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Study on the foaming behaviour of allyl ether-based polycarboxylate superplasticizers

A. Lange, J. Plank [*]

Lehrstuhl für Bauchemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

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ABSTRACT

In this study, the foaming behaviour of allyl ether-based polycarboxylate (PCE) superplasticizers and the mechanism underlying this effect is presented. It was found that both purified allyl ether-*co*-maleic acid PCE and individual allyl ether macromonomer possess moderate surfactant properties but do not cause the excessive foaming known from industrially manufactured PCEs. Whereas, a mixture of purified PCE polymer and only small amounts (≥10%) of allyl ether macromonomer shows very strong foaming. This combination exhibits similar foaming action like industrially manufactured PCE superplasticizers. Apparently, the allyl ether macromonomer acts as a co-surfactant (foam stabilizer) to PCE which already presents a macro tenside. Minimizing the amount of unreacted allylether monomer in commercial PCEs provides a solution to obtain a less foaming product.

1. Introduction

Polycarboxylate-based superplasticizers (PCEs) are frequently used in concrete applications since their invention in Japan [1]. These comb-type polymers possessing polyethylene oxide side chains show a very high water reducing capability, much higher compared to that of polycondensates [2–5]. Even small amounts of PCE added to concrete can greatly improve flowability and, when used at low water-to-cement ratios, allow the fabrication of high performance concretes such as self-compacting or ultra-high strength concrete. Methacrylate (MPEG)-, allyl ether (APEG)- and isoprenol (IPEG)-based superplasticizers are the kinds of polycarboxylates which are most frequently used in concrete applications [6–8].

Air content in concrete can have a great impact on its properties. Small amounts (4–5 vol.%) of air voids possessing a specific size of 10–300 μm enhance freeze–thaw resistance and thus are desirable under certain conditions [9]. High air content and large air pores, however, reduce final strength considerably and must be avoided. Unfortunately, common PCEs obtained from the industrial manufacturing process exhibit high foaming action. Under intensive mixing of the concrete, the air content can be such high that the gain in strength stemming from the lower water-to-cement ratio might be lost completely. This is why typical admixture formulations containing PCE mostly incorporate a defoaming agent [10]. Because defoamers add to the cost, their addition to PCE should be avoided if possible. Additionally, the oily defoamers often separate from the aqueous PCE solution, thus forming a top layer. As a result, the remaining PCE solution is depleted of defoamer and strong foaming in concrete will occur.

In this study, the mechanism behind the foaming action of an allyl ether-based polycarboxylate was investigated. Allyl ether-based PCE was chosen because it possesses a well defined chemical structure with a fairly narrow molecular weight distribution [11]. At first, the foaming action of the PCE as obtained from the synthesis was compared to that of the PCE after purification which removed unreacted monomers and impurities. Foaming tendency of PCE was determined by measuring surface tension and foam decay times of aqueous PCE solutions and the air void content of a standard mortar formulation. Second, the foaming effects of pure allylether macromonomer, and that of a mixture of purified PCE and the macromonomer were compared. From the experiments, the root cause for the foaming behaviour of PCE was detected and measures for prevention of this undesired effect are presented.

2. Materials and methods

2.1. Cement

The cement chosen for the experiments was an ordinary Portland cement (CEM I 52.5 N from HeidelbergCement, Geseke plant) which contains 8.4 wt.% C_3A and therefore requires a relatively high dosage of superplasticizer. The phase composition as determined by quantitative X-ray diffraction (Q-XRD; instrument: Bruker axs D8, software: Topas 3.0) is shown in Table 1. Average particle size (d_{50} value) of the cement sample was 12 μm and density of 3.14 g/cm³ (Helium pycnometer). The particle size was determined utilizing a laser granulometer (Cilas 1064, Cilas Company, Marseille, France).

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[*] Corresponding author. Tel.: +49 89 289 13151; fax: +49 89 289 13152.
E-mail address: sekretariat@bauchemie.ch.tum.de (J. Plank).

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Table 1
Phase composition of cement sample (CEM I 52.5 N) as determined by Q-XRD using *Rietveld* refinement.

