

## Synthesis and Performance of a Modified Polycarboxylate Dispersant for Concrete Possessing Enhanced Cement Compatibility

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**ABSTRACT:** It is well established that the performance of polycarboxylate (PCE) superplasticizers can be severely affected by the composition of individual cements. Here, a novel allylether/maleic anhydride (APEG)-based PCE was synthesized using allyl maleate monomer as a new, additional building block. When polymerized into the PCE main chain, this building block was found to form a cyclic lactone structure. The resulting PCE molecule was tested with respect to the dispersing force in cements possessing different phase compositions and alkali sulfate ( $K_2SO_4$ ) contents. These data were compared with those from conventional APEG- and methacrylate ester (MPEG)-type PCEs. Results obtained from cement paste flowability and adsorption measurements suggest that the modified PCE disperses all cement samples well and hence is more robust against variations in cement composition. Apparently, the new building block induces a higher affinity of the polymer to the surface of cement and can form a denser polymer layer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 346–353, 2013

**KEYWORDS:** adsorption; rheology; plasticizer; radical polymerization

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### INTRODUCTION

Polycarboxylate (PCE) superplasticizers are applied in the construction industry to produce highly flowable concretes such as e.g. self-compacting or high strength concrete which are characterized by a low water-to-cement ratio (w/c). Also, specially modified PCE superplasticizers can provide excellent fluidity retention over a time period of 2 h and more. Generally, PCEs are comb-shaped copolymers which consist of a negatively charged backbone holding carboxylate groups and grafted side chains commonly composed of polyethylene oxide units. The charged backbone can adsorb onto the surface of hydrating cement particles in three different ways, namely in train, loop or tail mode, while the nonadsorbed graft chains protrude from the cement surface into the pore solution.<sup>1</sup> The interaction between superplasticizers and cement is generally well understood.<sup>2,3</sup> The mechanism behind the dispersing effect of PCEs is based on steric hindrance between cement particles as well as electrostatic repulsion forces.<sup>4–6</sup>

It was observed that in concrete manufacturing, certain PCE molecules do not work well with specific cements, thus the flowability obtained at a given dosage of these PCEs was rather poor. Moreover, in some cases, the PCEs failed completely to provide any fluidity. This phenomenon is commonly referred to as “incompatibility” between cement and specific PCE products.

Various explanations have been presented for this behavior, such as the variation in clinker composition of cement, contamination of the concrete with clay or silt, and perturbation of PCE adsorption by sulfate ions released from cement (“sulfate effect”).<sup>7</sup> Because of these undesired effects, the usage of PCE superplasticizers in the concrete manufacturing industry has experienced some setback recently and prompted a partial revival of polycondensate-based superplasticizers.

The sulfate components present in cement can occur in four different forms: gypsum, hemihydrate ( $CaSO_4 \cdot 1/2H_2O$ ), anhydrite and alkali sulfates. Generally, sulfate has a remarkable impact on the properties of cement. Overdosing results in a false set which is owed to spontaneous crystallization of gypsum while a lack of sulfate in cements possessing a high calcium aluminate ( $C_3A$ ) content may lead to a flash set during the initial stage of hydration.<sup>8</sup>

Previous works have clearly shown the strong influence of alkali sulfates present in cement on the performance of PCEs as a result of their rapid dissolution and thus release of sulfate ions.<sup>7,9,10</sup> First, some researchers found that the sulfate content present in cement can significantly impede the flowability of the slurries containing PCE.<sup>9,10</sup> Opposite to this trend it was demonstrated that a high dosage of  $K_2SO_4$  may in fact enhance the workability retention (“slump loss behavior”) of certain PCEs.<sup>10</sup>

Consequently, some researchers believe that an optimum content of alkali sulfate exists for PCE performance.<sup>11</sup> As mechanistic explanation, it is presented that higher sulfate concentrations existing in cement paste cause lower adsorption of PCE.<sup>12</sup> Other researchers reported evidence that the side chain of PCE comb polymers might become compressed when elevated contents of sulfate ions are present in the cement pore solution. The corresponding shrinkage of the PCE molecule decreases the steric hindrance effect.<sup>9</sup>

Here, we report on the impact of different cement compositions and sulfate concentrations on the workability of concrete achieved by a specifically designed polycarboxylate molecule. First, its tolerance against three different cement samples possessing distinctly different tricalcium aluminate (C<sub>3</sub>A) contents was compared. Second, the behavior in the presence of increased amounts (0–2 wt %) of free dissolved sulfates (added as K<sub>2</sub>SO<sub>4</sub>) was probed utilizing the “mini slump” test. Additionally, adsorption isotherms were obtained to assess whether this PCE and sulfate actually involve in competitive adsorption. From this data it was aimed to propose a model explaining the difference in cement compatibility between conventional PCE and the novel PCE molecule which incorporates a new structural feature.

