

Superplasticizers and Other Chemical Admixtures in Concrete

Proceedings
Eleventh International Conference
Ottawa, ON, Canada

July 2015

V. Mohan Malhotra
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American Concrete Institute

SP-302

Eleventh International Conference on Superplasticizers and Other Chemical Admixtures in Concrete

Editors:

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First printing, June 2015

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Printed in the United States of America

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ISBN-13: 978-1-942727-22-4



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Preface

In May 1978, the Canada Center for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute (ACI) sponsored a three-day conference in Ottawa, ON, Canada, on the use of superplasticizers in concrete. Selected papers from the symposium were published as ACI SP-62.

In 1981, CANMET, again in association with the ACI, sponsored a second three-day international conference in Ottawa on the use of superplasticizers in concrete. Proceedings of the conference were published as ACI SP-68.

The purpose of the third international conference in Ottawa in 1989 was to review the progress made since the meetings in 1978 and 1981, and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. Proceedings of the conference were published as ACI SP-119.

In October 1994, CANMET, in association with the ACI and several other organizations, sponsored the fourth conference in Montreal, QC, Canada. The objective of this conference was to bring attention to new developments in chemical admixtures since the last conference in 1998. Proceedings of the conference were published as ACI SP-148.

In October 1997, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with the ACI and several cement and concrete organizations in Italy, sponsored the fifth conference in Rome, Italy. The conference was aimed at transferring technology in the fast-moving field of chemical admixtures. Proceedings of the conference were published as ACI SP-173.

In October 2000, the Committee of the Organization of CANMET/ACI International Conferences (ACI Council), in association with several organizations in Canada and France, sponsored the sixth conference in Nice, France. More than 50 papers from more than 20 countries were received and reviewed by the ACI review panel, and 37 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-195.

In October 2003, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with several organizations in Canada and Germany, sponsored the seventh conference in Berlin, Germany. The conference attracted more than 275 delegates and proceedings of the conference, consisting of 39 papers, were published as ACI SP-217.

In October 2006, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), sponsored the eight conference in Sorrento, Italy. More than 60 papers from more than 25 countries were received and peer reviewed by the CANMET/ACI review panel in Budapest, and 36 were accepted for publication as ACI SP-239.

In October 2009, the Committee for the Organization of International Conferences (COIC) (formerly CANMET/ACI International Conferences), sponsored the ninth ACI International Conference in Seville, Spain. More than 50 papers from more than 20 countries were received and peer reviewed, and 35 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-262.

In October 28 to 31, 2012, COIC, sponsored the Tenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in Prague, Czech Republic. More than 70 papers from the world over were peer reviewed, and 33 were accepted for publication.

publication in the proceedings of the conference. The proceedings were published as ACI SP-288.

In July 10-13, 2015, the COIC, in association with ACI, sponsored the Eleventh International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in Ottawa, Canada. More than 60 papers from the world over were peer reviewed, and 28 were accepted for publication in the proceedings of the conference. The proceedings were published by ACI as SP-302. Also, additional papers were presented at the conference that were published in the Supplementary Papers Volume.

Thanks are extended to members of the Technical Paper Review Panel that met in the Bahamas from October 3 to 11, 2014. Without their dedicated effort and hard work, it would not have been possible to publish the proceedings. Cooperation of the authors in accepting the reviewers' suggestions and in revising the manuscripts accordingly is appreciated greatly.

The help and assistance of Dr. Pawan R. Gupta and Prabha Gupta are acknowledged gratefully in the administrative work associated with the conference and processing of the manuscripts for both the conference proceedings (ACI SP-302) and the Supplementary Papers Volume.

V. Mohan Malhotra

Pawan R. Gupta

Terence C. Holland

Editors

Eleventh International Conference on Superplasticizers and Other Chemical Admixtures

July 12 to 15, 2015

Ottawa, Canada

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Effect of Clinker Grinding Aids on Static Yield Stress of Cement Pastes

by Joseph J. Assaad and Salim E. Asseily

The impact of clinker grinding aids (GAs) based on amine, glycol, or phenol on static yield stress (τ_0) of cement pastes is not well understood. Results obtained from this project have shown that GA molecules remain active after the grinding process and provide variations in cement properties, whether in the fresh or hardened states. Flowability improved and τ_0 decreased when the cement is ground using increased GA concentrations. This was attributed to the adsorption of these molecules onto the cement grains and saturation of surface charges, thus creating repulsive forces between neighboring particles. The decrease in τ_0 was particularly pronounced when phenol-based GA was used, given the presence of polycarboxylate polymers that help dispersing cement particles upon mixing with water.

Keywords: amine; cement; clinker; glycol; grinding aids; phenol; static yield stress.

INTRODUCTION

Grinding aids (GAs) are incorporated during comminution of clinker to reduce electrostatic forces and minimize agglomeration of cement grains.¹⁻³ Because of their highly organic polar nature, such additives are preferentially adsorbed on surfaces formed by the fracture of electrovalent bonds (Ca-O and Si-O). For a given cement fineness, this helps in improving mill productivity and/or reducing grinding energy consumption. Typical dosage rates vary from 0.01% to 0.15% of the manufactured cement mass.

After the grinding process, GAs may not preserve their original molecular structures; however, they do remain adsorbed onto the cement particles to provide variations of cement properties whether in the fresh or hardened states. The setting and hardening properties of cement containing GAs are well documented in literature. For instance, the hydration of C₃A was accelerated in the presence of triethanolamine (TEA) due to the rapid formation of hexagonal aluminate hydrate and its transformation to a cubic form.⁴ Heren and Olmez found that the addition of increased ethanolamine concentrations alters cement hydration and leads to retardation in setting times in the order of TEA > diethanolamine (DEA) > monoethanolamine (MEA).⁵ Triisopropanolamine (TIPA), which is an amino-alcohol and belongs to the group of alkanolamines, was found to change hydration reactions and particularly increase cement strengths. Perez et al. reported that TIPA remains in the interstitial paste solution (not adsorbed to the cement surface, as the TEA) and form iron complexes

to accelerate hydration of C_3S and C_4AF .⁶ Ichikawa et al. presented evidence that TIPA promotes hydration of limestone and densifies the interfacial transition zone (ITZ) between hydrated cement paste and sand or aggregate particles.⁷

Limited data exists in literature pertaining to the effect of GAs added during clinker grinding on rheology of cement-based materials. Aiad et al. found that viscosity of cement pastes is dependent on the type and dosage rate of ethanolamine used, whereby a decrease in viscosity was noticed following the sequence of TEA > poly-TEA > MEA.⁸ This was related to the number of O-H groups in the ethanolamine molecules that are adsorbed on the surface of cement grains, causing different repulsive forces and leading to variations in fluidity levels. However, it is important to note that the tests carried out by Aiad et al.⁸ cannot be conclusive as the ethanolamines were post-added to the cement (i.e., not added during the grinding process) at concentrations varying from 0.1% to 2% of cement weight (i.e., substantially higher than in real situations). Anna et al. compared the Z-potential of clinker containing TEA with others ground with polycarboxylate (PC) or poly-naphthalene sulphonate (PNS) concrete superplasticisers.⁹ They found that the TEA fluidifying mechanism for the dry cement system lies between the steric hindrance associated with PC polymers and electrostatic interaction of PNS with the positive charges of cement grains.⁹ While characterizing GAs and their impact on cement performance, Katsioti et al. noted an improvement in workability of cement pastes containing TIPA.¹⁰ This was related to the breaking down of cement agglomerates and balance modification between inter-particle forces.

The objective of this paper is to assess the effect of GAs on variations in flow and static yield stress of cement pastes prepared with different water-to-cement ratios (w/c). Grinding tests were performed by adjusting the specific energy consumption (E_c) in order to maintain similar Blaine fineness. Amine, glycol, and phenol-based GAs were used at various concentrations. Relevant parameters including flowability, yield stress, water demand, setting time, and compressive strength were evaluated.

RESEARCH SIGNIFICANCE

Grinding aids are increasingly used during comminution of clinker to prevent cement particle attraction and re-agglomeration, thus resulting in clinker and energy savings that can both lead to reduced carbon dioxide (CO_2) emissions. Results presented in this paper aim at assessing the effect of such additions on flow and yield stress of cement pastes. Such data can be of particular interest to cement manufacturers and concrete technologists as well as standardization committees dealing with specifications for GAs.

EXPERIMENTAL INVESTIGATION

Materials

Industrial clinker used for the production of ASTM C150 Type I cement, ground granulated blast furnace slag meeting the requirements of ASTM C989 Grade 80, and gypsum materials were employed in this study. The C_3S , C_2S , C_3A , and C_4AF of clinker were 54.6%, 17.4%, 9.2%, and 13.7%, respectively. The slag activity index with cement at 28 days is 86.4%. The relative hardness of the clinker, slag, and gypsum determined according to the Mohs hardness scale were around 5.5, 6, and 2, respectively.



Figure 1—Photo of the grinding mill used for testing.

Two commercially available GAs and a third one specially formulated for this study were tested. First, the amine-based GA is commonly used as a grinding aid and strength enhancer in the cement industry. It had 68% active chemicals when determined by the Karl Fischer method, and specific gravity and pH values of 1.09 and 7.2, respectively. The second GA is glycol-based composed by diethylene glycol (DEG) and monoethylene glycol (MEG) chemicals. It is commonly referred to as a grinding aid and pack-set inhibitor in the cement industry. Its active chemicals, pH, and specific gravity were 72%, 7.8, and 1.107, respectively. Finally, a specially formulated phenol-derivative GA with 70% active chemicals, pH of 5.8, and specific gravity of 1.09 was used. This latter GA was blended with 17.5% oleic fatty acids and 30% polycarboxylate ester molecules that are usually used in concrete admixtures to improve cement dispersion and workability during mixing.

Production of cement used for testing—A 50-L (13.25-gal) grinding mill connected to an electric counter for monitoring E_c was used^{2,3} (Fig. 1). The mill's drum diameter, width, and rotational speed were 400 mm (15.7 in.), 400 mm (15.7 in.), and 50 rpm, respectively. It contained a total of 80 kg (176 lb) steel balls among which 36 kg (79.2 lb) have 20-mm (0.7 in.) diameter and 44 kg (96.8 lb) have 30-mm (1.18 in.) diameter. Prior to grinding, the clinker, gypsum, and slag materials were crushed and sieved so that all particles were smaller than 10 mm (0.4 in.).

All grinding tests were conducted using 7 kg (15.4 lb) of a mix composed of 90% clinker, 5% gypsum, and 5% slag. First, a mix ground without GA at 42 kWh/ton was tested and considered in this project as being the control cement; its Blaine fineness was 3460 cm²/g. Then, GAs were introduced at pre-selected concentrations varying from low to high levels; the Ec was adjusted accordingly in a way to maintain the fineness equivalent to the control cement, i.e. Blaine of 3460 ±100 cm²/g. The high GA levels were determined following previous studies,^{2,3} thus ensuring that ASTM C465 requirements for water demand, setting time, and compressive strength are satisfactorily fulfilled.¹¹ The method for cement production consisted on grinding the materials for a certain elapsed time, stopping the mill, and sampling around 100 grams to check whether the Blaine was close to the targeted value. If not, additional grinding was performed. At the end of grinding, the temperature of the charge was found to increase from ambient (i.e., 23 °C (73 °F)) to around 37 °C (99 °F).

Testing equipment and procedures

Tests on powder cement—Following grinding, the cement fineness was determined using the Blaine apparatus, as per ASTM C204 Test Method, and by mechanical sieving on 106, 90, and 38 µm mesh openings. The R-90 and R-38 values given in this paper refer to the individual percentages retained on the 90-µm and 38-µm sieve, respectively. The residues on the 106-µm sieve were in the range of 0.2% to 3.5%, depending mostly on the Ec used (note that all particles retained on this later sieve were not included in the cement mix used for subsequent testing).

Tests on cement pastes—All pastes were batched with a laboratory mixer using water cooled to a temperature of around 23 °C (73 °F). Water was first introduced in the mixer followed gradually by the ground cement over 2 minutes. After a rest period of 30 s, the mixing was resumed for one additional minute. The ambient temperature and relative humidity during testing were maintained at 23 ±2 °C (73 ±36 °F) and 55 ±5%, respectively. The water demand required to achieve normal consistency was determined following ASTM C187 Test Method. Using the same cement paste, the Vicat initial and final setting times were then determined as per ASTM C191 Test Method.