Phase	wt.%
C_3S, m	67.2
C_2S, m	14.0
C_3A, c	7.2
C_3A, o	1.2
C_4AF, o	2.7
Free Lime (*Franke*)	0.1
Periclas (MgO)	0.0
Anhydrite	2.4
Hemihydrate[a]	0.0
Dihydrate[a]	0.0
Calcite + quartz	4.6

[a] Measured by thermogravimetry.

2.2. Preparation and analysis of allyl ether-based PCE

The APEG-type PCE was prepared by the process of aqueous free radical polymerization. This method produces higher conversion rates, but shorter main chains than the alternative method of bulk polymerization. Consequently, the resulting PCE molecules possess the shape of star polymers [12]. In a typical experiment, 50.0 g α-allyl-ω-methoxy poly(ethylene glycol) macromonomer containing 34 ethylene oxide units and an equimolar amount of maleic anhydride (3.13 g) were added to a five neck round bottom flask and dissolved in 53 mL DI water to yield a 50 wt.% solution. 0.49 g ammonium persulfate dissolved in 5.3 mL of DI water was used as radical initiator. Initiator dosage was one fifteenth of the molar quantity of the allyl ether macromonomer. The reaction mixture was heated to 70 °C, flushed with nitrogen throughout the entire reaction period and the solution of ammonium persulfate was added dropwise over a time period of 1.5 h. At the end of initiator addition, the temperature was kept at 70 °C for another 30 min before it was heated to 90 °C for 2 h. After cooling to ambient temperature, the aqueous PCE solution (solid content ~ 45 wt.%) was adjusted to pH 7 using 30 wt.% aqueous NaOH solution, thus producing a yellow, low viscous, odourless liquid.

A 30 mg/mL PCE solution was prepared for size exclusion chromatography (SEC) analysis. Measurement was performed on a Waters 2695 Separation Module equipped with three Ultrahydrogel™ columns (120, 250, and 500) and an Ultrahydrogel™ guard column from Waters, Eschborn Germany, and a subsequent 3 angle static light scattering detector ("mini Dawn" from Wyatt Technology Corp., Santa Barbara, CA USA). The polymer concentration was monitored with a differential refractive index detector (RI 2414, Waters, Eschborn/Germany). Aqueous 0.1 N $NaNO_3$ solution adjusted to pH 12 with NaOH was used as an eluent at a flow rate of 1.0 mL/min. From the SEC measurements, the polydispersity index (PDI), the molar masses (M_w and M_n) as well as the hydrodynamic radius (R_h) were obtained. The value of dn/dc used to calculate M_w and M_n was 0.135 mL/g (value for polyethylene glycol) [13].

2.3. Purification of PCE

2.3.1. By aqueous dialysis

The 45 wt.% PCE solution was continuously dialysed for three days through a MWCO 15.000 membrane (Spectra/Por Membrane, Carl Roth GmbH, Germany). Excessive water introduced by the dialysis was removed by distillation under reduced pressure at 60 hPa. Thereafter, the product was freeze-dried under high vacuum (0.05 hPa) to yield a colourless powder. This method only removes unreacted maleic anhydride and salts, but residual unreacted allylether macromonomer will remain in the PCE solution.

2.3.2. By solvent extraction

Highly purified PCE free of allyl ether macromonomer was obtained from solvent extraction. A saturated NaCl solution was prepared and its pH adjusted to 10 with NaOH. Dried PCE powder from a) was added to this solution until PCE no longer dissolved (about 5 g/100 mL). 100 mL of this solution was extracted three times with 50 mL ethyl acetate. Using this method, any residual unreacted allyl ether macromonomer will accumulate in the organic phase, whereas the polycarboxylate will remain in the aqueous phase. The organic phase was discarded. Residual NaCl and ethyl acetate left in the aqueous solution were removed by continuous dialysis over three days. The resulting purified polymer solution again was freeze-dried under vacuum. Total NaCl removal was probed by adding a droplet of $AgNO_3$ solution to a small portion of the purified PCE solution. No precipitation of AgCl occurred. Complete removal of the allylether macromonomer and thus successful purification of the PCE were confirmed by ^1H NMR spectroscopy and SEC.