## MATERIALS AND METHODS

### Cement Samples

Three different cement samples (CEM I 32.5 R from HeidelbergCement, Rohrdorf plant/Germany; CEM I 42.5 R from HeidelbergCement, Geseke plant/Germany; and CEM I 52.5 R from Holcim, Lägerdorf plant/Germany), all ordinary Portland cements, were used in this work. Table I lists their phase compositions as determined by quantitative X-ray diffraction (XRD) analysis using *Rietveld* refinement and thermogravimetry. D8 advance instrument from Bruker-AXS (Karlsruhe/Germany) was used in the XRD analysis while thermogravimetry was performed on a STA 409 PC apparatus from NETZSCH, Selb/Germany. Specific surface area and particle size distribution (*d*<sub>50</sub> value) were determined using a *Blaine* instrument (Toni Technik, Berlin/Germany) and a laser granulometer (Cilas 1064, Marseille/France), respectively.

### Chemicals

K<sub>2</sub>SO<sub>4</sub> powder, maleic anhydride, allyl alcohol, and benzoyl peroxide, all analytically pure grade, were purchased from Merck KGaA, Darmstadt/Germany. The allyl ether macromonomer  $\alpha$ -allyl- $\omega$ -methoxy polyethylene glycol (*n*<sub>EO</sub> = 34) was obtained from NOF CORPORATION, Tokyo, Japan.

### Polycarboxylate Samples

Five PCE superplasticizers were synthesized and tested. As first polymer, the novel PCE copolymer was prepared from  $\alpha$ -allyl- $\omega$ -methoxypolyethylene glycol ether macromonomer, maleic anhydride, and allyl maleate as a new building block.

A typical synthesis is carried out following the principal process described in a patent application.<sup>13</sup> First, the building block is synthesized by reacting 6.25 g (64 mmol) of maleic anhydride with 3.72 g (64 mmol) of allyl alcohol at 60°C for 1 h. Note that it is critical to avoid any molar excess of allyl alcohol, for the reason explained below. During the reaction, the maleic anhydride

**Table I.** Phase Compositions and Properties of the Cement Samples Employed in the Study

Phase	CEM I 32.5R wt %	CEM I 42.5R wt %	CEM I 52.5R wt %
C <sub>3</sub> S	60.4	67.2	70.3
C <sub>2</sub> S	11.9	14.0	12.0
C <sub>3</sub> A	9.3	8.4	1.1
C <sub>4</sub> AF	7.3	2.7	12.5
Free lime	1.9	0.1	0.5
Periklas	2.0	0.0	0.0
Anhydrite	3.1	2.4	0.3
Hemihydrate	1.3	0.0	1.8
Gypsum	0.0	0.0	0.2
Calcite	2.6	3.8	0.6
Quartz	0.3	0.8	0.0
K <sub>2</sub> O	0.9	0.7	0.4
Na <sub>2</sub> O	0.3	0.2	0.2
Spec. surface area (Blaine) (cm <sup>2</sup> g <sup>-1</sup> )	3 040	3 300	4 700
<i>d</i> <sub>50</sub> value (μm)	16.16	10.82	6.80
water/cement ratio (w/c) <sup>a</sup>	0.48	0.55	0.505

<sup>a</sup>Value to obtain a paste spread of 18 ± 0.5 cm.

will melt and form a homogeneous reaction product with the allyl alcohol which is allyl maleate with a purity of about 96%. The synthesis method described here inevitably produces a small amount of diallyl maleate (~2%) which can act as a crosslinking agent during subsequent PCE synthesis which makes the polymer ineffective as cement dispersant. Therefore, higher concentrations of diallyl maleate must be avoided, and the best way is to react maleic anhydride with a slight substoichiometric amount of allyl alcohol. To further purify the allyl maleate, it was distilled under vacuum (3 h Pa) to yield a colorless, nearly odorless liquid. The allyl maleate should be stored in a cool, dark place and should be consumed rapidly as it was found to undergo self polymerization.

Second, synthesis of the novel PCE is carried out by mixing 100 g (64 mmol) of allylether macromonomer (*n*<sub>EO</sub> = 34), 6.25 (64 mmol) g of maleic anhydride and 10.0 g (64 mmol) of purified allyl maleate. This mixture is heated to 90°C and the reaction vessel is flushed with an inert gas, preferably nitrogen. While stirring, 2.00 g of benzoyl peroxide are added as powder continuously over a time period of 90 min. The quality of the resulting polymer greatly depends on accurate and uninterrupted addition of this radical initiator. After complete addition of the benzoyl peroxide, the mixture is heated to 100°C and is stirred for another 90 min. The viscosity of the mixture will gradually increase, but remains stirrable over the whole reaction period. During the polymerization process, the color of the reaction mixture will change to yellowish. At the end, ~120 mL of deionized water are added to the reaction mixture while it is still hot to yield a polycarboxylate solution of ~50 wt % solid content. The solution can be neutralized with 30 wt % aqueous NaOH which will produce the

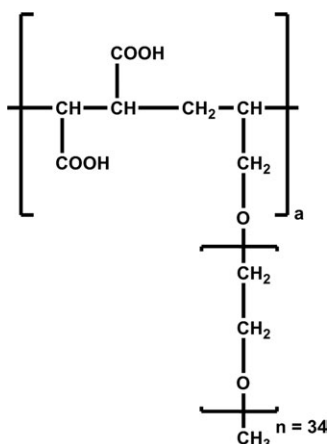


Figure 1. Chemical structure of the synthesized APEG-based PCE sample.

sodium salt of the PCE. This polymer was designated as modified PCE (*m*34APEG).