The effect of GA types and concentrations on flow and rheological properties was evaluated using cement pastes prepared at 0.48 and 0.42 w/c. These w/c were selected in order to produce pastes with different consistency levels ranging from highly flowable to relatively cohesive. The flow was determined as the average diameter of the paste after spreading on a horizontal surface using an ASTM C230 mini-slump cone. A rotational viscometer connected to a data logger was used to evaluate static yield stress (τ_0). The vane used consisted of four blades arranged at equal angles around the main shaft; it measured 24 mm (0.95 in.) in height and 12 mm (0.47 in.) in diameter. Right after mixing, the cement paste was poured in a cylindrical bowl and allowed to rest for one min prior to measuring the τ_0 value. The testing protocol consisted on subjecting the paste to a very low rotational speed of 0.3 rpm and recording the changes in torque as a function of time. The τ_0 was determined in accordance to Nguyen and Boger,¹² by considering the maximum torque registered that indicates the initiation of flow. It is important to note that the total elapsed time from the initial contact of cement with water until the flow and τ_0 measurements was around 10 minutes.

Table 1—Properties when cement is ground with amine-based GA

Ec, kWh/ton		42	40.4	38.6	37.1	35.7	34.8
GA dosage, % of mass		0	0.03	0.06	0.09	0.11	0.13
Blaine, cm ² /g		3460	3430	3495	3360	3405	3375
R-90, %		8.6	8.1	8.2	9.3	9.8	9.5
R-38, %		28.3	25.8	22	30.1	28.6	32.8
Water demand, %		27.25	27.3	27.45	27.2	27.5	27.05
Final set, min		235	240	235	255	275	290
w/c = 0.48	Flow, mm	195	190	200	195	200	205
	τ_0 , Pa	9.2	10	8.8	7.6	7.2	7.6
w/c = 0.42	Flow, mm	150	150	160	155	160	165
	τ_0 , Pa	30.4	28.8	29.6	28	28.8	26.4
7-d compression, MPa		35.6	35.9	38.1	38	39	36.9
28-d compression, MPa		47.2	48.8	49.7	49.6	52.1	50.3

Notes: 1 cm²/g = 6.8×10^{-5} in²/lb; 1 MPa = 145 psi; 1 in. = 25.4 mm

Table 2—Properties when cement is ground with glycol-based GA

Ec, kWh/ton		42	40.7	39.2	38.4	37.5
GA dosage, % of mass		0	0.03	0.06	0.08	0.1
Blaine, cm ² /g		3460	3415	3475	3520	3515
R-90, %		8.6	7.8	8.4	9	8.9
R-38, %		28.3	25.2	24	29.1	34.3
Water demand, %		27.25	27.05	27.2	27.1	27.3
Final set, min		235	255	265	260	300
w/c = 0.48	Flow, mm	195	210	210	225	220
	τ_0 , Pa	9.2	8.8	8	7.6	7.6
w/c = 0.42	Flow, mm	150	145	160	175	170
	τ_0 , Pa	30.4	28.8	25.6	21.6	22.4
7-d compression, MPa		35.6	34.8	37	36.7	35.3
28-d compression, MPa		47.2	48	47	49.5	45

Notes: 1 cm²/g = 6.8×10^{-5} in²/lb; 1 MPa = 145 psi; 1 in. = 25.4 mm

Tests on mortars—The compressive strength was determined as per ASTM C109 Test Method. The 50-mm (2-in.) cubes were cured in water until testing at 7 and 28 days.

TEST RESULTS AND DISCUSSION

The various cement properties determined following clinker grinding at fixed Blaine fineness of 3460 ± 100 cm²/g using either amine, glycol, or phenol-based GA are summarized in Tables 1, 2, and 3, respectively. It is to be noted that several cement mixtures were ground two to three times to evaluate reproducibility of testing. Acceptable coefficients of variation (COV) were obtained; as these were equal to 3.8%, 5.1%, 4.6%, 7.4%, and 5.7% for the Blaine, R-38, water demand, setting time, and compressive strength, respectively. The COV increased to 8.8% for τ_0 responses, given the variations in Blaine fineness that could lead to different restructuring rates during the rest period prior to shearing. Also, confinement and yielding of paste within the rotating vane impeller could lead to some

Table 3—Properties when cement is ground with phenol-based GA

Ec, kWh/ton		42	41.1	40.8	39.8	39	38.5
GA dosage, % of mass		0	0.02	0.03	0.06	0.08	0.09
Blaine, cm ² /g		3460	3390	3475	3405	3420	3370
R-90, %		8.6	8	8.2	8	9.1	9.3
R-38, %		28.3	24.1	23	27.4	30.2	33
Water demand, %		27.25	27.3	27.1	26.75	26.4	26.1
Final set, min		235	250	230	215	205	195
w/c = 0.48	Flow, mm	195	205	220	235	250	260
	τ ₀ , Pa	9.2	8.4	8.2	6.5	4.6	3.7
w/c = 0.42	Flow, mm	150	160	165	180	190	210
	τ ₀ , Pa	30.4	28.9	26.4	21.6	20.7	16.5
7-d compression, MPa		35.6	37	36.8	37.2	34.4	33
28-d compression, MPa		47.2	48.1	45.6	47.1	43.5	42.6

Notes: 1 cm²/g = 6.8 × 10⁻⁵ in²/lb; 1 MPa = 145 psi; 1 in. = 25.4 mm

discrepancies in rheological measurements.¹² The COV is taken as the ratio between standard deviation and mean values, multiplied by 100.

Effect of GA on Ec values

Regardless of GA type, the addition of increased concentration led to consecutively reduced Ec values. For example, Ec decreased from 42 kWh/ton for the control cement to 37.5 kWh/ton with the use of 0.1% glycol-based GA, corresponding to 10.7% reduction in energy consumption. Such decrease reached 34.8 and 38.5 kWh/ton with the use of 0.13% amine-based GA and 0.09% phenol-based GA, respectively (i.e., 17.1% and 8.3% energy decrease, respectively). This can normally be related to the GA molecules that are adsorbed onto newly fractured surface grains, thus attenuating electrostatic forces and improving cement fineness.²

It is to be noted that the decrease in Ec provided during the grinding process led to an increase in R-38 and R-90 values, particularly at high GA concentrations (Tables 1, 2, and 3). Hence, R-38 increased from 28.3% for the control cement to 32.8% and 34.3% when the amine or glycol-based GA were used, respectively, at a rate of 0.13% or 0.1%, respectively. This indicates that the sieve residues that are functions of the maximum particle size are directly affected by the amount of grinding energy.³ Nevertheless, data provided by the particle size analysis has shown an increased fraction of particles finer than around 5 μm for those later mixtures, which allowed maintaining the Blaine fineness within 3460 ± 100 cm²/g.

For a given GA concentration, higher decreases in Ec were achieved with the use of amine-based GA. For example, at a rate of 0.06%, the targeted Blaine was ensured at Ec of 38.6, 39.2, and 39.8 kWh/ton for cement ground with amine, glycol, or phenol-based GA, respectively.

Effect of GA on variations in water demand and setting time

Water demand—The effect of incorporating various dosages of amine or glycol-based GA did not lead to remarkable variations in water demand, as compared to the 27.25% value

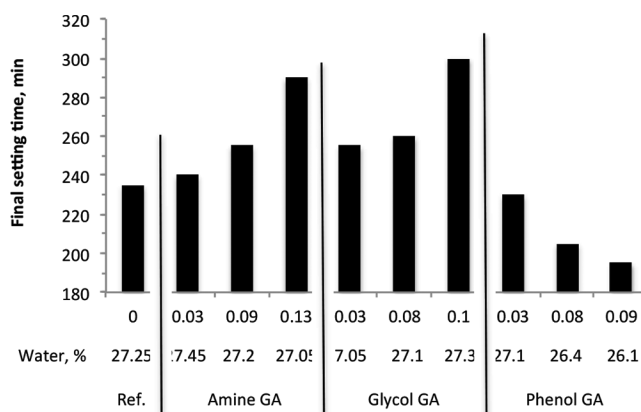


Figure 2—Variations in setting times for cement ground with various concentrations of amine, glycol, or phenol-based GA.

determined on the control mixture (i.e., values given in Tables 1 and 2 remained within $27.25\% \pm 0.25\%$). Conversely, water demand necessary to achieve normal consistency considerably decreased with the use of phenol-based GA; this reduction reached 26.1% with the addition of 0.09% dosage rate (Table 3). This can essentially be attributed to the presence of polycarboxylate molecules that improve cement dispersion upon mixing with water. In other words, this indicates that the GA molecules added during grinding preserve, to a certain extent, their original functionality to effect variations in cement properties.^{3,13}

Setting time—The variations in final setting time for cement ground with various concentrations of amine, glycol, or phenol-based GA are plotted in Fig. 2. In the case of amine and glycol-based GA, the setting time slightly increased at low to relatively moderate GA dosages, and then increased sharply at higher dosages. For example, the setting increased from 235 min for the control cement to 240 and 255 min when the amine-based GA was added at a rate of 0.03% and 0.09%, and then reached 290 min at a rate of 0.13%. Such increase was equal to 255, 260, and then 300 min when the glycol-based GA was used at dosages of 0.03%, 0.08%, and 0.1%, respectively. The delay in setting with increased GA concentrations is in complete agreement with other data published in literature. Teoreanu and Guslicov suggested the existence of an optimum GA concentration that can be correlated with the achievement of a continuous absorption monolayer onto the micro-fractured cement particles.¹⁴ Beyond such optimum, the adsorbed monolayer may partly blocks the hydration reactions and leads to retardation in setting times,^{5,14} just like what happens with the use of water reducers and superplasticizers in concrete mixtures.

Unlike the variations obtained for cement ground with amine or glycol-based GA, the incorporation of phenol-based GA accelerated the setting times, as compared to the control mix (Fig. 2). Hence, a decrease in final setting from 235 to 205 and 195 min was measured for the control cement containing 0.08% and 0.09% GA, respectively. This can indirectly be related to the reduced water demand added to the cement paste that was used for testing normal consistency. The reduced w/c leads to increased cement hydration rates, thereby

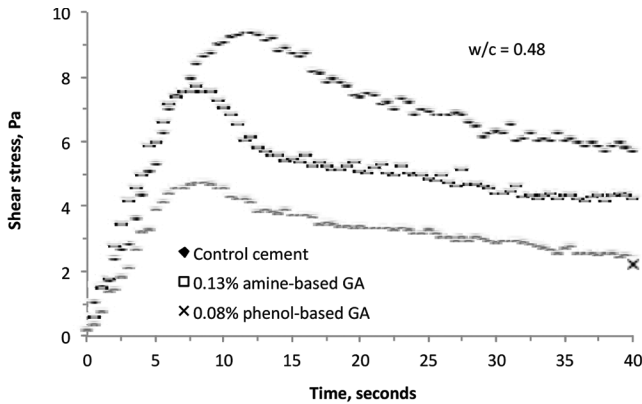


Figure 3—Typical variations in shear stress for 0.48 w/c cement pastes.

shortening setting times.⁴ Additionally, phenol molecules are reported to remain in pore water and form insoluble complexes that react with calcium ions released from cement,¹⁵ thus possibly contributing in accelerated hydration reactions and setting times.

Effect of GA on variations in τ_0 values

Typical plots of shear stress as a function of time determined on various cement pastes are shown in Fig. 3. All profiles exhibited an elastic linear region whereby the material resists shearing, until reaching a maximum shear stress indicating breakage of majority of bonds and yielding of structure. The maximum value required to initiate flow is considered as τ_0 .