Purity of the APEG macromonomer used in the synthesis was probed using a MALDI-TOF instrument from Bruker Daltonics, Bremen/Germany.

2.4. Testing of foaming behaviour

2.4.1. Foaming in aqueous solution

To quantify the foaming capacity of PCE samples in a simple experiment, their solutions in deionised water (concentration 10 g/L) were prepared. Portions of 10 mL of these solutions placed in 15 mL glass tubes were intensively shaken for 2 min by a mechanical shaker (Vortex Mixer, VWR International GmbH, Darmstadt/Germany). Thereafter, the height of the foam developed and its decay was recorded over time.

2.4.2. Air entrainment in mortar

A mortar consisting of 1350 g norm sand according to DIN EN 196-1, 450 g CEM I 52.5 R (HeidelbergCement, Milke Classic) and 225 g DI water (w/c = 0.5) was prepared according to DIN EN 196. Its initial spread when no PCE was present was 8 cm, indicating an extremely stiff consistency. When PCE was added, it was dissolved in the mixing water prior to mortar preparation. The mortar was mixed in a Toni-MIX agitator (Toni Technik GmbH, Berlin/Germany) using an automated program according to DIN EN 196. The resulting mortar was filled into the container of the air void tester and compacted for 30 s by vibration. The kettle was closed and remaining space was filled with water. The amount of air voids was measured according to DIN EN 12350-7:2000-11 by applying air pressure.

2.5. Measurement of surface tension

The surface-active properties of the polymers were determined from the surface tension of aqueous solutions. Solutions of 10 g/L were prepared and the droplet shape was measured using a droplet shape analyser (Krüss GmbH, Hamburg/Germany). This instrument measures the droplet volume and surface area and uses this data to calculate the surface tension of the solution.

2.6. Determination of hydrodynamic radius (R_h) of PCE

The hydrodynamic radius (R_h) of the polymers was measured by dynamic light scattering (DLS) using a ZetaSizer Nano ZS (Malvern Instruments Ltd, Worcestershire, England). Polymer solutions of 10 g/L in DI water were prepared and measured three times at a constant temperature of 25 °C. The final result was generated from the average of the three independent measurements.