For comparison, the same APEG-type PCE as above, but in the absence of the building block allyl maleate was prepared following the description as before. This reference polymer was designated as 34APEG. The chemical structure of this type of PCE polymer which is strictly tactical because allyl ether does not homopolymerize is displayed in Figure 1.

For further comparison, three more PCEs (*x*MPEG<sub>y</sub>) based on methacrylic acid-*ω-ω*-methoxy poly(ethylene glycol) (MPEG) methacrylate ester were prepared. This kind of PCE is among the most commonly used PCE products which are applied in concrete. Their general chemical structure is shown in Figure 2. There, “*x*” refers to the number of ethylene oxide units (*n*<sub>EO</sub>) present in the side chain of the PCE comb polymers and was 25 or 45, respectively, whereas “*y*” refers to the molar ratio of methacrylic acid to MPEG methacrylate ester which was 6 : 1, 3 : 1, and 1.5 : 1, respectively. Aqueous radical copolymerization was utilized to synthesize these copolymers. The initiator used was sodium peroxodisulfate, and methallyl sulfonic acid was employed as a chain transfer agent. Details of the synthesis process have been disclosed before.<sup>14</sup>

After copolymerization, polymer solutions were generally neutralized with sodium hydroxide and dialyzed using a 6000–8000 Da cellulose cut-off membrane (Spectra/Pro, Spectrum Laboratories, Rancho Dominguez, CA). After concentration under vacuum in a rotary evaporator (“Rotovap” Laborota 4003 from Heidolph Instruments GmbH & Co. KG in Schwabach/Germany), viscous polymer solutions possessing solid contents of ~40 wt % were obtained.

All copolymers were characterized using Waters 2695 gel permeation chromatography (GPC) separation module equipped with a refractory index detector (2414 module, Waters, Eschborn/Germany) and a Dawn EOS 3 angle static light scattering detector (Wyatt Technology, Clinton, SC). A  $d_w/d_c$  of 0.135 mL g<sup>-1</sup> (value for poly(ethylene oxide)) was utilized to determine molar masses.<sup>15</sup> Ultrahydrogel columns 500, 250, 120 (Waters, Eschborn/Germany) with an operating range (PEO/PEG) of  $M_w$  between 100 and 1,000,000 Da were used. Eluent was 0.1N NaNO<sub>3</sub> at pH = 12 adjusted with NaOH.

### Cement Pore Solution

The term “pore solution” (PS) generally describes the aqueous phase loaded with electrolytes which exists between cement particles when cement is dispersed in water at a specific water-to-solids ratio. Here, the pore solution was gained via vacuum filtration of the cement paste prepared from CEM I 32.5 R ( $w/c = 0.48$ ) in the absence or the presence of 1 wt % ( $w/c = 0.5$ ) or 2 wt % ( $w/c = 0.55$ ) of K<sub>2</sub>SO<sub>4</sub>, respectively.

### Anionic Charge Amounts of PCE Samples

The anionic charge amounts of the copolymers were determined by polyelectrolyte titration using a particle charge detector PCD 03 pH (BTG Mütek GmbH, Herrsching/Germany). The charge detector consists of a PTFE cylinder with an oscillating PTFE piston in the center. The polyanionic polymer adsorbs onto the Teflon surface, while the counter ions are being separated from the polymer when the piston is moving. This creates a streaming current, which is measured by two Pt electrodes inside the Teflon cylinder. The anionic charges were determined by titrating the PCEs dissolved in cement pore solutions using 0.001N poly(diallyldimethylammoniumchloride), PolyDADMAC as cationic counter-polyelectrolyte.

### Mini Slump Test

Flowability of pastes obtained by dispersion of the neat cement samples or of cement plus K<sub>2</sub>SO<sub>4</sub> was determined utilizing a “mini slump test” according to DIN EN 1015. The test was carried out as follows: Over a period of 1 min, 300 g of cement were filled into a porcelain cup which contained the specific amount of DI water. The  $w/c$  ratio was 0.3 for the cement compatibility test (Cement Compatibility section), while for all other tests the ratios provided in Table I were used to obtain a spread of  $18 \pm 0.5$  cm. The mixture was allowed to soak for 1 min, stirred manually with a spoon for 2 min. Immediately after stirring, the slurry was poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) placed on a glass plate, filled to the brim and the cone was removed vertically. The resulting diameter (spread) of the paste represents the flow value of the slurry. The spread was measured twice; the second measurement being perpendicular to the first one, and an average was obtained to give the slump value. Each test was repeated three times, and the average of the paste flow diameter was reported as the slump flow