The variations of τ_0 for tested cement pastes containing various GA types and concentrations at w/c of 0.42 and 0.48 are illustrated in Fig. 4 and 5, respectively (variations in flow are also shown). As can be seen, the τ_0 appears to decrease when the cement is ground using increased GA concentrations. For example, at w/c of 0.42, a decrease from 30.4 Pa for the control cement to 28 and 26.4 Pa is noted when the amine-based GA was used at a rate of 0.09% and 0.13%, respectively. The corresponding flow improved from 150 to 155 and 165 mm, respectively (5.9 to 6.1 and 6.5 in., respectively) (Fig. 4). Given that Blaine fineness and water demand were almost similar for cement mixtures ground with amine-based GA, this indicates that the GA molecules remained active after the grinding process and resulted in certain variations in rheological properties. The τ_0 decrease in presence of GA can be due to the adsorption of these molecules onto cement particles and saturation of surface charges, thus creating repulsive forces between neighboring cement and improving flowability.^{10,13}

It is interesting to note that the decrease in τ_0 was more pronounced when the glycol-based GA was used, as compared to the cement ground using amine-based GA. For example, at a dosage rate of 0.06%, τ_0 decreased from 29.6 to 25.6 Pa for mixtures prepared at 0.42 w/c using cement ground with amine or glycol-based GA, respectively. When cement comes into contact with water, it is the aluminate phases (C_3A and C_4AF) that react first to form a gel based on complex sulfoaluminate hydrates. This gel exerts a barrier effect and governs the mass flow between the inner part of the cement grain and pore water, thus controlling the

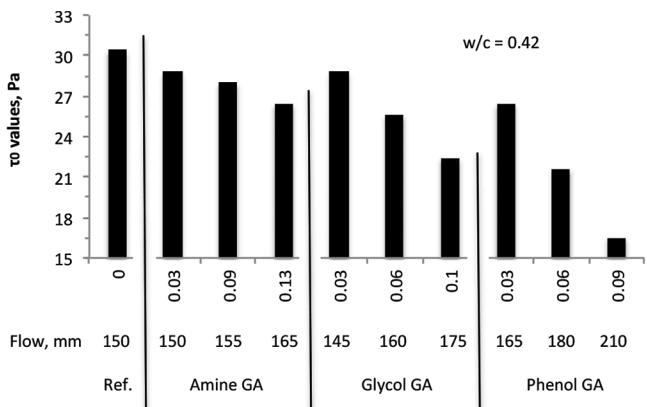


Figure 4—Variations in τ_0 for 0.42 w/c pastes made using cement ground with various concentrations of amine, glycol, or phenol-based GA (1 MPa = 145 psi; 1 in. = 25.4 mm).

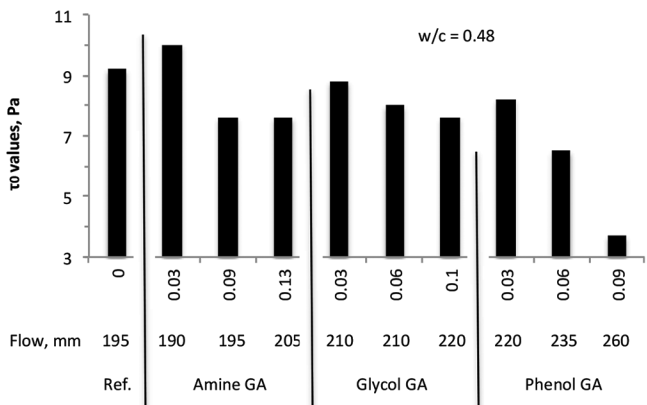


Figure 5—Variations in τ_0 for 0.48 w/c pastes made using cement ground with various concentrations of amine, glycol, or phenol-based GA (1 MPa = 145 psi; 1 in. = 25.4 mm).

rheological behavior and hydration of the silicate phases.⁹ Given that TEA and TIPA have been identified to rapidly react with the aluminate phases,^{4,5} this may increase viscosity of the interstitial phase and formation of colloidal crystals between connected cement grains. This therefore explains the relative increase in τ_0 measurements for pastes prepared with cement ground with amine-based GA, as compared to those containing glycol-based GA.

The pastes prepared using cement ground with phenol-based GA exhibited the highest improvements in flowability and decrease in τ_0 . For example, at 0.42 w/c, the flow increased to 210 mm and τ_0 decreased to 16.5 Pa with the addition of 0.09% phenol-based GA (Fig. 4). As already explained, this can be related to the polycarboxylate polymers present in this GA that help dispersing cement particles upon mixing with water. There

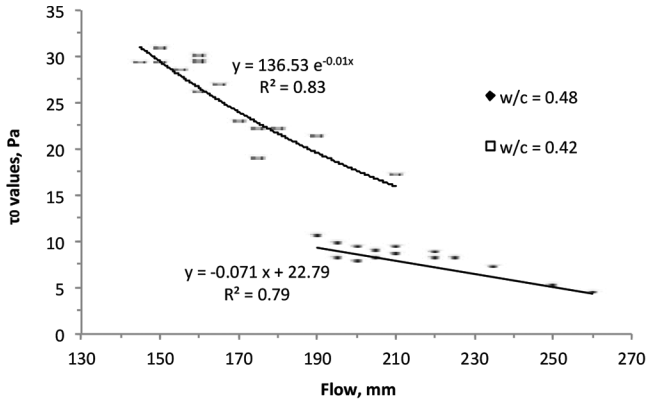


Figure 6–Relationships between τ_0 and flow for all tested cement pastes (1 MPa = 145 psi; 1 in. = 25.4 mm).

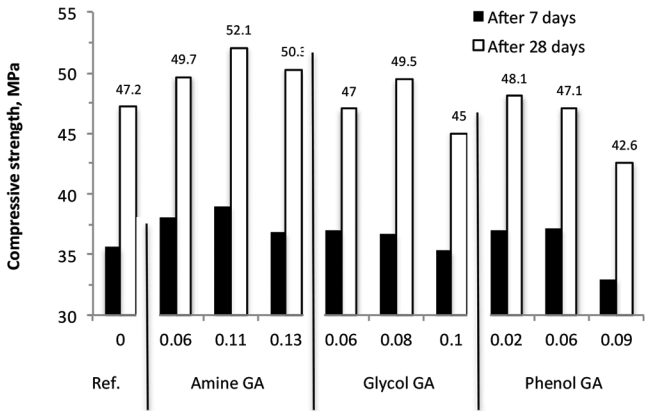


Figure 7–Variations in compressive strength for mortars made using cement ground with various concentrations of amine, glycol, or phenol-based GA (1 MPa = 145 psi).

fore, given that the tested pastes were prepared at given w/c of 0.42 or 0.48, this explains the improvement in flowability and corresponding decrease in τ_0 .

Acceptable correlations exist between τ_0 and flow values of all tested cement pastes, as shown in Fig. 6. The correlation coefficients (R^2) were equal to 0.79 and 0.83 for pastes made with w/c of 0.42 and 0.48, respectively. Hence, the higher the flow, the lower τ_0 responses.

Effect of GA on compressive strength development

The variations in compression strength determined after 7 and 28 days for mortars made with cement ground with various GA types and concentrations are plotted in Fig. 7. As can be seen, the increase in strength was much more pronounced for mortars prepared

using cement ground with amine-based GA, as compared to those containing the glycol or phenol-based GA. For example, the strength increased from 47.2 MPa (6.84 ksi) for the control mortar to 52.1 MPa (7.55 ksi) after 28 days for the mixture containing cement ground with 0.11% amine-based GA. For given Blaine, this can mainly be attributed to the presence of TIPA that strengthens the C-S-H compounds and densifies the interfacial transition zone between the cement paste and sand particles.^{3,6,7}

At high GA concentrations, the hydration reactions can be altered by the adsorbed GA molecules,^{10,14} thus leading to decreased strength (Fig. 7). Such decrease was particularly pronounced in the case of mortars prepared with cement ground with glycol and phenol-based GA. Hence, at 0.1% rate of glycol-based GA, the compressive strength dropped to 45 MPa (6.52 ksi) after 28 days. A value of 42.6 MPa (6.17 ksi) was registered for mortar prepared using cement ground with phenol-based GA at a rate of 0.09%. In literature, the decline in strength for cement containing fatty acids was related to oxidation with dissolved oxygen of mixing water during the curing period, thus causing microscopic cracks in the mortar skeleton.¹⁶

CONCLUSIONS

Based on the above results, the following conclusions can be warranted:

- The incorporation of amine or glycol-based GA did not lead to remarkable variations in water demand, as compared to control mix. Conversely, water demand necessary to achieve normal consistency considerably decreased with the use of phenol-based GA, due to the presence of polycarboxylate molecules that improve cement dispersion.
- The setting time slightly increased at low to relatively moderate dosages of amine and glycol-based GA, and then increased sharply at higher dosages. Such delay in setting can be correlated to the GA adsorption onto the micro-fractured cement particles, thus partly blocking the hydration reactions and leading to retardation in setting times. Conversely, the use of phenol-based GA accelerated setting times, given the reduced w/c and creation of insoluble complexes that react with calcium ions released from the cement.
- The flowability improved and τ_0 decreased when the cement is ground using increased concentrations of amine-based GA. For a given Blaine fineness and water demand, this was attributed to the adsorption of these molecules onto the cement particles and saturation of their surface charges, thus creating repulsive forces between neighboring and improving flowability.
- The decrease in τ_0 was more pronounced when the glycol-based GA was used, as compared to the cement ground using amine-based GA. This was related to the presence of TEA and TIPA in this later GA that can rapidly react with the cement aluminate phases, thereby increasing viscosity of the solution and formation of colloidal crystals between connected cement grains.
- The pastes prepared using cement ground with phenol-based GA exhibited the highest decreases in τ_0 , given the presence of polycarboxylate polymers that help dispersing cement particles upon mixing with water and improving flowability.
- The increase in strength was particularly pronounced for mortars prepared using cement ground with amine-based GA, as compared to those containing glycol or phenol-based GA. This was attributed to the presence of TIPA that strengthens the

C-S-H compounds and densifies the interfacial transition zone between the cement paste and sand particles.

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A ^{13}C NMR Spectroscopic Study on the Reparation of Acid and Ester Groups in MPEG Type PCEs Prepared via Radical Copolymerization and Grafting Techniques

by Julia Pickelmann, Huiqun Li, Robert Baumann, and
Johann Plank

The microstructure of MPEG-type polycarboxylate (PCE) copolymers, i.e. the distribution of side chains along the main chain was investigated via ^{13}C NMR spectroscopy and the effect on the interaction with cement was determined. For this purpose, two series of polycarboxylate samples (one series synthesized by radical copolymerization, the other one via grafting/esterification) at molar ratios of $-\text{COO}^-$ to side chain of 2 to 10 were compared. The ^{13}C NMR spectra suggest that the copolymerized PCEs possess a gradient-like distribution of side chains along the main chain while the grafted PCEs exhibit a statistical (random) repartition. Owing to those microstructural differences the grafted PCE copolymers show a tendency to adsorb in lower amount on cement. The reason is that in the copolymerized PCEs, large blocks of $-\text{COO}^-$ groups are present which exhibit high affinity to the surface of cement and therefore promote adsorption.

Keywords: copolymerization; dispersing force; grafting; microstructure; polycarboxylates.

INTRODUCTION

Superplasticizers possessing PEO side chains which are connected with the backbone via methacrylic ester groups are known as PCEs of the first generation. They are widely used to improve the rheology of mortar and concrete or to reduce the water demand resulting in higher durability of the concrete. Generally, a major advantage of polycarboxylates is their variability in chemical composition and structure. This feature allows tailoring PCE molecules to specific needs in highly diverse applications. For example, PCE polymers exhibiting a long slump retention can be designed.¹

In the past, PCEs have been studied intensively with respect to the effects of their composition (e.g. side chain length, side chain density, anionic charge, hydrodynamic size of the polymer, etc.) on their dispersing force and the adsorbed amounts.²⁻⁶ However, only limited information on the correlation between the dispersing power in cement and the microstructure of PCEs is available. The reason is the complexity of the analysis of the microstructural composition of the polymer, especially the repartition of the side chains along the polymer trunk. *Borget et al.* were the first to propose an analytical method to elucidate the microstructure of polymethacrylic acid- ω -methoxy polyethyleneglycol graft copolymers using ^{13}C NMR spectroscopic measurements. According to them, the grafting process results in a copolymer with a random distribution of the side chains along the main chain.⁷ *Rozzoni* and *Belotto* also used ^{13}C NMR spectroscopy to study the molecular configuration and tacticity of two copolymerized MPEG-type PCEs. They found a correlation between the tacticity of the copolymer and its macroscopic properties such as e.g. a lower critical solution temperature (LCST, cloud point).⁸

Still, the most interesting point is the correlation between the microstructure of the polymers and their behavior in cement. In a first attempt *Pourchet et al.* compared two well-defined polymers possessing a high side chain density but different repartition of the pendant groups.⁹ The first PCE sample exhibited a gradient distribution of the side chains while the second one possessed a random distribution. They found that the different microstructures significantly impacted the adsorption behavior of the polymers and their sulfate resistance. However, a major drawback of this study is that both copolymers were synthesized via RAFT copolymerization which is not performed in industrial manufacturing of PCEs. Therefore, at present no information is available which describes the relationship between the microstructure of commonly produced MPEG PCEs and their interaction with cement. Furthermore, no data on PCEs possessing low grafting density have ever been published.