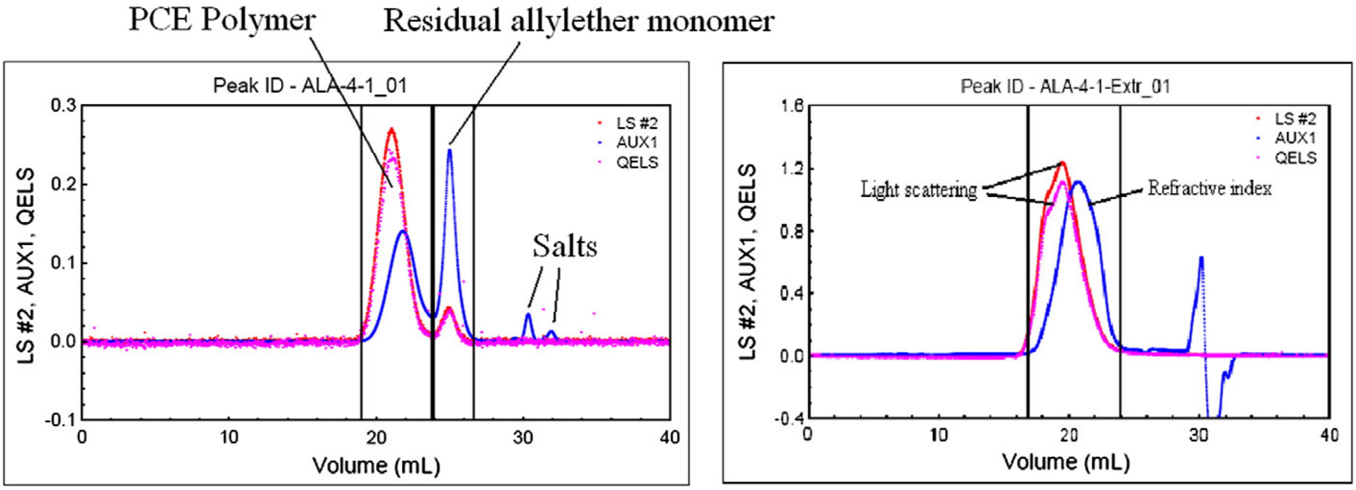

Fig. 1. Gel permeation chromatograms of dialysed PCE (left) and PCE after solvent extraction (right).

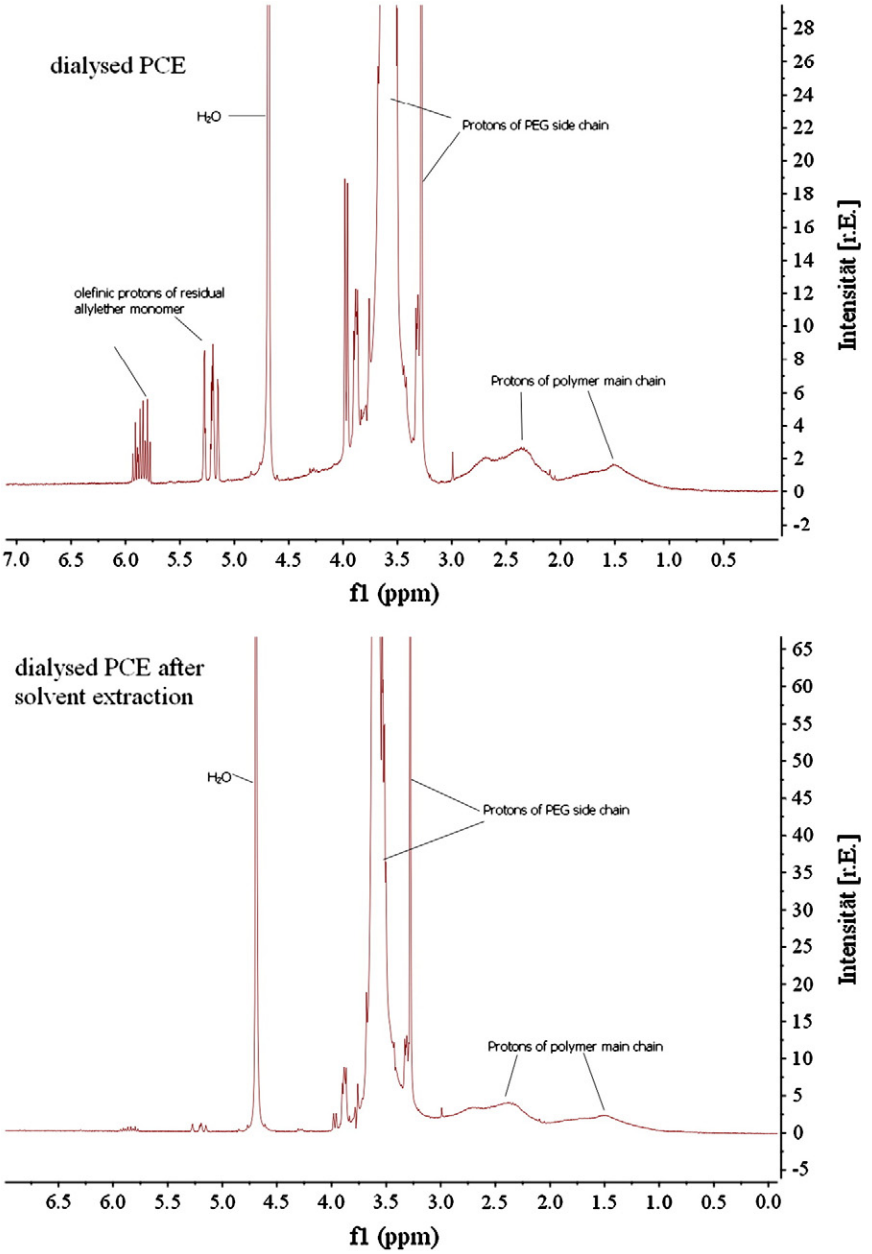

Fig. 2. ^{1}H NMR spectra of dialysed PCE before (top) and after purification (bottom) by solvent extraction.