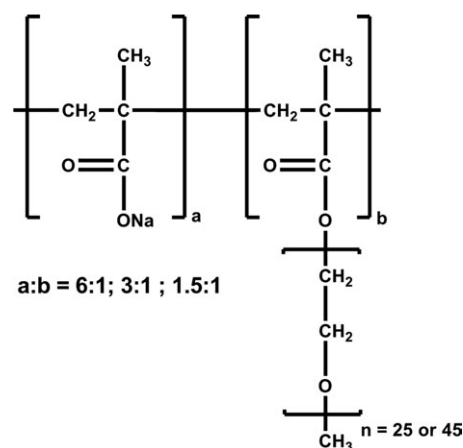
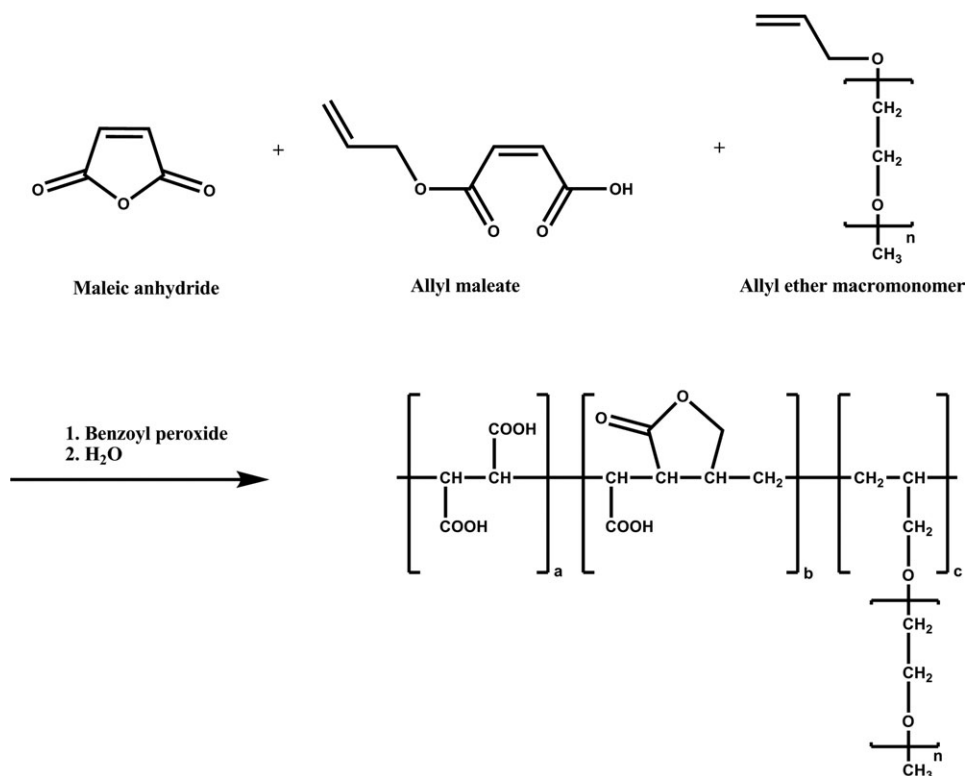


Figure 2. Chemical structure of the synthesized MPEG-based PCE samples.



**Scheme 1.** Reaction sequence leading to the formation of modified PCE polymer *m34APEG*.

value. The margin of error was  $\pm 3\%$ . Using this test protocol, the PCE dosages required to reach a spread of  $26 \pm 0.5$  cm were determined.

#### Adsorption of PCE Samples

The adsorbed amounts of the PCEs on cement were determined according to the depletion method. Different dosages of copolymer were added to the slurries of the cement sample CEM I 32.5 R blended with different amounts of  $\text{K}_2\text{SO}_4$  (w/c = 0.5 and 0.55 for cement blended with 1 and 2 wt % sulfate, respectively). The pastes were filled into 50 mL centrifuge tubes, shaken for 2 min at 2400 rpm in a wobbler (VWR International, Darmstadt/Germany) and centrifuged for 10 min at 8500 rpm in a centrifuge (Heraeus International, Osterode/Germany). For quantification of the organic carbon content in the supernatant, a High TOC II apparatus from Elementar (Hanau/Germany) was used. Centrifugates were diluted at 20 : 1 (v/v) with 0.1N HCl to remove inorganic carbonates and to prevent the dissolution of carbon dioxide in the alkaline solution. The samples were oxidized in a glass tube at 1000°C on a platinum catalyst using synthetic air, the exhaust gas was dried over phosphorous pentoxide and the carbon dioxide was determined in a NDIR cell. The amount of organic carbon present in the sample was calculated based on the values obtained for monopotassium phthalate which was used as calibration standard. The adsorbed amounts of individual PCEs were obtained by subtracting the concentration of PCE found in the centrifugate from the initial PCE concentration existing prior to contact with cement. All measurements were repeated three times and averaged.

#### Hydrodynamic Radius of PCE Molecules

Different polymer solutions were prepared by dissolving 1 g of PCE powder in 100 mL of cement pore solution (see Cement

Pore Solution section), and the average particle sizes of individual PCE molecules were determined by dynamic light scattering measurement using a Horiba LB-550 instrument (HORIBA, Kyoto/Japan). Each sample was measured four times, and the average was reported as the hydrodynamic radius of PCE.

