allowed to expect a similar strength development in mortar (see 3.4). Furthermore, for the MAPTAC modified zwitterionic polymer the heat release was more comparable to that of the blend without admixture which indicates a faster early hydration.

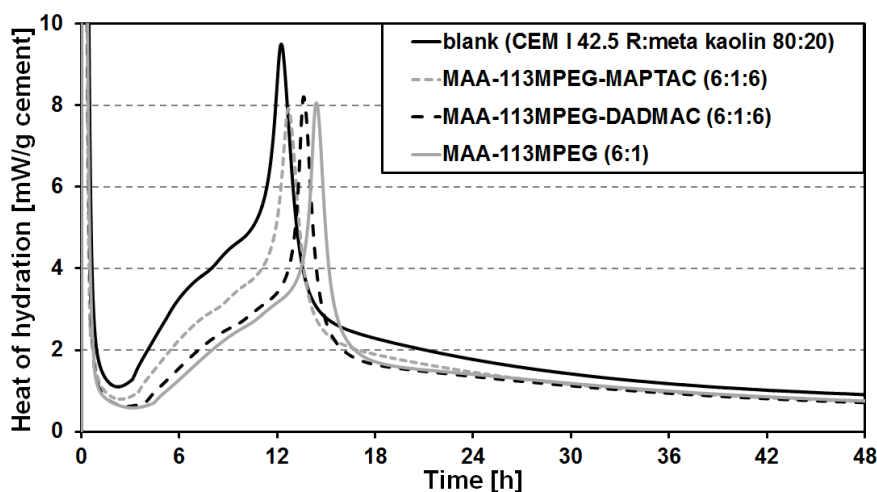


Figure 4. Heat evolution during hydration of CEM I 42.5 R blended with 20 wt. % meta kaolin and admixed with 0.3 wt. % of synthesized polymers

3.4 Effect on early strength of mortar

Mortars blended with 20 wt. % of the calcined clay samples and admixed with 0.3 % bwob of the synthesized polymers were tested after 24 hours of curing. Their compressive and tensile strengths were determined at comparable mortar densities (variation $\pm 40 \text{ kg/m}^3$). The strength results are displayed in **Figures 5** and **6**.

Relative to the compressive strengths, both amphoteric superplasticizers were slightly superior when meta illite was present (12.4, 12.2 and 12.7 N/mm^2 vs. 12.0 N/mm^2 for the anionic PCE). The amphoteric superplasticizers seem slightly to improve the compressive strength in meta illite blended mortars, while in mixtures holding meta kaolin and meta muscovite, the anionic superplasticizer provides the highest early compressive strength. Additional tests at earlier times (e. g. 6 h, 12 h) are planned which should give a more detailed information on the influence of the polymers on the very early strength development.

Furthermore, it was found that the flexural strengths of the mortars are quite comparable except for meta kaolin in which the DADMAC-modified amphoteric terpolymers exhibit slightly superior strength values.

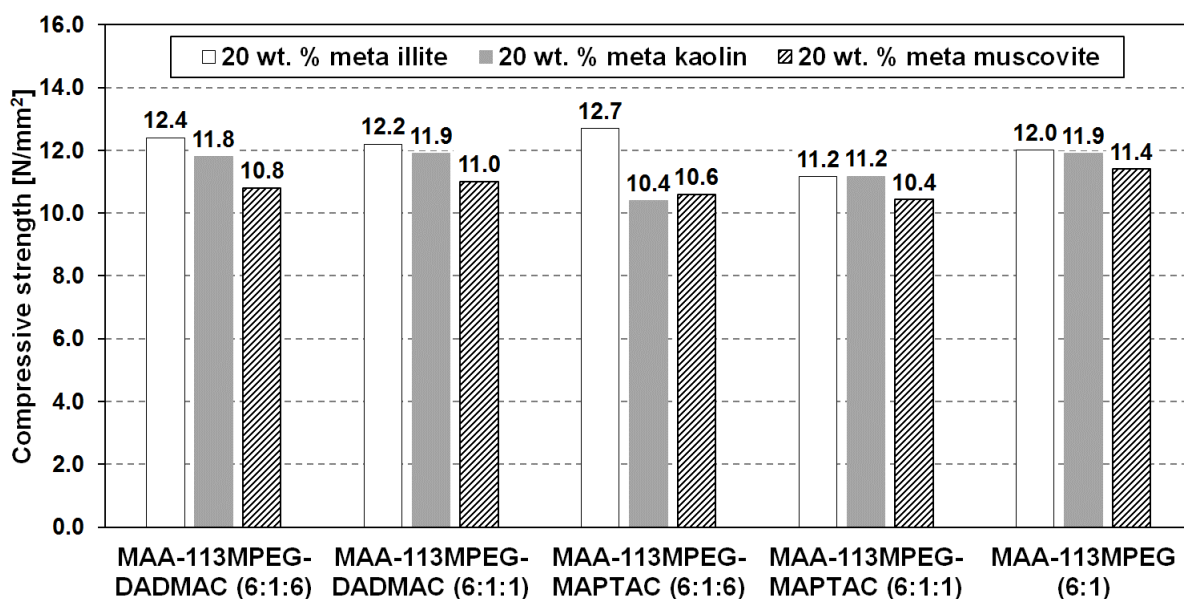


Figure 5. Compressive strengths of mortars blended with pure calcined clays cured for 24 hours and admixed with 0.3 % bwob of the synthesized zwitterionic superplasticizers