3. Results and discussion

3.1. Characterization of synthesized PCE

The synthesized PCE was analysed by SEC. Its molar masses were found at 63,100 Da (M_w) and 22,500 Da (M_n). Thus, the polydispersity index (PDI) was 2.8. Further purification steps carried out in this study had no influence on the molecular weight of the polymer. SEC analysis of purified PCE samples revealed values for M_w of 63,000 ± 1000 Da which is within accuracy of the method.

From the SEC spectra, a conversion rate for the monomers of 82% was calculated. This value common for industrially made PCEs indicates that the PCE as prepared contained a mixture of polycarboxylate copolymer, residual APEG macromonomer and maleic acid, and salts from initiator and pH adjustment.

3.2. Purification of PCE

At first, purification of the PCE was attempted by dialysis in water over a period of three days. However, gel permeation chromatography (GPC) performed after dialysis revealed that this method only allows to remove unreacted maleic anhydride and salts (e.g. from the initiator) while unreacted allyl ether macromonomer (~20% based on total mass) was found to be still present (Fig. 1, left). Consequently, further purification of the dialysed PCE utilizing extraction with ethyl acetate solvent was performed. The GPC spectra obtained after this step confirmed successful removal of the macromonomer (Fig. 1, right), and pure polycarboxylate copolymer was obtained.

The same result was obtained from ^{1}H NMR spectroscopy (Fig. 2). There, after the extraction step, the proton signals characteristic for the allyl ether macromonomer (δ ~ 5.2–5.9 ppm) had practically disappeared. According to the NMR spectrum of the solvent treated PCE, a purity of > 99% was obtained for this sample. This purity was considered to be satisfactory for the study of the foaming behaviour of pure PCE.

3.3. Purity of allyl ether macromonomer

^{1}H NMR analysis of the allyl ether macromonomer used in the PCE synthesis showed that it was free of any impurities (Fig. 3). However, the integrated area from the signals of the PEG protons was found to be less than expected (found 42; expected 68). Therefore, the molecular mass distribution of the APEG macromonomer was analysed by MALDI-TOF mass spectrometry.

The MALDI-TOF spectrum shown in Fig. 4 reveals the overall composition of the macromonomer. The number average molecular weight (M_n) was found at 1548 g/mol. This value corresponds to exactly 34 ethylene oxide units which is in perfect agreement with the length of the PEG chain as stated by the producer. The molecular weight distribution of the monomer is fairly narrow and *Gauss*-shaped. It ranges from about 20 to 50 ethylene oxide units. No further impurities were detected, as was already indicated by NMR analysis.

The MALDI-TOF analysis confirms that the APEG macromonomer does not consist of one specific and uniform molecule, but clearly exhibits a molecular weight distribution. Such composition is characteristic for industrially made APEG monomers. As a result, the synthesized PCE copolymer possesses side chains of different lengths ranging between those of 20 and 50 EO units, with the most frequent one containing 34 EO units.

3.4. Foaming behaviour of PCE

3.4.1. Foaming in aqueous solution

This property was tested from 10 g/L aqueous solutions of PCE as synthesized, PCE dialysed, PCE solvent extracted, APEG macromonomer and of a 1:1 mixture of PCE solvent extracted and APEG macromonomer.

As is shown in Fig. 5, all products tested generate some foam, thus indicating that they generally possess surface-active properties while the differences between individual products lie in the specific decay times of the foams which are a result of different foam stabilities. First, individual allyl ether macromonomer as well as solvent extracted PCE produces foam which contains very few, but large bubbles, thus is very unstable and collapses within seconds. Consequently, neither pure PCE nor pure individual APEG macromonomer can be responsible for the excessive foaming behaviour observed for most commercial APEG-type PCEs.