#### Other Instruments

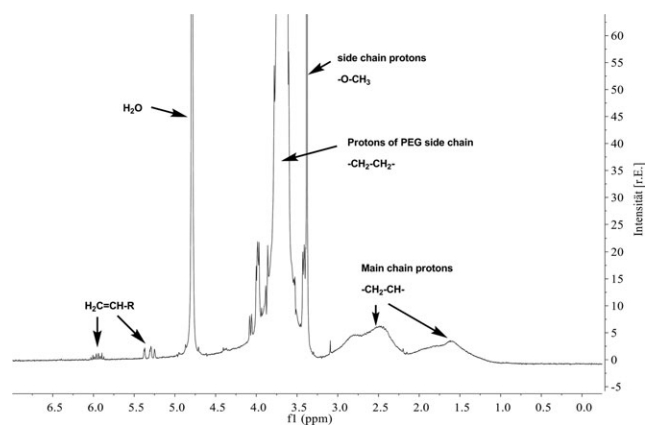
For  $^1\text{H}$  NMR analysis, a 250 MHz spectrometer from Bruker Bio-Spin, Karlsruhe/Germany was utilized while IR was conducted using a Vertex 70 FTIR—ATR instrument from Bruker Optics, Karlsruhe/Germany. Quantification of sulfate concentration contained in cement pore solutions was performed on an ICS-2000 ion chromatograph from Dionex, Sunnyvale, CA.

## RESULTS AND DISCUSSION

### Synthesis and Chemical Structure of the Modified PCE

The novel type of PCE was synthesized by free radical copolymerization in bulk from allyl ether macromonomer, maleic anhydride, and allyl maleate at a molar ratio of 1 : 1 : 1. The sequence of reactions occurring in the synthesis is described in Scheme 1.

Surprisingly, it was found that allyl maleate which presents a potential crosslinking agent for PCE does not much increase the molecular weight and viscosity of the aqueous *m34APEG* solution. Also, in the  $^1\text{H}$  NMR spectrum of the purified terpolymer, only traces of protons characteristic for the allyl C=C double bond were detected (Figure 3). These observations prompted the idea that during the copolymerization process, the allyl maleate building block undergoes cyclization to a five-membered heterocycle, as is shown in Scheme 1. Such ring formation has



**Figure 3.**  $^1\text{H}$  NMR spectrum of the purified  $m34\text{APEG}$  copolymer, measured in  $\text{D}_2\text{O}$ .

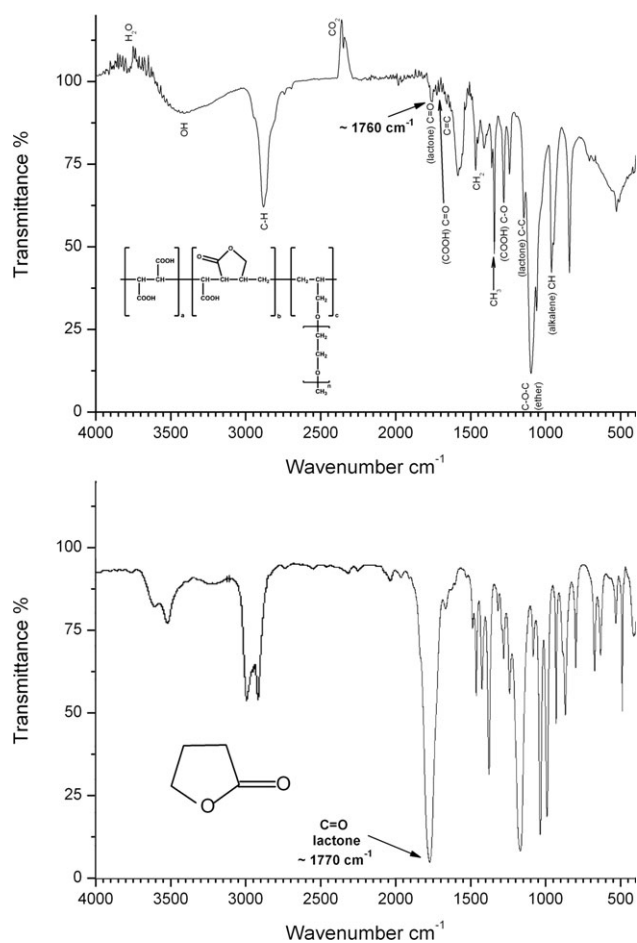
been reported before for unconjugated dienes.<sup>16</sup> Further evidence for the formation of a lactone ring was provided by FT-IR spectroscopy. There, a signal at  $\sim 1760\text{ cm}^{-1}$  which is characteristic for the  $\text{C}=\text{O}$  absorption in a five-membered lactone ring appeared (Figure 4). For comparison, in  $\gamma$ -butyrolactone, the same group produces an absorption at  $1770\text{ cm}^{-1}$ .<sup>17</sup> Another indirect proof for cyclization lies in the fact that when the reaction products of acrylic or itaconic acid with allyl alcohol are used in the PCE synthesis, the resulting terpolymers exhibit significantly higher  $M_w$  than the nonmodified reference polymer, as a result of crosslinking plausibly induced by the unreacted  $\text{C}=\text{C}$  double bond present in allyl acrylate or allyl itaconate which apparently did not undergo cyclization. Also, in these copolymers, no IR absorption characteristic for a lactone  $\text{CO}$  groups was found. These observations signify that an  $\alpha$ -olefinic proton is required to undergo this reaction, and such proton is only available in maleic anhydride. To conclude, with the lactone cycle the newly synthesized PCE possesses a specific structural feature which clearly distinguishes it from conventional PCE molecules.