To close this gap, two series of MPEG-type PCEs were prepared employing the common industrial manufacturing methods of radical copolymerization and grafting (esterification) of ω -methoxy polyethylene glycol and a polymethacrylic acid (PMAA) backbone. Within each series, the molar ratios between the $-\text{COO}^-$ and the side chain bearing monomers were varied between 2 and 10 to represent the common PCE products used in actual applications. Their individual microstructures were determined by ^{13}C NMR spectroscopic measurements and then related with their adsorption behavior in cement.

RESEARCH SIGNIFICANCE

The repartition of $-\text{COO}^-$ groups present in MPEG type PCEs synthesized via the two routes practiced in the industry (radical copolymerization and grafting/esterification) was determined analytically. It was found that copolymerized PCEs exhibit a gradient distribution of the $-\text{COO}^-$ groups and therefore generally adsorb in higher amounts on cement than grafted PCEs. The study reveals that different preparation methods for PCEs may result in different microstructures which can impact the interaction of those PCEs with cement. Furthermore, it provides evidence for the existence of different reactivity ratios for methacrylic acid and the macromonomer in radical copolymerization.

A ¹³C NMR Spectroscopic Study on the Reparation of Acid and Ester Groups in MPEG Type PCEs Prepared via Radical Copolymerization and Grafting Techniques 27

Table 1 – Phase composition of the CEM I 52.5 N sample, as determined by Q-XRD analysis.

Phase [wt. %]											
C ₃ S _m	C ₂ S _m	C ₃ A _c	C ₃ A ₀	C ₄ AF ₀	CaSO ₄	CaSO ₄ . ½ H ₂ O*	CaSO ₄ . 2 H ₂ O*	Calcite	Quartz	Arcanite	LOI
52.0	27.6	4.4	3.6	4.3	2.1	0.7	0.4	3.3	0.8	0.5	0.01

* determined by thermogravimetry

EXPERIMENTAL PROCEDURES

Cement

A CEM I 52.5 N ('Milke classic', HeidelbergCement, Geseke plant, Germany) was used. Its phase composition as determined by Q-XRD employing *Rietveld* refinement is shown in **Table 1**. Furthermore, a mean particle size (d_{50} value, determined by laser granulometry) of 10.2 μm and a *Blaine* fineness of 3316 cm^2/g (Helium pycnometry) were found for this sample.

Synthesis of PCE samples

PCE via copolymerization – For preparation, two solutions were prepared. Solution I contained water, the monomers methacrylic acid (MAA, Sigma Aldrich, Steinheim/Germany) and polyethylene glycol methacrylate ester (PEG-MA 1000, Clariant, Burgkirchen/Germany), and the chain transfer agent mercapto propionic acid (MPA, aber, Karlsruhe/Germany). Solution II constituted of an aqueous solution (100 mL) of the initiator sodium persulfate (SPS) which was kept at 0°C during the entire synthesis. In preparation, 50 mL of water were placed in a 500 mL five neck round bottom flask equipped with a reflux condenser and stirrer, flushed for 20 min with N₂ and then heated to 85°C. Using two peristaltic pumps, solution I was added to the flask over 4 h and solution II over 5 h. After cooling the polymer solution to ambient, its pH value was adjusted to ~ 7 by adding NaOH (30 wt. %). The resulting PCE solutions exhibit a solid content of ~ 30 wt.% and are yellowish and slightly viscous. The individual quantities and molar ratios of all reactants used in the different syntheses are shown in **Table 2**.

PCE via grafting (esterification) – Polymethacrylic acid (PMAA, Dow, Walsrode/Germany) and ω -methoxy polyethyleneglycol (PEG-M 1000, Clariant, Burgkirchen/Germany) were placed in a 250 mL flask and then homogenized at 95°C. Esterification was initiated by gradually heating to 175°C under vacuum (0.1 mbar, 0.75 Torr) while water was distilled off and collected in a cooling trap. After ~ 6 h of reaction time, the final product was cooled to ambient, diluted with water to a solid content of ~ 30 wt. % and adjusted to pH ~ 7 by adding NaOH (30 wt. %). The resulting polymer solutions are colorless and slightly viscous. The quantities of raw materials and the molar ratios for all polymers prepared are shown in **Table 2**.

Characterization of PCE samples

Size exclusion chromatography – Molar masses (M_w , M_n), polydispersity index (PDI), hydrodynamic radius ($R_{h(z)}$) and conversion of all PCE samples were determined by size exclusion chromatography (SEC). PCE solutions (concentration 10 g/L) were injected into

Table 2 – Quantities and molar ratios of reactants used in the preparation of copolymerized and grafted PCE samples

molar ratio COO- to side chain	PCEs via copolymerization					PCEs via grafting	
	MAA	Macro- monomer	MPA	water	SPS	PMAA	MPEG
2	10.0 g 116 mmol	58.08 g 58 mmol	1.23 g 12 mmol	42.0 g	1.38 g 5.8 mmol	15.5 g 180 mmol	60.0 g 60 mmol
3	15.0 g 174 mmol	58.08 g 58 mmol	1.64 g 15 mmol	45.0 g	1.22 g 5.2 mmol	20.66 g 240 mmol	60.0 g 60 mmol
5	25.0 g 290 mmol	58.08 g 58 mmol	2.07 g 23 mmol	51.0 g	2.77 g 11.6 mmol	31.0 g 360 mmol	60.0 g 60 mmol
6	30.0 g 348 mmol	58.08 g 58 mmol	2.71 g 23 mmol	54.0 g	3.23 g 13.6 mmol	36.16 g 420 mmol	60.0 g 60 mmol
10	50.0 g 581 mmol	58.08 g 58 mmol	4.52 g 43 mmol	66.0 g	5.07 g 21.3 mmol	56.8 g 660 mmol	60.0 g 60 mmol

a Waters 2695 Separation Module equipped with three Ultrahydrogel™ columns (120, 250, 500) and a Ultrahydrogel™ guard column (Waters, Eschborn/Germany) and a subsequent 3 angle static light scattering detector (mini Dawn, Wyatt Technology Corp., Santa Barbara, CA/USA). After separation, the polymer concentrations were monitored with a differential refractive index detector (RI 2414, Waters, Eschborn/Germany). Aqueous 0.1 M NaNO₃ solution adjusted to pH = 12 with NaOH was used as an eluent at a flow rate of 1.0 mL/min. The value of *dn/dc* used to calculate Mw was 0.135 mL/g (value for polyethylene oxide).¹⁰

Specific anionic charge amount – The specific anionic charge of the polymers was determined in alkaline solution (pH = 12) utilizing a particle charge detector PCD 03 pH (Mütek Analytic, Herrsching, Germany). In this experiment, solutions of 0.2 g/L of the polymer samples were adjusted to pH = 12 with NaOH and titrated against an aqueous 0.162 g/L solution of polydiallyl dimethyl ammonium chloride (polyDADMAC) until charge neutralization (zero potential) was reached. From the amount of polyDADMAC consumed to reach a zero potential, the amount of negative charge per gram of polymer was calculated.

Adsorbed amounts – Adsorption on cement was determined using the depletion method, i.e. the non-adsorbed amount of polymer remaining in solution at equilibrium was measured by analyzing the total organic carbon (TOC) content of the solution. In a typical experiment, 30 g of cement, 9.0 g of DI water and the amount of superplasticizer to be tested were filled into a 50 mL centrifuge tube, shaken in a wobbler (VWR International, Darmstadt, Germany) for 2 minutes at 2,400 rpm and then centrifuged for 10 minutes at 8,500 rpm. The supernatant was filtered through a 0.2 µm syringe filter and diluted with 0.1 M HCl. The TOC content of the solution was determined by combustion at 890°C on a High TOC II instrument (Elementar Analysensysteme, Hanau, Germany). The difference between the carbon content of the reference polymer and the TOC content of the supernatant reflects the adsorbed amount of superplasticizer. Measurements were generally repeated twice and the average was reported as adsorbed amount.

¹³C NMR measurements – All ¹³C NMR spectra were recorded in D₂O at 25°C and a polymer concentration of 30 mg/mL using a Bruker AV500cryo spectrometer operating at

500 MHz and equipped with a cryo magnet. In each measurement, 512 scans and a relaxation delay of 8 s were performed to obtain quantitative results.

RESULTS AND DISCUSSION

Characterization of synthesized PCE samples

Two different synthesis methods (copolymerization and grafting) were selected to prepare PCE samples which were then compared with respect to their individual microstructures. Based on some of our previous experiments where representative samples were pulled during the copolymerization process and analyzed it was expected that the two methods will produce PCEs with different distribution of the side chains along the main chain. According to our earlier observations, MAA and MPEG-MA exhibit different reactivities, with the macromonomer reacting faster than methacrylic acid. This result differs from earlier findings of *Smith* and *Klier*.¹¹ They reported that in D_2O , MAA and PEG-MA show comparable reactivity ratios while in a 50/50 ethanol- D_2O mixture, the macromonomer reacts faster, confirming our observation. Consequently, these discrepancies required clarification.

Based on our conception of different reactivity ratios for the monomers in radical copolymerization it was expected that this method will produce PCEs with a gradient-like distribution of the $-\text{COO}^-$ group whereas from the grafting process, polymers possessing a statistical (random) distribution of the side chains should result. To investigate this point, PCE polymers possessing molar ratios of $-\text{COO}^-$ to side chain of 2, 3, 5, 6 and 10 were synthesized using both methods, free radical copolymerization and grafting technique. The general chemical structures of the two series of PCEs used in this study are shown in **Figure 1**.

The synthesized polymer samples were characterized by SEC. The chromatograms (not shown here) confirmed high purity and uniformity for all polymers. Molar masses (M_w , M_n), PDI, hydrodynamic radii and conversion of the PCE samples are shown in **Table 3**. The data show that the grafted PCEs have a slightly more narrow molecular weight distribution and therefore lower PDIs in comparison to the copolymerized PCE samples. All copolymerized PCEs exhibit molecular weights in the range of 13,500 to 30,000 g/mol whereas the molar masses of the grafted PCEs decrease as a result of the decreasing number of side chains at constant length of the PMAA backbone. For all PCE samples, the anionic charge amounts increase linearly with increasing MAA content. Interestingly, the specific anionic charge of grafted PCE samples consistently is slightly lower than those of the copolymerized samples. The reason behind this difference remained unclear, because the additional charge contribution provided by the chain transfer agent used in the copolymerization process should be almost negligible.

Microstructural analysis via ^{13}C NMR spectroscopy

To determine the chemical shift of the ^{13}C resonance signals representing the carboxylate and the ester carbon atoms, the spectra of pure PMMA and of a PCE without carboxylate groups holding only side chains designated as 23PC0 were captured first. From **Figure 2** it is evident that the carbon atoms present in the carboxylate groups ($-\text{COO}^-$) appear as a sharp signal at a chemical shift δ of ~ 187 ppm while the carbon atoms of the ester group ($-\text{COOR}$) occur as a broad signal in the range from ~ 176 –181 ppm. According to literature,

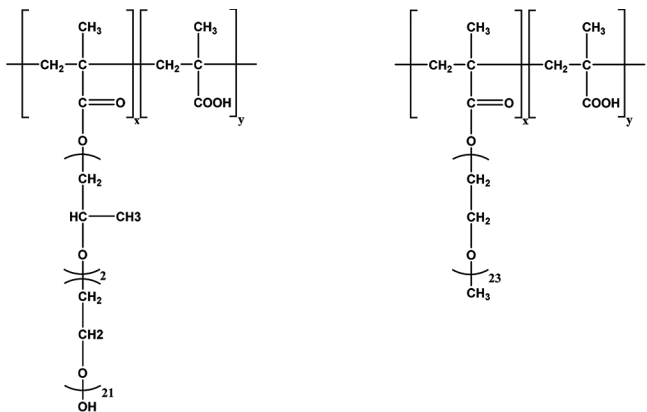


Figure 1 – General structures of the copolymerized (left) and grafted (right) MPEG type PCE samples prepared for this study.