Interestingly, dialysed PCE (which still contains ~20% of residual APEG macromonomer) develops a much more stable micro foam which even after 3 min has not collapsed completely. Even more stable and lasting is the foam produced by the PCE obtained from the synthesis. This result instigates that the simultaneous presence of

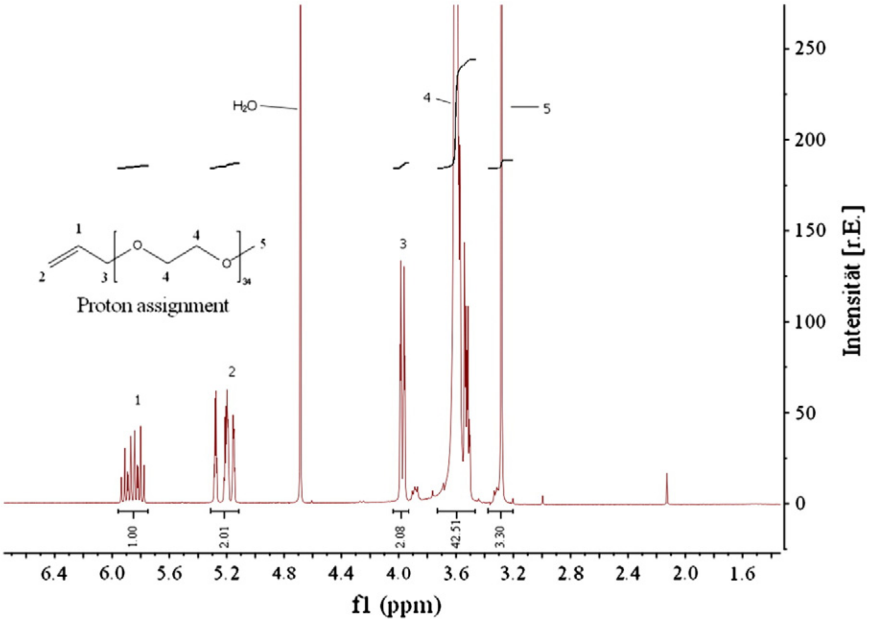

Fig. 3. ^{1}H NMR spectrum of the allyl ether macromonomer.

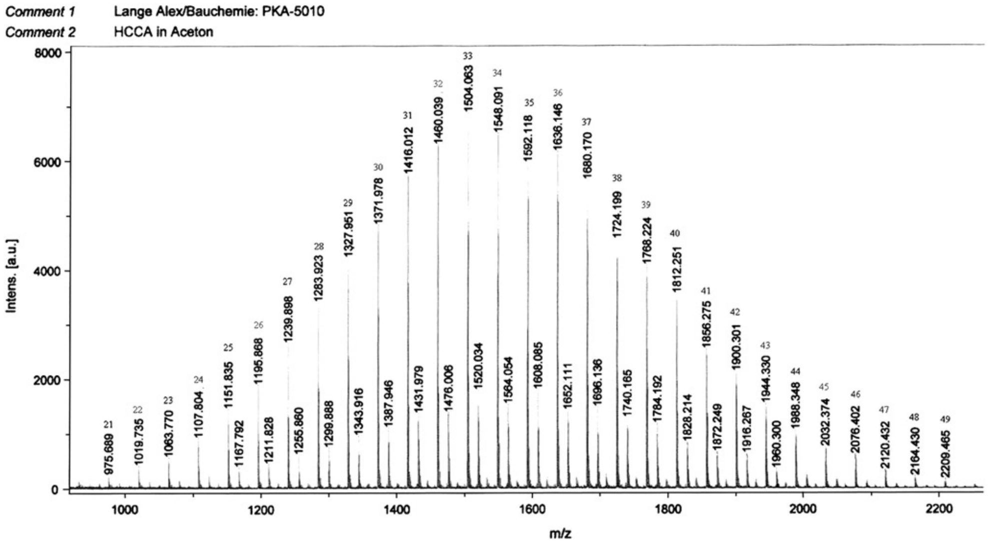

Fig. 4. MALDI-TOF spectrum of the allyl ether macromonomer used in the synthesis.