Next, the characteristic molecular properties of  $m34\text{APEG}$  sample were compared with those of the non-modified reference polymer. The results are exhibited in Table II. According to this data, it is evident that the modified and nonmodified PCE samples possess very comparable properties with respect to molar masses, polydispersity and hydrodynamic radius. The differences lie in their specific anionic charge amounts, as is shown in

**Table II.** Characteristic Properties of the Synthesized PCE Comb Polymers

Copolymer	Side chain $n_{\text{EO}}$	Molar masses		Polydispersity index ( $M_w/M_n$ )	Hydrodynamic radius $R_{h(\text{avg})}$ (nm)	Spec. anionic charge in CPS <sup>a</sup> ( $\mu\text{eq g}^{-1}$ )
		$M_w$ ( $\text{g mol}^{-1}$ )	$M_n$ ( $\text{g mol}^{-1}$ )			
$m34\text{APEG}$	34	78,430	24,830	3.2	7.0	195
34APEG	34	63,100	22,900	2.8	6.2	140
25MPEG3	25	67,590	28,290	2.4	6.0	1100
45MPEG1.5	45	196,300	51,900	3.8	8.7	145
45MPEG6	45	163,100	45,570	3.6	10.2	910

<sup>a</sup>CPS = cement pore solution gained from cement sample CEM I 32.5 R.



**Figure 4.** FT IR spectra of modified PCE polymer  $m34\text{APEG}$  containing the allyl maleate building block (top) and of  $\gamma$ -butyrolactone (bottom).

Table II. There, it becomes evident that  $m34\text{APEG}$  possesses a higher anionic charge than 34APEG, as a result of incorporation of the charged building block.

### Cement Compatibility

In the following, the dispersion ability of this new PCE molecule was compared with those from PCEs possessing conventional structures. To probe the robustness against variations in cement compositions, namely the tricalcium aluminate ( $\text{C}_3\text{A}$ ) content, distinctly different cement samples were selected and tested. Here, a w/c ratio of 0.3 was chosen for all cement pastes



to challenge the polymer's ability to disperse under particularly difficult conditions. The results are shown in Figure 5.

The data suggests that sample CEM I 32.5R is particularly difficult to disperse by PCE, plausibly because of a combination of high  $C_3A$  and free lime content (Table I). All nonmodified PCE samples 34APEG and 25MPEG3 (the latter was chosen as an example for MPEG-type PCEs; the two other MPEG samples produced similar results) require substantially higher dosages than the modified PCE sample *m*34APEG. We attribute its superior behavior to incorporation of the new building block allyl maleate which apparently renders the PCE molecule more robust against high contents of  $C_3A$  and free lime.

In practical concrete manufacturing, the robustness of the modified PCE presents a huge advantage because it allows to switch cement suppliers without the need of reformulating the entire mix design. This way, extensive lab testing can be avoided.

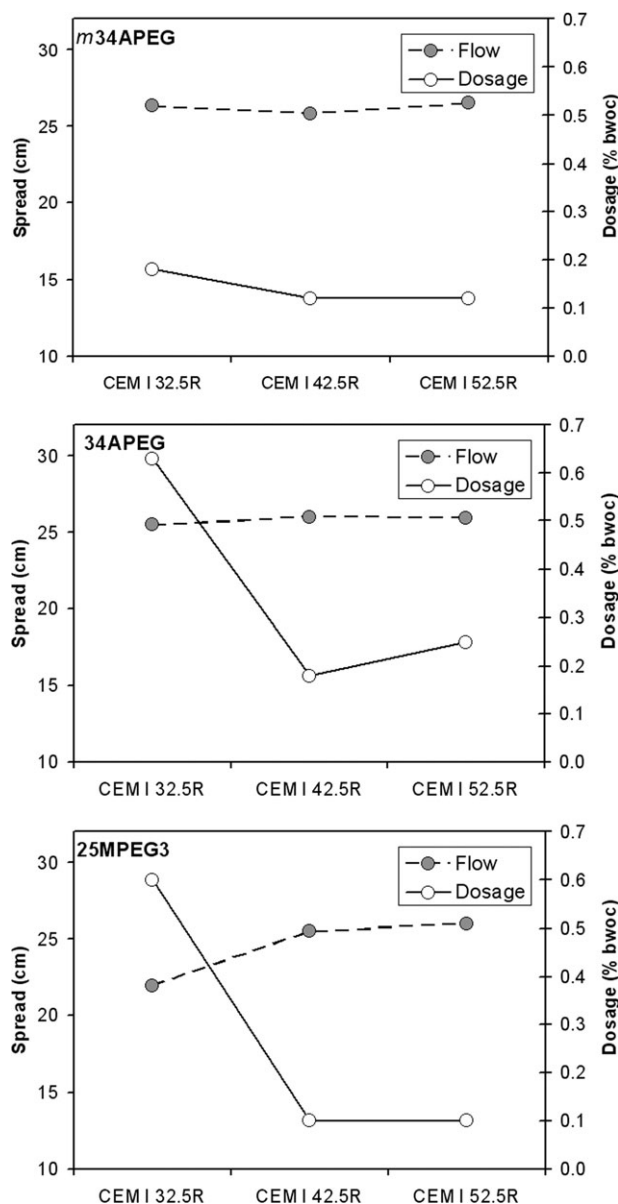
#### Tolerance to Sulfate

Sulfates are contained in every Portland cement, both as alkali sulfates originating from the combustion of sulfurous fuel which produces  $SO_3$ , and from the addition of calcium sulfates for set control of cement. Depending on the manufacturer, significant variations in the sulfate contents of individual cement samples can occur, whereby high sulfate concentrations can severely impede the effectiveness of PCE polymers ("sulfate effect").<sup>10</sup>