Table 3 – Molecular weights, polydispersity index, hydrodynamic radius, anionic charge 226 and conversion of the PCE samples prepared via copolymerization or grafting.

Polymer sample	M_w [g/mol]	M_n [g/mol]	PDI	$R_{h(z)}$ [nm]	anionic charge in NaOH (pH = 12) [μeq/g]	conversion [%]
23PC2	25,000	12,600	2.0	4.3	2,200	92
G-23PC2	29,500	14,900	2.0	4.7	1,600	95
23PC3	26,900	11,900	2.3	4.5	2,800	93
G-23PC3	22,400	11,800	1.9	3.9	2,200	96
23PC5	24,000	12,200	2.0	4.0	3,600	92
G-23PC5	18,000	9,700	1.9	3.4	3,100	97
23PC6	30,000	11,900	2.5	5.8	4,400	93
G-23PC6	16,800	8,800	1.9	3.5	3,700	96
23PC10	26,700	13,100	2.0	4.7	11,300	92
G-23PC10	13,500	7,300	1.8	3.0	9,700	96
PMAA	6,800	5,700	1.2	1.5	14,500	—

the carbon signals will shift depending on whether electron accepting or electron donating groups are present in the vicinity of these carbon atoms.⁸ For example, a high amount of acid groups in the vicinity of a carboxylate carbon atom causes a shift to a lower field (= higher value of chemical shift δ) while a high amount of electron donating ester groups next to a carboxylate group leads to a high field shift of the signal. Using this approach it can be determined whether a PCE molecule holds large blocks of $-\text{COO}^-$ groups, or whether a rather homogeneous (statistical) distribution of side chains along the main chain exists.

As an example the complete ^{13}C NMR spectrum of PCE sample G-23PC5 is presented in **Figure 3**. There, the section at $\delta = 176\text{--}187$ ppm which holds the information about the repartition of $-\text{COO}^-$ groups in the PCE copolymer is shown enlarged. Thus, in further

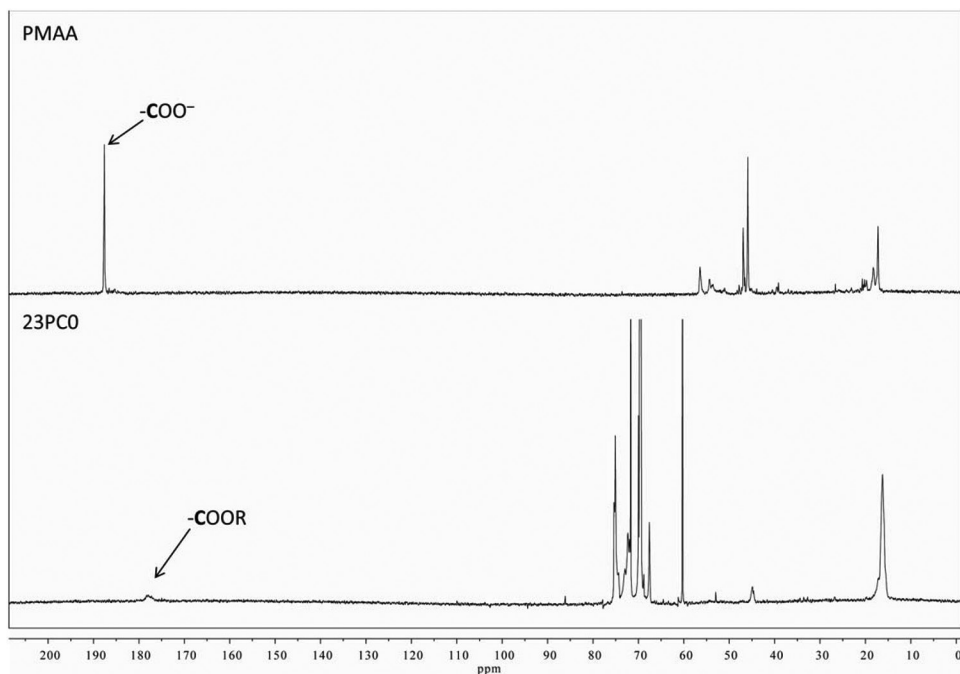


Figure 2 – ^{13}C NMR spectra of the reference polymers PMAA (top) and 23PC0 (bottom), measured in D_2O

analysis of all PCE samples only the range of chemical shifts between $\delta = 176\text{--}187$ ppm signifying the carboxylate/ester carbon atoms was looked at.

For analysis of the PCE samples, the carboxylate carbon atom signals were divided into two segments: carbon atoms mainly surrounded by $-\text{COO}^-$ carbons as represented in area (a) (see **Figure 4**), and carbon atoms surrounded by $-\text{COO}^-$ and ester or mainly ester carbon atoms in area (b). According to **Figure 4** it becomes obvious that copolymerized PCEs generally contain larger segments of (a) than the grafted PCEs. This signifies that the copolymerized PCEs contain larger blocks of $-\text{COO}^-$ along the main chain, compared to the gradient-like distribution of comonomers in the copolymerized PCE samples which apparently is owed to the different reactivities of MAA and the macromonomer. Such disparaged incorporation of the monomers leads to blocks of methacrylic acid within the copolymer and therefore to increased intensity of the signals in range (a) (see **Figure 4**). In contrast to that, for the grafted polymers G-23PC2 to G-23PC5 this signal is either weak in intensity or completely missing which confirms a statistical distribution of $-\text{COO}^-$ and ester groups along the polymer trunk.

However, for the PCE samples G-23PC6 and G-23PC10 possessing high charge density (= low grafting density) the difference between the carbon signals of grafted and copolymerized PCEs becomes smaller. Thus, for the corresponding copolymerized and grafted polymer samples, both the shape of the carboxylate signal and its chemical shift are comparable. This suggests that at high anionic charge density, the microstructures of copolymer-

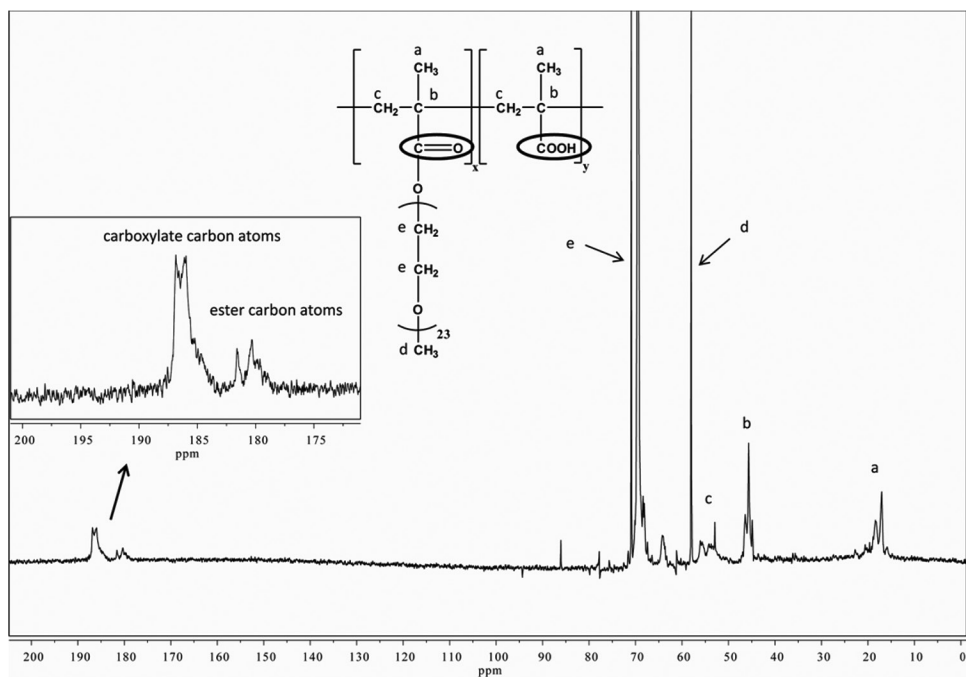


Figure 3 – Typical ^{13}C NMR spectrum of PCE sample G-23PC5, measured in D_2O at $\text{pH} = 7$; insert: magnification of the carbonyl region.

ized and grafted PCE samples converge, as is schematically shown in **Figure 5**. Whereas at low anionic charge density, the copolymerized PCE samples still possess significant blocks of polymethacrylic acid and of the PEG polyester. Such structural disparities do not occur in the grafted PCE samples.

In order to understand whether those microstructural differences translate into a different interaction with cement, adsorption isotherms of the PCE samples on cement were determined (see **Figure 6**). Note that under the experimental conditions chosen here the adsorption behavior of the PCE samples is mainly influenced by the type and reactivity of C_3A (i.e. the surface area of the ettringite produced).

For all PCE samples, the tendency as expected was observed: at increased charge density, the maximum adsorbed amount of polymer increases. When comparing the copolymerized and the grafted PCE polymers, however, it becomes obvious that the grafted copolymers consistently produce lower saturated adsorbed amounts than the copolymerized ones. Those variations appear to become smaller at increased charge density. For example, sample G-23PC2 adsorbs only half of the amount of 23PC2 while the maximum adsorbed amounts of samples G-23PC10 and 23PC10 are similar. This conversion of copolymerized and grafted copolymers exhibiting high charge density correlates well with the observations made in the ^{13}C NMR spectra and the microstructural analysis (see **Figure 4**).

To confirm the model that the adsorption tendency of PCE is owed to the amount of COO^- groups present, a PCE molecule without carboxylate groups (a homopolymer of the

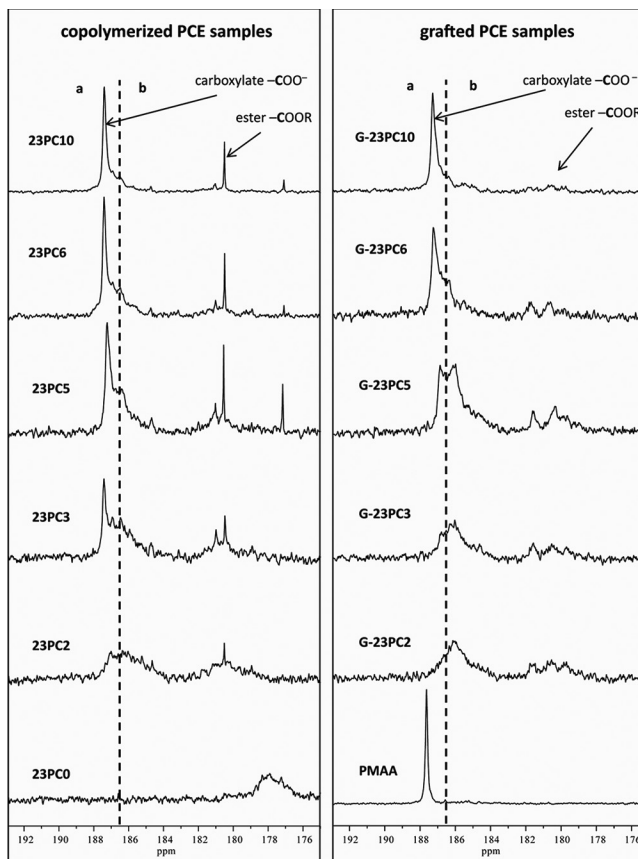


Figure 4 – ^{13}C NMR signals of the carboxylate and the ester carbon atoms of copolymerized (left) and grafted PCEs (right), recorded in D_2O at $\text{pH} = 7$. Spectra of polymethacrylic acid (PMAA) and of a completely esterified polymer (23PC0) are shown for reference (bottom).

macromonomer) was synthesized via radical copolymerization. When mixed into cement paste, no adsorption at all was detected thus confirming the strong influence of the $-\text{COO}^-$ blocks on the adsorption behavior of PCEs.