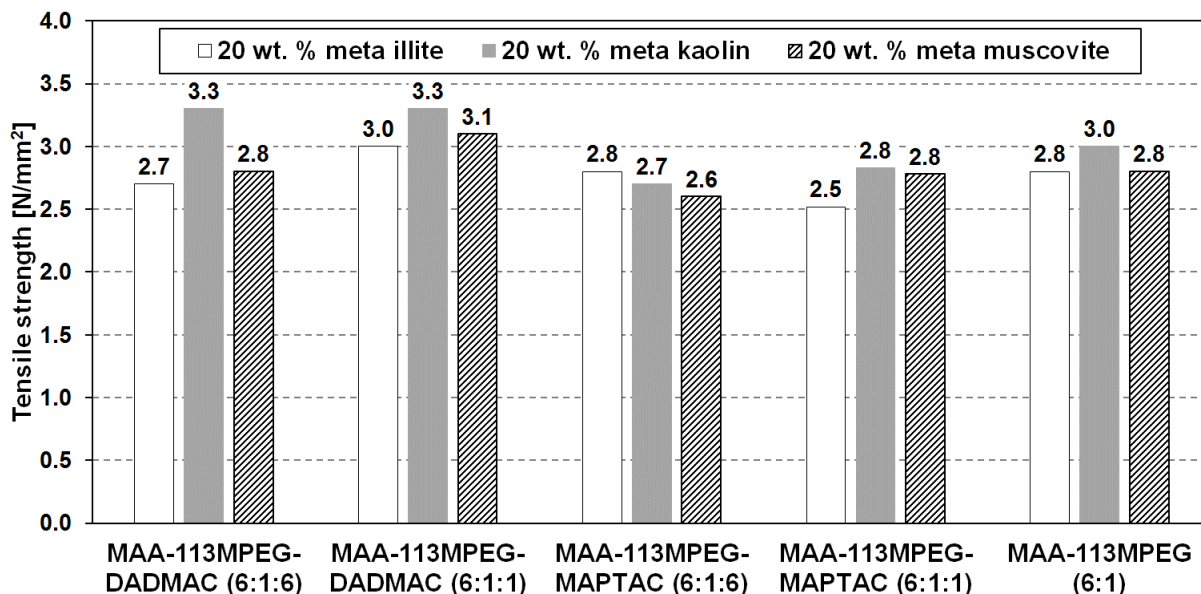


Figure 6. Tensile strengths of mortars blended with pure calcined clays, cured for 24 hours and admixed with 0.3 % bwob of the synthesized zwitterionic superplasticizers

4. CONCLUSIONS

In this work, four amphoteric comb polymers composed of methacrylic acid, MPEG-methacrylate macromonomer and DADMAC or MAPTAC as cationic monomers were synthesized and their efficiency to disperse OPC blended with three different calcined clays was investigated. Based on the results obtained it is concluded that their dispersing effectiveness is higher at lower contents of the cationic monomer. Furthermore, DADMAC proved to be more effective than MAPTAC monomer. However, at best their dispersing effectiveness was found to be only slightly superior to that of the anionic reference polymer.

In cement paste, both meta kaolin and meta muscovite can be dispersed rather well whereas meta illite is more difficult to fluidize which can be explained by its very small particle size and a subsequent high BET surface area compared to the other calcined clays investigated. In mortar, all three types of calcined clays behave similarly in the blended cement, whereby here meta illite shows a tendency to produce higher flow values than the two other calcined clay phases.

In all binder systems the amphoteric polymers show no or only a slight retarding effect on early cement hydration, compared to a conventional anionic polycarboxylate.

Further investigations should evaluate the strength development at very early times (6 - 12 hours) as it is known that most conventional anionic PCE superplasticizers reduce those early strengths.

5. ACKNOWLEDGEMENTS

The authors greatly thank Clariant Produkte GmbH (Burgkirchen, Germany), Evonik Performance Materials GmbH (Darmstadt, Germany) and SNF SAS (Andrézieux, France) for generously supplying monomers for the PCE syntheses. Moreover, this study is part of the research project "Ecological and energetic optimization of concrete: Interaction of structurally divergent superplasticizers with calcined clays" funded by Deutsche Forschungsgemeinschaft (DFG), Bonn, Germany under the grants PL 472/11-1 and TH 1383/3-1. The financial support provided by DFG is gratefully acknowledged.

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