In the literature, two mechanisms are discussed to explain the negative effect of sulfate on PCEs: First, competitive adsorption between sulfate and PCE, whereby the highly anionic sulfate ions preferably adsorb onto cement and occupy most of the surface sites on hydrates available for adsorption. This way, PCE is prevented from adsorbing in sufficient amount on cement. The second mechanism involves shrinkage of the PCE molecule, which leads to a more coiled conformation that cannot adsorb as easily on cement.<sup>9</sup>

According to that, we studied the behavior of our PCEs in two steps: at first, the impact of sulfate on the workability of the PCEs in cement paste was determined utilizing mini slump tests. Second, the effect of sulfate on the adsorbed amounts of the PCEs was studied. For these tests, the "difficult" cement sample CEM I 32.5 R ( $w/c = 0.48$ ) was used. To this cement, 1 wt % ( $w/c = 0.5$ ) or 2 wt % ( $w/c = 0.55$ ) of  $K_2SO_4$ , respectively were added to generate an elevated sulfate content in cement. Utilizing ion chromatography, the sulfate concentrations as follows were determined in the pore solutions: (a) neat cement:  $12.8 \text{ g L}^{-1}$ ; (b) cement + 1 wt %  $K_2SO_4$ :  $20.8 \text{ g L}^{-1}$ ; (c) cement + 2 wt %  $K_2SO_4$ :  $23.6 \text{ g L}^{-1}$  of  $SO_4^{2-}$ .

**Impact on Workability.** The following experiments were carried out using the CEM I 32.5 R sample, a cement which was demonstrated before to possess high "incompatibility" with conventional PCEs, as a result of its high  $C_3A$  and free lime content (Figure 5). The initial spread of this cement paste ( $w/c = 0.48$ ) was  $18 \pm 0.5 \text{ cm}$ . To achieve the target flow of  $26 \pm 0.5 \text{ cm}$ , the required dosages of the PCE samples were 0.095; 0.11; 0.10; 0.18, and 0.21 % bwoc (by weight of cement) for *m*34APEG, 34APEG, 25MPEG3, 45MPEG6, and 45MPEG1.5, respectively.

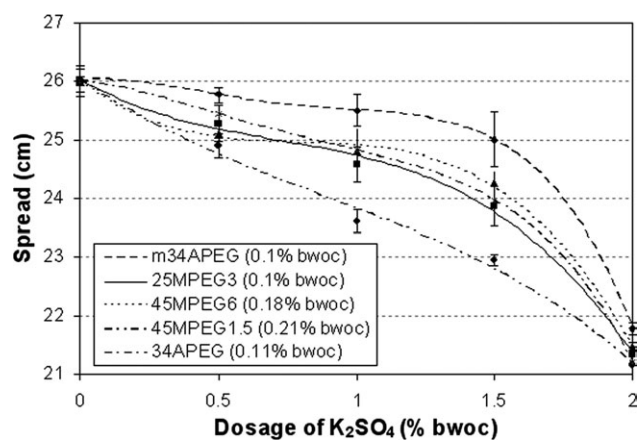


**Figure 5.** Dispersing ability of PCE polymers *m*34APEG, 34APEG, and 25MPEG3 in pastes ( $w/c = 0.3$ ) prepared from different cement samples.

At these dosages, the influence of  $K_2SO_4$  on the dispersing effectiveness of the PCEs in the cement slurries was determined. Up to 2 % bwoc of  $K_2SO_4$  were added as solid to the freshly mixed cement paste and worked into the slurry by stirring for 5 min before measurements were taken. The results are presented in Figure 6.

It was found that the modified PCE sample *m*34APEG exhibits the highest robustness against sulfate, while its reference polymer 34APEG shows a particularly weak tolerance against  $K_2SO_4$ . All MPEG-type PCE samples behave comparably with sulfate, their dispersion power is affected, but less than for the nonmodified APEG polymer 34APEG.