Generally, a polymer with a gradient distribution of carboxylate groups is more likely to adsorb in a “tail” conformation, as the blocks of $-\text{COO}^-$ groups provide particularly strong electrostatic attraction to the surface of cement. However, such adsorbed conformation leads to only partial coverage of the surface of cement particles, as is schematically illustrated in **Figure 7**. Whereas, polymers exhibiting a statistical repartition of carboxylate groups can be expected to adsorb in a “loop” conformation whereby a larger area of the surface is covered (**Figure 7**). Consequently, there a lower amount of polymer should be required to achieve the same surface coverage as from a copolymer with a gradient-like

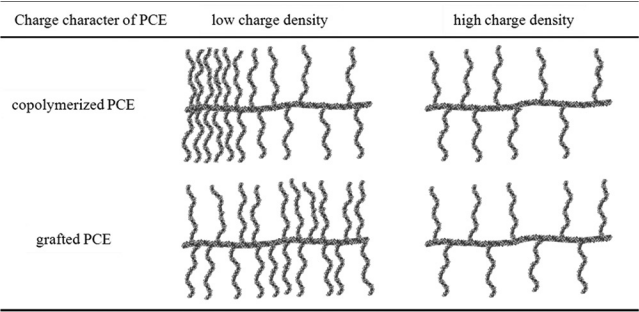


Figure 5 - Schematic illustration of the microstructure of copolymerized and grafted PCE samples in dependence of their charge density.

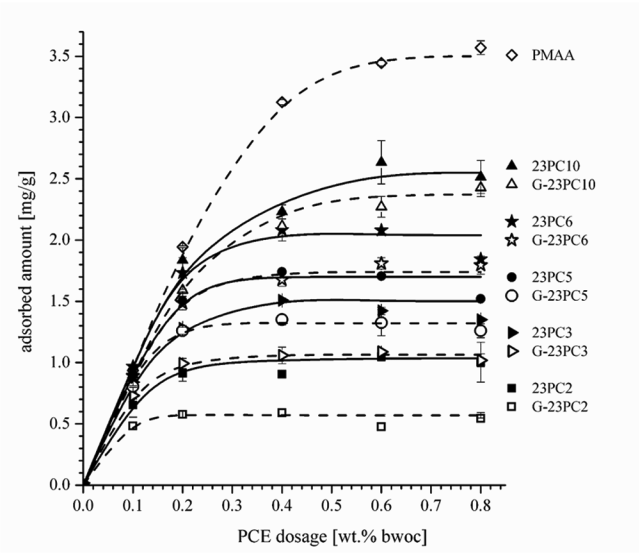


Figure 6 - Adsorption isotherms on cement of PCE samples synthesized via copolymerization or grafting.

microstructure. This effect can also explain the lower adsorbed amounts for the grafted PCEs. However, at increasing charge density the gradient structure converges into a more random one which is similar to that of the grafted PCE (Figure 5). Accordingly, both types of PCE (copolymerized and grafted) now adsorb in a “loop” conformation which results in quite comparable maximum adsorbed amounts.

CONCLUSION

MPEG-type PCE superplasticizers were synthesized via two different methods resulting in polymers possessing different microstructures. ¹³C NMR spectroscopic measurements

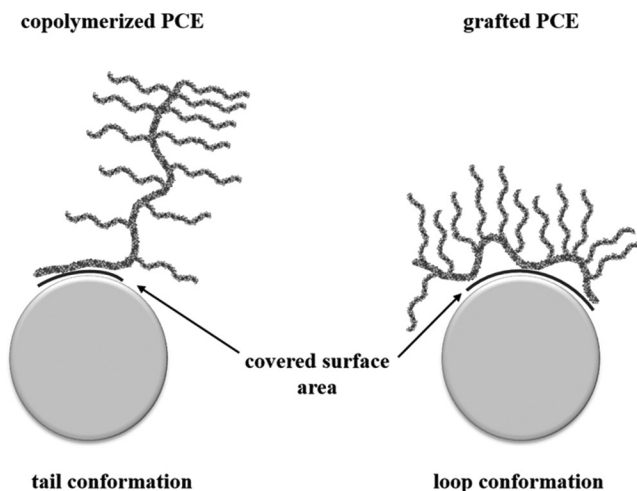


Figure 7 – Idealized illustration of the adsorbed conformations of PCE samples with gradient (left) and statistical (right) distribution of carboxylate groups along the trunk chain.

revealed a gradient-like distribution of the side chains for the copolymerized PCEs and a statistical (more regular) distribution of the side chains for the grafted PCEs. With increasing charge density those structural differences become smaller which is also reflected in the interaction between the polymers and cement. At high side chain density, copolymerized PCEs possessing a gradient structure adsorb in higher amounts on cement due to enhanced accessibility of the charged parts. However, for PCE polymers exhibiting high charge density (= low side chain density), such differences in the maximum adsorbed amounts for the copolymerized and the grafted PCEs disappear.

The study demonstrates that a microstructural analysis of individual PCE polymers is possible and that differences in the microstructure can affect the behavior of PCE superplasticizers in cement.

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ACKNOWLEDGEMENTS

Julia Pickelmann wishes to thank Dow Europe for sponsoring her Ph.D. and Li Huiqun expresses her gratitude to “TUM Center For Advanced PCE Studies” for supporting her stay as a guest researcher.

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Effects of Particle Volume Fraction and Size on Polysaccharide Stabilizing Agents

by Wolfram Schmidt, Sarah Peters, and Hans-Carsten Kühne

Polysaccharides modify the rheological properties of cement based systems. Depending upon their chemistry, molecular architecture, and adsorption tendency, they have different modes of action. Some polysaccharides like diutan gum have strong effect on the fluid phase; others like starch strongly interact with particles. This paper presents effects of diutan gum and starches in presence of polycarboxylates. Rheometric investigations with varied particle volume fractions and increasing coarse aggregate diameters were conducted. The results show that starches have stronger influence on the rheology at high particle volume fractions than diutan gum. At lower particle volume fractions this trend is inverted. Experiments with aggregates sizes up to 16 mm (0.63 in.) indicate that stabilizing agent influences on the effects of aggregates on yield stress were small; however up to 1.0 mm (0.04 in.), a significant effect on the plastic viscosity could be observed, which levelled off at larger diameters.

Keywords: diutan gum; starch; polysaccharides; polycarboxylate ether; volume fraction.

INTRODUCTION

Today, the fresh properties have become a characteristic item to designate various classes of concrete. For many concrete types, such as self-consolidating concrete (SCC) or ultra-high performance concrete (UHPC), the rheological properties directly affect their performance at hardened state. The major driving force for innovations in concrete technology over the last three decades has been brought by the invention and steady enhancement of superplasticizers, since they allow uncoupling the workability properties from the water content.¹ The main relevant rheological properties for cement based systems are the yield stress (τ_0) and the plastic viscosity (η_{pl}), which describe the minimum shear stress that needs to be exceeded in order to make a system flow and the resistance of a flowable system against a shear deformation, respectively.

However, sophisticated rheological properties in complex multi-phase systems like concrete come along with a high risk of failure as soon as the boundary framework changes. Since the function of superplasticizers depends upon the adsorption on the early cement hydration phases AFt and AFm, any influence that accelerates or slows down cement

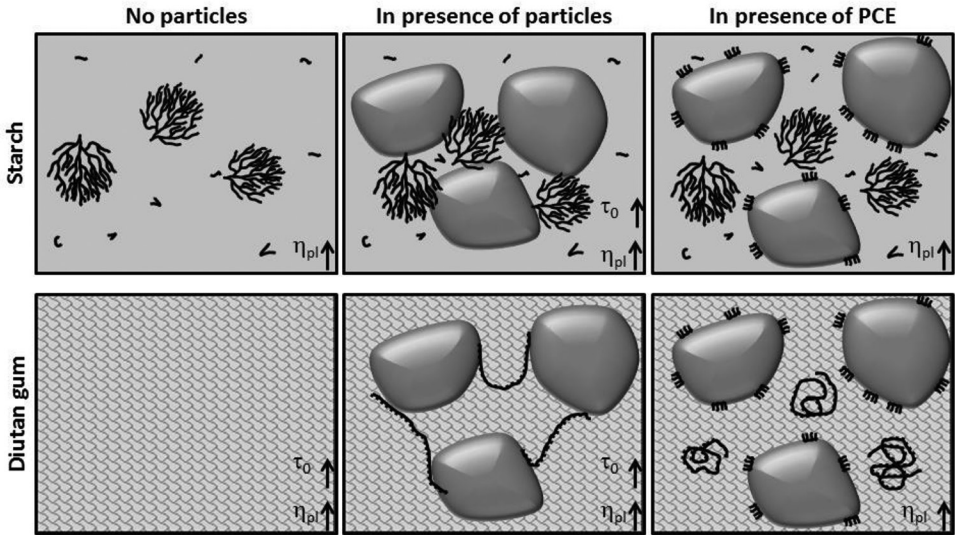


Fig. 1—Possible effects of diutan gum and starch based STA without and in presence of PCE.

hydration at a very early point in time after water addition can automatically affect the rheological properties.²⁻⁴ Therefore, unexpected effects that affect the cement hydration at early age can yield both, unwanted stagnation or segregation.

A stabilizing agent (STA) can help reduce unwanted loss of flowability or segregation. Therefore, their application has gained increasing interest in the scientific research.⁵⁻¹⁵ For the stabilization of cement based systems, polysaccharides such as cellulose, starch, or bio-gums (e.g. sphingans) are typically used. Depending on their molecular weight, radius of gyration, and ionic charges, they affect the rheology of cement based systems in different ways. The stabilizing mechanisms can be based on the water binding capacity,^{5,7} the viscosity modification of the pore solution,^{8,15} depletion forces,^{9,14} or effects induced by the sheer size of the polymers causing interactions with particles,^{8,9} which can have radii of gyration as large as 500 nm, or if still agglomerated even larger.

For the understanding of the working mechanism of STAs, it is also of highest importance to take into account that superplasticizers can have a significant influence on their efficiency. These influences are shown in Fig. 1. It was found that in systems without superplasticizers, starch had only a tangible effect on the yield stress (τ_0) at higher particle volume fractions, while diutan gum increased τ_0 already without the presence of particles. Approximately 20% of the starch consists of amylose, a linear glucose chain, and about 80% consists of amylopectin, which is a huge branched molecule formed by glucose chains. The effect of the starch was mainly attributed to the effects of the amylopectin molecules, which interact with small solid particles like spacers but require interacting particles for activating their stabilizing effect. The effect of the diutan gum, which contains anionic groups in the backbone, was attributed to water absorption and thickening of the fluid phase as well as adsorption on cement and hydration phases. However, in the presence

Table 1—Stabilizing agent modifications used for the investigations and dosages required to achieve η_{PI} of 3.5 mPa•s

	Diutan gum	Starch with low degree of modification	Starch with high degree of modification	Cationic starch	Anionic starch
Abbreviation	DGUM	ST-low	ST-high	ST-cat	ST-an
Dosage to achieve $\eta_{PI} = 3.5 \text{ mPa}\cdot\text{s}$ in water [% by mass of water]	0.04%	0.84%	1.3%	1.04%	0.44%

of superplasticizer, effects of STA adsorption retreated into the background and both STAs showed only negligible effects on τ_0 but maintained a strong effect on the plastic viscosity η_{PI} .^{9,13}

It is hence becoming obvious that for the understanding of STAs, it is necessary to distinguish between systems with and without superplasticizers as well as to take into account the particle volume fraction Φ_p and possible interactions between STAs and particles. This study aims at understanding these influences for diutan gum and various starch modifications in limestone filler (LSF) and cement based flowable systems as well as to look at whether the aggregate size and volume fraction may have an effect on the efficiency of STAs.

RESEARCH SIGNIFICANCE

Today, the use of superplasticizers has become common practice for flowable concrete. However, flowable concrete systems often lack stability, and therefore may need to be amended by stabilizing admixtures, which are typically based on polysaccharides. Their mode of operation is not very well understood today. Being able to manipulate the rheology has become of utmost importance for bringing innovative concrete into practice. The present study investigates interactions of polysaccharides with superplasticizers, cement hydration, particle volume fraction, and the sand and aggregates. The goal is better understanding of the mode of operation of these materials.

EXPERIMENTAL INVESTIGATION

Materials

In order to understand effects of different STA modifications, investigations were conducted on paste, mortar, and concrete matrices. The observations were focused on diutan gum and a variety of starches. Two starches were modified at different degrees with hydroxypropyl groups, another starch was modified with cationic groups, and another with anionic groups. The STAs that were evaluated are listed in Table 1. Their dosages were adjusted in a way that a plastic viscosity (η_{PI}) of 3.5 mPa•s in water was achieved. These required dosages to achieve this property are listed for each STA in Table 1.