PCE and APEG monomer might present the root cause for excessive foaming of PCE in concrete.

To investigate, combinations of purified PCE polymer with APEG macromonomer (1:1 wt./wt.) were prepared and tested. It was found that such combinations generally produced very fine bubbles (micro foam) which were very stable and decayed only slowly (Fig. 5). After 3 min, still a significant layer of finely dispersed foam was observed in the upper part of the solution. Even when the allyl ether monomer content in the mixture was reduced to only 10% of the PCE dosage, foaming behaviour similar to that of the 50:50 mixture continued to persist. Only further reduction of the allyl ether macromonomer content to <10% by weight of PCE significantly reduced foam formation.

Obviously, a synergistic effect between the pure PCE polymer and the allyl ether macromonomer exists whereby enhanced surface activity of the mixture and a more stable micro foam result. This way, the APEG macromonomer acts as a co-surfactant (foam stabilizer) for PCE.

3.4.2. Air entrainment in standard mortar

A mortar according to DIN EN 196 was prepared to assess the foaming behaviour of PCE under realistic application conditions. First, the total air void content of the mortar in the absence of PCE was established as reference value. It was found at 3.2 vol.% (Fig. 6).

Next, a dosage of 0.1% bwoc of PCE as obtained from the synthesis (raw PCE) was added to achieve a mortar spread value of 26 ± 0.5 cm. For comparability of the results, this dosage was maintained for all polymers tested in the following.

The non-purified raw PCE gained from the synthesis developed the highest air content of ~15 vol.% (Fig. 6). Dialysis of this PCE which only removed salts and maleic acid did not help much to reduce the air entraining effect. At ~13 vol.%, the air content is still very high. Whereas, highly purified PCE entrains considerably less air (~8 vol.%) and the mortar appears much smoother than the mortar containing raw PCE. Similarly, the mortar containing 0.1% bwoc of pure allyl ether macromonomer exhibits an air content of ~7 vol.%, thus revealing that also the pure macromonomer exhibits only a slight foaming action. However, a 1:1 mixture of pure PCE with pure APEG monomer shows a considerably increased air content (~14 vol.%) which is comparable to that of the non-purified PCE obtained in the synthesis. Thus, it is again confirmed that the simultaneous presence of PCE molecule and residual APEG macromonomer is the root cause for strong foaming behaviour of industrially manufactured PCE products.

3.5. Study on the mechanism causing foaming behaviour of PCE

From the previous results it was speculated that the PCE polymer and the allyl ether macromonomer form micelle-type associates with much increased surface-active properties. Plausibly, in the micelle-

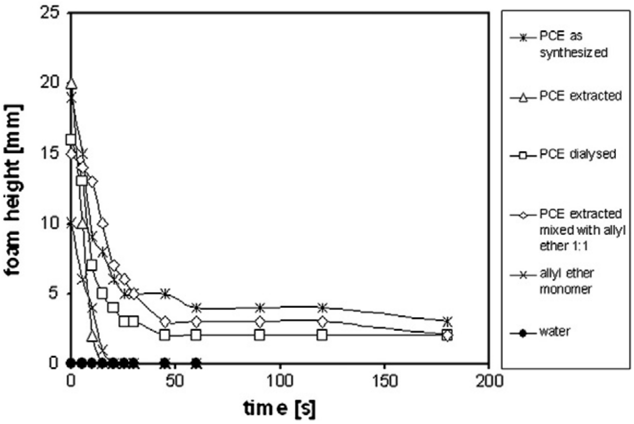

Fig. 5. Foaming behaviour of PCE samples and mixtures of PCE with APEG monomer measured by height of foam after agitation and its time-dependent decay.