Again, the test results demonstrate that the new building block allyl maleate renders a PCE polymer with enhanced cement



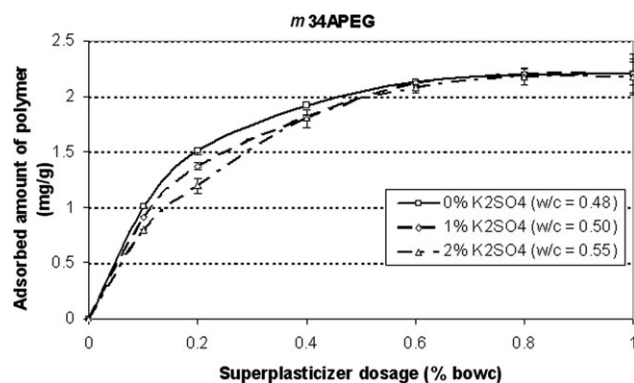
**Figure 6.** Effect of  $K_2SO_4$  addition on the fluidity of cement pastes (CEM I 32.5 R,  $w/c = 0.48$ ) holding different PCE samples.

compatibility, here with respect to variation in the sulfate content.

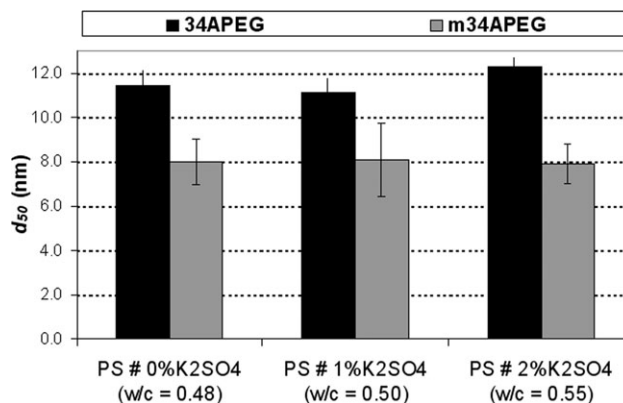
**Mechanism for Sulfate Tolerance.** To understand the mechanism underlying the robustness in presence of sulfate, adsorbed amounts of the modified PCE on cement as a function of the  $K_2SO_4$  amount added were determined. The results are shown in Figure 7.

Normally, the dispersing effectiveness of a superplasticizer directly correlates with the adsorbed amount of polymer. Consequently, adsorption of a sulfate tolerant PCE polymer can be expected to be quite independent of the sulfate concentration. Here, for *m34APEG* PCE it was found indeed that its adsorbed amounts are not much affected by different  $K_2SO_4$  additions. This result instigates that the novel terpolymer possesses such high affinity to the surface of cement that even in competition with highly anionic sulfate ions, its adsorption still can take place. We attribute this enhanced affinity to its specific chemical structure as well as the higher anionic charge compared to 34APEG, as was shown in Table II.

In earlier literature, it was postulated that PCE molecules can shrink as a result of elevated sulfate content and thus become less effective.<sup>9</sup> This mechanism could provide another potential



**Figure 7.** Adsorption isotherms for PCE polymer *m34APEG* on CEM I 32.5 R at 0–2% bwoc  $K_2SO_4$  addition.



**Figure 8.** Hydrodynamic radius of PCE samples 34APEG and *m34APEG*, measured in filtrates of CEM I 32.5 R pastes at increased  $K_2SO_4$  additions.

explanation for the increased sulfate tolerance of the novel PCE polymer. To investigate, the steric size (hydrodynamic radius,  $R_h$ ) of *m34APEG* in the pore solutions of the cement/ $K_2SO_4$  blends was determined. This experiment provides information on whether the PCE molecule is indeed compressed by dissolved sulfate ions and attains a coiled conformation. The results are presented in Figure 8.

Obviously, the hydrodynamic radius of *m34APEG* remains stable at  $\sim 8$  nm and is independent of the  $K_2SO_4$  amount present. This clarifies that the molecule is not shrunk by dissolved sulfate ions. Thus, the sulfate concentration present in the pore solution has no influence on the steric size of this PCE polymer.

As a comparison, the steric size of the reference polymer 34APEG was measured. Again, it was found that its radius was independent of the sulfate concentration. This way, it was demonstrated that for the two APEG-type PCE molecules tested here, sulfate induced coiling of the macromolecules is not occurring. More important, however, is the observation that nonmodified 34APEG generally possesses a significantly larger steric size ( $d_{50} = 12$  nm, Figure 8), compared to *m34APEG* ( $\sim 8$  nm). This instigates that upon adsorption, the modified PCE polymer can form a much denser polymer layer on the surface of cement, and thus can develop a considerably stronger dispersion force, in particular as it carries a higher anionic charge than 34APEG.

## CONCLUSIONS

The experiments demonstrate that a PCE polymer containing a five-membered lactone ring as a novel building block exhibits improved cement compatibility, because it is less affected by high  $C_3A$ , free lime and sulfate concentrations occurring in different cement samples.

During the hydration process of cement, sulfate ions are originated from dissolving calcium sulfates and alkali sulfates which can significantly perturb the dispersing performance of specific PCE molecules as a result of decreased adsorption. From the experiments conducted it is suggested that in the presence of sulfates, the PCE polymer containing the lactone ring is

performing more robust than conventional PCE polymers. This property is attributed to its higher anionic charge and its smaller steric size which allows the formation of a more densely packed polymer layer on the surface of cement particles.

While the favorable behavior of the novel PCE polymer with sulfate anions can be explained, its high tolerance toward cements containing large amounts of  $C_3A$  and free lime was not clarified. Further studies are necessary to uncover the reason behind the negative effects of this combination on conventional PCE polymers.

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