Paste investigations were conducted at varied particle volume fractions Φ_p with LSF and with cement, respectively. Their specific gravities can be found in Table 2. For the LSF pastes, Φ_p was varied between 0%, 33%, and 50%. For the cement pastes, Φ_p was varied

Table 2—Specific gravities of mixture constituents and mixture composition for SCC

	Cement	Lime stone filler	Water	Sand				Aggregate	
				0.1-0.5 mm	0.5-1.0 mm	1.0-2.0 mm	2.0-4.0 mm	4.0-8.0 mm	8.0-16 mm
Spec. Gravity [-]	3.13	2.74	1.00	2.60	2.60	2.60	2.60	2.60	2.60
Net weight [kg/m ³]	354	130	177	331	192	192	126	126	702
Volume frac- tion [%]	11.3	4.8	17.7	12.7	7.4	7.4	4.9	4.9	27.0

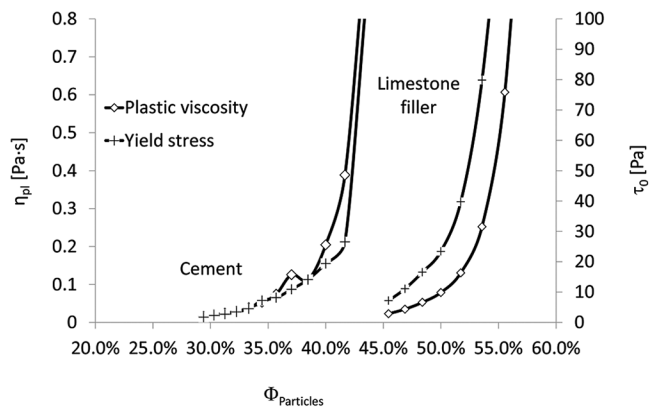


Fig. 2—Influence of the particle volume fraction on τ_0 and η_{pl} of LSF and cement pastes.

between 0%, 25%, and 40%. The reason is the stronger influence of Φ_p on the increase of both yield stress (τ_0) and η_{pl} in cement based systems, as can be found in Fig. 2.

The influence of different dosages of polycarboxylate ether superplasticizer (PCE) was also investigated in LSF and cement pastes. These investigations were conducted at Φ_p of 50% and 40% for LSF and cement pastes, respectively. The dosages of PCE were varied between 0% and 1% by mass of solid PCE related to the mass of solid particles.

Mortar and concrete investigations were conducted on a mixture composition for SCC, which is shown in Table 2. The aim was to identify influences of Φ_p and the maximum particle diameter. Therefore, rheometric investigations were conducted on paste, mortar and concrete with varied solid volume contents and maximum grain sizes according to Table 2. Pure systems without STA were compared with systems incorporating DGUM and ST-low. The STA dosages were as in Table 1 and the PCE dosage was 0.68% solids by the cement mass. The PCE in use was a low charge density PCE. The respective dosage provided a long flow retention at a slump flow value of 650 mm (25.6 in.) at 30 minutes after water addition.

Table 3—Measurement regime for rheometric paste investigations.

Profile characteristic	Upward ramp	Plateau	Downward ramp
Time	0 s - 30 s	30 s - 60 s	60 s- 240 s
(max.) Shear rate [1/s]	0 to 73.5	73.5	73.5 to 0
Purpose	-	-	Flow curve determination

Mixing of pastes and mortars

For all mixes, the STAs were always first dissolved in a blender mixer in the water for the mixture addition. The mixing of the pastes and mortars was conducted in a mortar mixer. After a 30 s dry mixing phase, water including STA was added and mixed for 2 minutes. Then (if required) PCE was added and mixing was continued for another minute. In order to avoid peculiar initial effects induced by the hydration of ettringite and monosulfate, the experiments were conducted approximately at 10 minutes after the water addition.

Paste rheometry

For the investigations of the rheological properties of pastes, a Couette type viscosimeter (Schleibinger NT) was used in combination with a double gap cell with a network structured grid as shear body. The cell allows the measurement of pastes and mortar up to a grain size of 2 mm. Since shear forces affect the cement hydration and the adsorption of polymers, for cementitious systems it is of utmost importance to keep the measurement time as short as possible. The applied profile is shown in Table 3. It is considered to be a reasonable compromise between precision and compactness. For the conversion of the flow curves, a Bingham approximation was chosen. Though this does not take into account shear thinning effects that were observed to certain extent in some systems, it is in good agreement with the results for all Φ_p and admixture dosages, and the comparison between the pastes is facilitated.

Mortar rheometry

For the rheometric mortar investigations in systems containing sand in the size fractions 0.1 mm to 4.0 mm (0.004 - 0.16 in.) the same rheometer was used as for the paste investigations. However, a mortar cell including a stirrer was used. The cell does not allow the conversion to fundamental units, but it allows determining an ordinate intercept and a slope of the measured torque, which can provide relative information on differences in yield stress and plastic viscosity.

Concrete rheometry

For concrete with aggregate sizes 4.0 mm to 16.0 mm (0.16 - 0.63 in.), a concrete rheometer (Rheometer-4SCC) was used. Like for the mortar equipment used in these investigations there is no reliable method for the conversion of torque and rotational velocity into shear stresses and shear rates, the results can only provide qualitative information on changes in yield stress and plastic viscosity. Therefore the measurements are referred to as G-Yield for qualitative observations of yield stress changes and H-Viscosity for qualitative changes of the plastic viscosity, respectively.

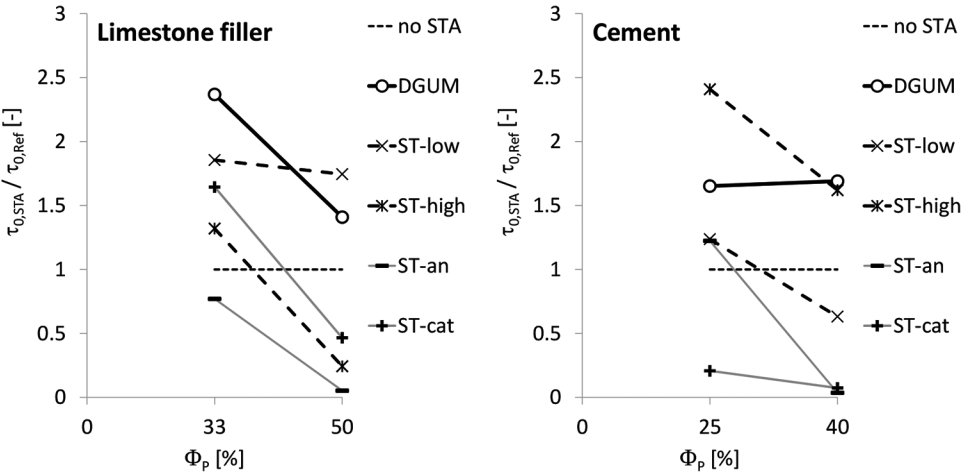


Fig. 3—Influence of Φ_p on τ_0 of LSF and cement pastes with different STAs

Paste slump flow tests

In addition to the rheometric investigations, slump flow tests were conducted with varied dosages of PCE. In order to avoid segregation, they were conducted at a water volume, which just surrounds the particles and fills the voids in between but without any excess water. This water demand was determined according to the so called Puntke test.^{2,16,17} The slump flow tests were conducted 10, 20, and 30 minutes after the addition of water. Furthermore, paste slump flow tests were conducted at fixed PCE and STA dosages with varied cement volume fractions varying between 69.8% and 63.5%. Below 63.5% the cement pastes were no longer free from segregation at the used dosage of PCE.

EXPERIMENTAL RESULTS AND DISCUSSION

Paste rheometry at varied particle volume fraction

The effect of the different STAs on τ_0 depending upon Φ_p can be observed for LSF and for cement pastes in Fig. 3. Since the differences in τ_0 were strongly affected by the Φ_p , the figure shows results normalized to reference mixtures without STA. The figure therefore shows the ratio of τ_0 of a paste modified with STA in the dosage given in Table 1 and an identical paste without STA.

Apart from the anionic starch ST-an, all STAs increase the τ_0 of LSF pastes at $\Phi_p = 33\%$. ST-an shows lower values for τ_0 than the reference at 33% and at 50%, indicating that the anionic charges may interact with the LSF and have a plasticizing effect regardless of the Φ_p . At 50%, the yield stress increasing effect of the other STAs is reduced significantly for all STAs. Only for the ST-low this reduction is less significant than for all other STAs. ST-cat and ST-high show lower τ_0 at that solid volume fraction than the reference.

In the cement pastes at low Φ_p all STAs apart from the cationic starch show higher τ_0 than the reference, while this effect is reduced at higher particle solid volume fraction. An exception is DGUM. No effect of Φ_p on how DGUM increases τ_0 can be observed, while

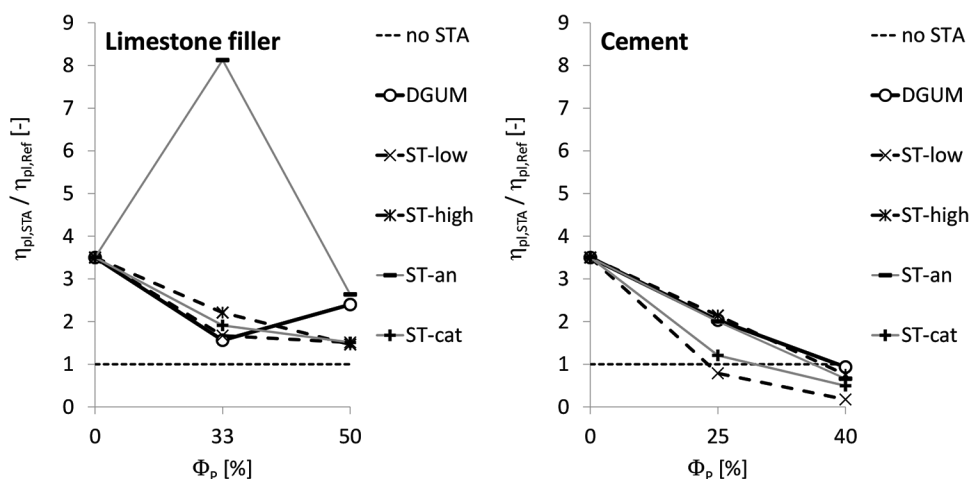


Fig. 4—Influence of Φ_p on η_{pl} of LSF and cement pastes with different STAs

in LSF paste this drop is significant. The attractive forces in a LSF system are significantly lower than in a cement system. Therefore, the lower influence of Φ_p on the effect of the DGUM in the cement system may be attributed to higher adsorption compared to the LSF system. The higher adsorption would withdraw polymers from the solution that would otherwise increase the solution's viscosity.

For ST-high, a similar drop of the yield stress effect can be observed in LSF and cement systems; however, the effect of this STA is much stronger in the cement system. For ST-low, which has a strong effect in limestone paste but not in cement paste, this observation is inverted. The reason for this effect could be that the higher ionic strength of the cement pore solution may negatively affect the performance of the slightly modified agent, e.g. by causing interactions within the huge amylopectin molecule or by linking amylose and amylopectin. The higher degree of modification of ST-high may more effectively prevent such interactions.

A prominent observation is that the anionic and the cationic starch exactly show inverted behavior in LSF and in cement systems. Both show a plasticizing effect at high Φ_p , indicating that they induce electrostatic repulsive forces. However, at low Φ_p this plasticizing effect can only be observed for ST-an in limestone and for ST-cat in cement pastes. It is known that LSF in water attracts anionic polymers.² It is therefore likely that in LSF pastes the adsorption of ST-an incorporates repulsive forces, while this adsorption is reduced in the cement system due to the presence of sulfates.