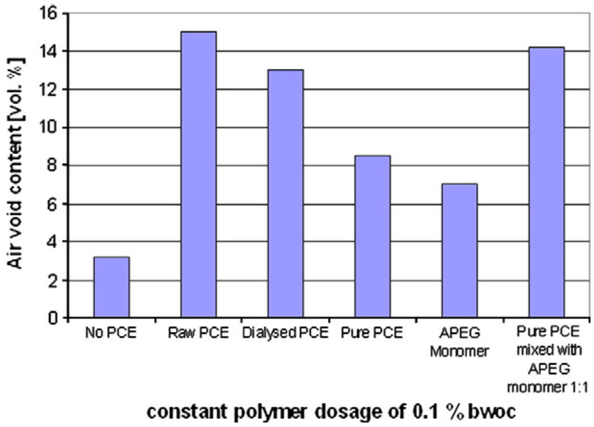

Fig. 6. Total air void content of mortar prepared according to DIN EN 196 with different polymer additions.

Table 2
Surface tension of aqueous polymer solutions.

Sample	Surface tension [mN/m]
Water	69.5
Raw PCE as synthesized	59.6
Dialysed PCE	59.2
Extracted PCE	58.1
APEG monomer	59.4
Extracted PCE mixed with APEG monomer 1:1 wt./wt.	57.2

type associates the allyl ether macromonomer aligns with the side chains present in the PCE molecule, thus enhancing the moderate surface-active properties of PCE which presents a mild macro tenside.

To clarify a potential associative mechanism underlying the foaming behaviour, the surface tension of aqueous polymer solutions (concentration 10 g/L) was measured. Pure water was chosen as reference value. The results are presented in Table 2.

The surface tension of pure water was found at 69.5 mN/m, which is close to the literature value of water at 25 °C [14]. To much surprise it was found that all polymer solutions tested including extracted PCE and APEG monomer are moderately surface active and produce comparable surface tensions in water. The distinct differences observed for the individual products in the foam decay and mortar tests were not evidenced by corresponding differences in surface activity.

Furthermore, to investigate a potential associate formation, the hydrodynamic radius (R_h) of pure PCE and APEG macromonomer were measured. Unfortunately, the hydrodynamic radius of the APEG monomer was too small to be detectable by the ZetaSizer. For extracted PCE, a hydrodynamic radius of 6.8 ± 0.5 nm was found. 50:50 mixtures of extracted PCE and APEG monomer produced the same value. Thus, it was not possible to determine whether association of the PCE with APEG macromonomer occurs at all.

To conclude, neither the measurement of surface tension nor that of the hydrodynamic radius of PCE in the presence of APEG macromonomer could explain why this combination produces a much more stable micro foam than the pure substances.

4. Conclusion

Polycarboxylates are generally macro tensides which always introduce some foam when mixed into concrete. Fortunately, the foam produced by pure PCE is an unstable macro foam which decays rapidly and is released by concrete. Therefore, the foaming behaviour of pure PCE does not constitute a major problem.

The problem of excessive foaming known from commercial PCEs occurs when a combination of PCE and residual, unreacted allyl ether macromonomer is present. They produce a very stable micro foam which is hardly released by concrete.

Similar results as reported here for APEG-type PCEs were obtained for MPEG-based PCEs [15]. There, again the combination of PCE polymer with MPEG-MA macromonomer created the strongest foaming action. Thus, the simultaneous presence of these two molecules (PCE and macromonomer or methoxy polyethylene glycol) indeed presents the root cause for the strong foaming action of PCE. Apparently, the macromonomers (MPEG-MA or APEG) act as foam stabilizers for PCE.

Industrially manufactured PCE superplasticizers most often contain an appreciable amount of unreacted macromonomer (on average ~10 wt.%), therefore strong foaming action is common and use of a defoamer becomes mandatory. Consequently, many commercial PCE superplasticizer solutions contain a defoaming agent.

To avoid this undesired property, the synthesis of PCE needs to be conducted in such manner that practically complete conversion of the macromonomers is achieved. It is however acknowledged that this goal will be hard to achieve in presently applied industrial manufacturing processes for PCE which are restricted by economical considerations. But only through this method, a PCE solution exhibiting acceptable low foaming behaviour will be accomplished and the problem of shelf-life stability of the PCE - defoamer combination in solution can be avoided.

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