Fig. 4 shows the effect of Φ_p on η_{pl} . For the LSF system, it can be observed that apart from ST-an, all starch based STAs showed reduced effects of the STAs with increasing amount of Φ_p . For DGUM at $\Phi_p = 50\%$, an increasing effect can be observed, which is similar to the effect of the ST-an. Both STAs have anionic charges, so that this effect is likely to be attributed to their adsorption on particles. The strong effect of the ST-an on the viscosity increase relative to the reference system at $\Phi_p = 33\%$ indicates that the huge amylopectin molecule may bridge particles with increasing effect on η_{pl} . In this context, it is interesting

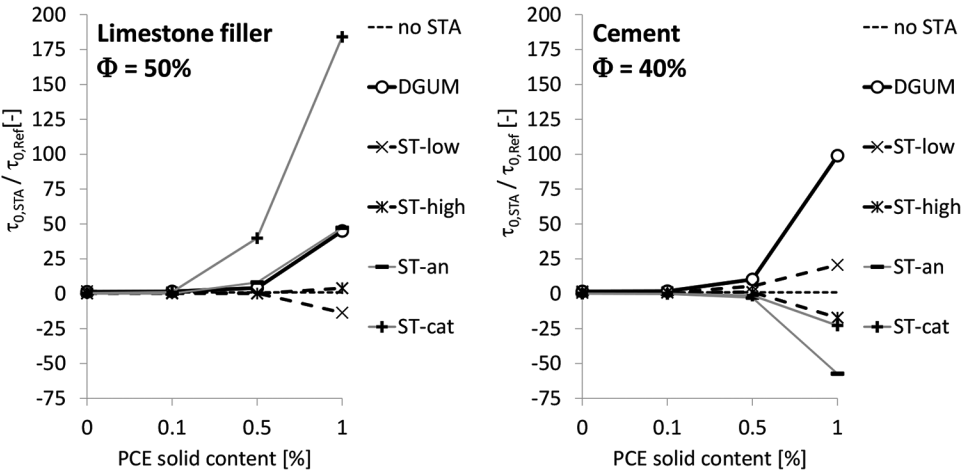


Fig. 5—Influence of the PCE dosage on τ_0 of LSF and cement pastes with different STAs

to observe that at $\Phi_p = 50\%$ both anionic STAs show higher effect on η_{pl} , but as shown in Fig. 3, in terms of τ_0 only the starch based agent had a plasticizing effect. It is assumable that this plasticizing effect may be induced by the adsorption of mainly the small amylose molecules, while the viscosity increase is caused rather by the huge amylopectin molecules and thus similar to the effect of the DGUM. In cement based systems, it can be observed that a Φ_p of 25% causes reduced effectiveness of the STAs, which further reduces at 40%. At 40%, the plastic viscosities of all systems were lower than the reference.

Paste rheometry at varied PCE dosage

In order to observe effects of STAs in presence of superplasticizers, LSF and cement pastes were evaluated at Φ_p of 50% and 40% for LSF and cement, respectively, at varied PCE dosages. Upon addition of PCE, τ_0 was reduced significantly for all mixtures. Fig. 5 shows the ratios of τ_0 with STA compared to systems without STA.

For the LSF system, it is interesting to see that the two non-ionic STAs both do not distinguish greatly from the reference paste, regardless of the PCE dosage. The anionic admixtures, ST-an and DGUM, both show a horizontal curve up to a PCE dosage of 0.5% above which they generate a higher τ_0 than the reference system. It is assumable that competitive adsorption between the STAs and the PCEs takes place causing less adsorption of PCE, which increases τ_0 . For the cationic starch, it can be observed that above a PCE dosage of 0.1% τ_0 is always higher than in the reference system. In this case it is most likely that the cationic starch interacts with the anionic PCEs, which reduces their adsorption, which automatically increases τ_0 .

In the cement system, up to a dosage of 0.5% the observations are similar to those of the limestone system with the only difference that the anionic starch ST-an does not have a different effect on τ_0 than the other agents. At 1% PCE dosage, the observations are more complex. What is common to the LSF system is the observation that the influence of the non-ionic starches is small also at 1% of PCE addition. The effect of the cationic starch

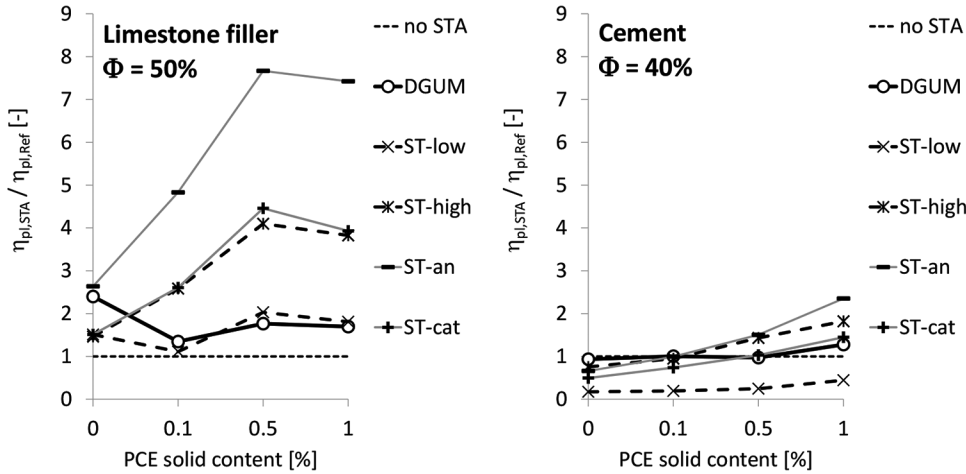


Fig. 6—Influence of the PCE dosage on η_{pl} of LSF and cement pastes with different STAs

is smaller than that of the other charged agents. In case of ST-cat τ_0 is lower than that of the reference, which is different to the limestone filler system. Also τ_0 of the paste with the anionic starch is lower than the reference. Only for the diutan gum STA a significantly higher τ_0 can be observed at 1% PCE. The reason for this can be attributed to a competitive adsorption that reduces the effect of the PCE. However, it is interesting to see that the anionic starch shows an adverse effect. This may be caused by adsorption mainly of the amylose molecules, which may be responsible for a supplementary fluidizing effect as already shown in Fig. 3. The large amylopectin molecule may not be found adsorbed directly on the surfaces. This would also explain why the anionic and the cationic starch show similar behavior.

The results for the ratio $\eta_{pl,STA}/\eta_{pl,Ref}$ is shown in Fig. 6. It can be found that in the LSF system, all STAs maintained η_{pl} significantly higher than in the reference system. The ST-an, ST-cat and the ST-high became particularly effective at high PCE 0.5% PCE dosage, and this effect was maintained also at 1% PCE.

In the cement system, all pastes with STAs had a lower η_{pl} than the reference. However, with increasing PCE dosage, they became increasingly more efficient in generating higher plastic viscosities than the references. At PCE dosages above 0.5% all STA modified systems apart from the system with ST-low showed higher plastic viscosities than the reference with an increasing trend for higher PCE dosages. The least effect could be observed for ST-low. Only at 1% PCE dosage a slightly viscosity enhancing effect can be observed.

It can be assumed that compared to the adsorption of PCE, adsorption of STAs has a negligible effect on η_{pl} (different from τ_0). Therefore, the yield stress enhancement compared to the reference is most likely induced mainly due to the pure presence of large polymers in the pore solution.

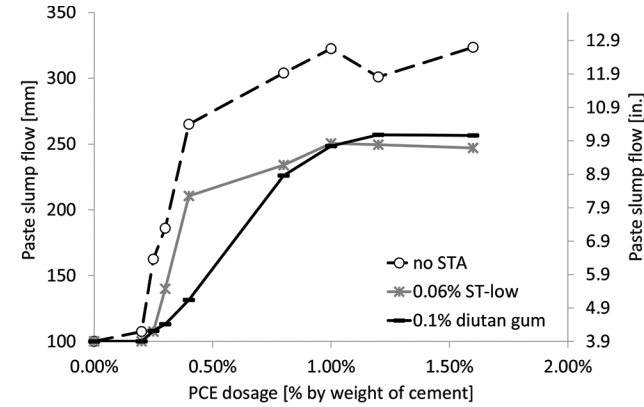


Fig. 7—Influence of the presence of STA on the slump flow of cement pastes with different dosages of high charge PCE at $\Phi_p = 0.6$. The dosage of starch was selected to achieve a similar slump flow reduction at the PCE dosage that yields the maximum slump flow.

Influence of STA on the effectiveness of PCE

It was shown that the presence of PCE can have a significant influence on how effective stabilizing admixtures are. In order to better assess this interaction, flow tests on cement pastes were conducted with increasing PCE dosages. Due to the high powder particle fraction, the observed pastes do not show any flow without PCE addition. For each PCE dosage, the water content of the PCE is reduced from the total water content, hence, the flow is only induced by the presence and dosage of PCE. A more detailed description of the experiment can be found elsewhere.² Without the presence of STA, the maximum flow of about 320 mm (12.6 in.) can be achieved at a PCE dosage of approximately 1% (Fig. 7), beyond which further addition of PCE does no longer contribute to a wider flow diameter. The flow initiation dosage is at approximately 0.2%. In a next step, it was observed how these values are changed by the addition of 0.1% DGUM, and it can be seen that the characteristic dosages for the flow initiation and maximum remain similar to the reference system without PCE. However, the maximum flow is significantly reduced to a value of approximately 250 mm (9.8 in.). In a further step, the dosage of ST-low was determined that causes a similar maximum flow as the system with DGUM. Based on the dosages listed in Table 1, the first attempts were conducted at significantly higher dosages than for the DGUM system. However, it was found that these systems were not flowable at all. Eventually, the dosage that showed performance like DGUM was only 0.06% of the starch.

The fact that in water and low Φ_p systems, the DGUM was required at significantly lower dosages than the starches for similar flow properties (Table 1). But since this is obviously inverted at very high Φ_p (Fig. 7), it is recommended to test the influence of the Φ_p . Fig. 8 shows results of slump flow values at 1.0% PCE and in the presence of 0.1% ST-low and DGUM dosage, respectively. This PCE dosage was the dosage that yielded the maximum flow for the reference systems in the tests shown in Fig. 7.

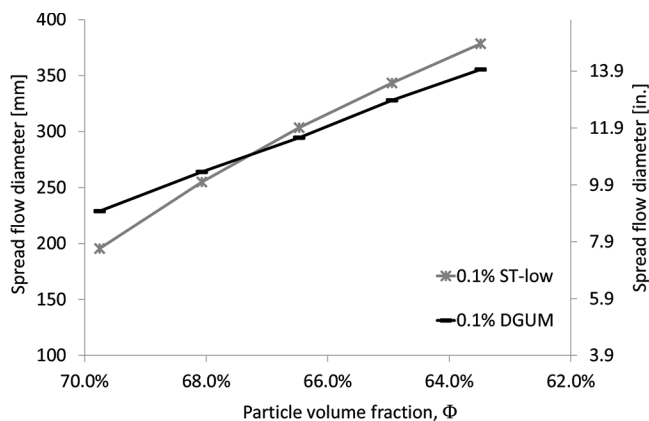


Fig. 8—Influence of the particle volume fraction of cement pastes on the effectiveness of starch based and diutan gum based STA.

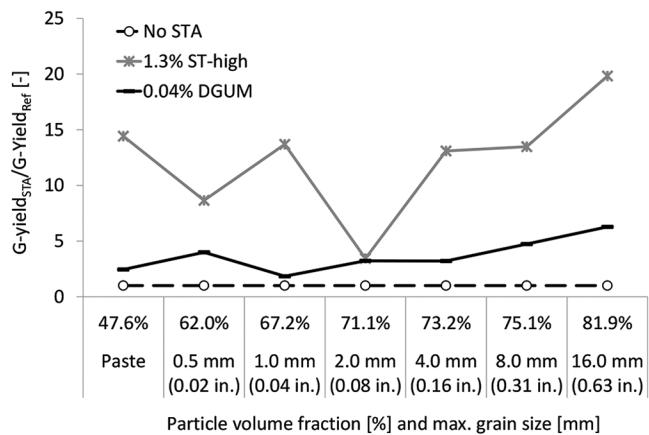


Fig. 9—Influence of the maximum particle size diameter and the particle volume fraction on the effectiveness of stabilizing agents to affect the τ_0 .

It can be clearly identified that indeed the starch addition causes a smaller slump flow than the diutan gum at a very high solid volume fraction of 69.8%. This effect is reduced with decreasing solid volume fraction. At a solid volume fraction of approximately 67%, both STAs have similar effects on the slump flow, while with decreasing Φ_P the diutan gum becomes more and more efficient. It is hence obvious that Φ_P has a very strong effect on the effectiveness of different STAs in flowable systems.