Research Article

A new method for the quantification of adsorbed styrene acrylate copolymer particles on cementitious surfaces: a critical comparative study

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Abstract
The amount of adsorbed styrene acrylate copolymer (SA) particles on cementitious surfaces at the early stage of hydration was quantitatively determined using three different methodological approaches: the depletion method, the visible spectrophotometry (VIS) and the thermo-gravimetry coupled with mass spectrometry (TG–MS). Considering the advantages and disadvantages of each method, including the respectively required sample preparation, the results for four polymer-modified cement pastes, varying in polymer content and cement fineness, were evaluated.
To some extent, significant discrepancies in the adsorption degrees were observed. There is a tendency that significantly lower amounts of adsorbed polymers were identified using TG-MS compared to values determined with the depletion method. Spectrophotometrically generated values were lying in between these extremes. This tendency was found for three of the four cement pastes examined and is originated in sample preparation and methodical limitations.
The main influencing factor is the falsification of the polymer concentration in the liquid phase during centrifugation. Interactions in the interface between sediment and supernatant are the cause. The newly developed method, using TG–MS for the quantification of SA particles, proved to be suitable for dealing with these revealed issues. Here, instead of the fluid phase, the sediment is examined with regard to the polymer content, on which the influence of centrifugation is considerably lower.

Keywords Polymer adsorption · Cement · Visible spectrophotometry · Depletion method · Mass spectrometry

1 Introduction

Beside the cement hydration, the polymer particle adsorption is the main driving process in microstructure formation of polymer-modified mortars and concretes. The adsorption of polymer particles is to be understood as the result of attractive intermolecular and interparticlular interactions taking place within the suspension between organic, inorganic components and the constitution of cement paste pore solution at early stages of the cement hydration. The physicochemical processes leading to the destabilization of colloidal polymer particles and the effect of these interactions on macroscopic properties were subject of numerous studies in the last 25 years (e.g. [1–13].).

There are numerous methods for quantifying macromolecules on inorganic surfaces. For example the adsorption of macromolecules on mesoporous materials can be studied by using the isothermal titration calorimetry [14] and the differential scanning calorimetry [15]. To characterize the adsorption behavior of particulate polymers on cementitious surfaces, beside qualitative observation methods like zeta potential measurements [7, 9], confocal laser scanning microscopy [10] or cryo-SEM [11], especially one method is usually used to quantify the amount

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of adsorbed polymers at early hydration stages, which is the depletion method (e.g. used in [7, 8, 10] and [12]). This is a well-known gravimetric method to determine components in the liquid phase of various systems, where a weight loss can be clearly assigned to a component. It was already applied in 1964 to determine the adsorption of gelatin to a silver bromide sol [16]. Differently to this system, the applicability of the depletion method for polymer-modified cementitious systems is questioned. Concerning the quantification of polymer particle adsorption, there are some peculiarities especially in the sample preparation, which are decisive factors that should be noted.

In [17] the authors compared experimentally determined amounts of adsorbed polymer particles with the theoretical maximum polymer adsorption and found that the determined amount of adsorbed polymer particles obtained from centrifugal separation of polymer-modified cement pastes with normal water / cement ratio were in some cases higher than the theoretically possible amount that the surface of cement grain can accept. When separating the fluid and the solid phases of a polymer-modified cement paste by centrifugation it is impossible to fully avoid the trapping of particles in the sediment [18]. Furthermore, it is not distinguishable if polymers in the sediment are adsorbed by the cement grain or coagulated together by themselves due to their instability in the cement paste during centrifugation process [17]. Finally, the centrifugal and interfacial forces can lead to an accumulation of polymers in the boundary layer between the sediment and the supernatant, as it was shown in [19]. All of these influences, individually or in total, inevitably lead to an overestimation of the amount of adsorbed polymer.

The intention of the hereafter-described experiments is a systematic comparison of the gravimetric procedure as it is described in [10] to two alternative analytical methods, with the aim of evaluation. The thermo-gravimetric analysis coupled with mass spectrometry (TG–MS) for the direct quantification of adsorbed SA particles in the solid phase/sediment, based on detection and quantification of fragmented polymers. The visible spectrophotometry (VIS) has been used to approximately quantify not-adsorbed SA particles in the fluid phase/supernatant of the polymer-modified cement paste by determination of its turbidity properties [19].

Each of the before mentioned methods has advantages and disadvantages, whose comparison and assessment will be attended in concluding considerations. These may be helpful finding the appropriate effective methodical solution for the scientific issue of quantifying polymer adsorption in cementitious systems.

2 Materials, sample preparation and adsorption measurements

2.1 Materials

2.1.1 Cementitious materials

Two ordinary Portland cements, a CEM I 32.5 R (Schwenk) and a CEM I 42.5 R (Erwitte/Seibel + Söhne) were used, differing slightly in density, chemical composition, mineral phase constituents but especially in specific surface. Thus a higher adsorption degree for the CEM I 42.5 is expected.

The mineral constituents of the cements were determined by XRD (device: XRD 3003 TT, Fa. Seifert) using Rietveld refinement according to [20], specific surface area was determined according to DIN 66126 using the BLAINE procedure [21] and the particle size distribution was investigated by laser granulometry according to [22] with the Coulter LS 230 (Fa. Beckmann). The explicit data are shown in Tables 1, 2, 3, 4.

2.1.2 Polymers

For cement paste modification, a styrene acrylate copolymer with a glass transition temperature of 23 °C was used. The anionic stabilized SA particles were colloidal distributed in a 49.9 percent aqueous dispersion, that exhibit a total particle charge of 0.13 C/g and a pH value of 7.8.

The characterization in terms of particle size of the primary SA particles is shown in Table 5. The

Table 1 Chemical constitution of the cements [%]

	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	K_2O_{wl}	Na_2O_{wl}	SO_3	CaO_{free}	MgO
CEM I 32.5 R	61.4	19.7	5.7	3.2	0.8	0.2	0.7	0.1	2.9	0.5	2.9
CEM I 42.5 R	61.4	21.6	4.0	4.6	0.7	0.2	0.4	0.1	3.1	2.1	0.9

Table 2 Mineralogical constitution of the cements – main components [%]

	C_2S	C_3A	C_3S	C_4AF	Gypsum	Bassanite	Anhydrite
CEM I 32.5 R	18.6	6.0	50.5	7.8	1.4	1.8	3.5
CEM I 42.5 R	21.7	3.8	50.0	11	1.9	1.7	3.7

Table 3 Physical characteristics of the cements

	Density [g/cm^3]	Specific surface [cm^2/g]	Water requirement [%]	Setting begin [h:min]	Setting end [h:min]
CEM I 32.5 R	3.14	2830	26.0	03:00	04:05
CEM I 42.5 R	3.18	3680	28.5	03:15	04:15

Table 4 Particle size characteristics of the cements

	Average grain size [µm]	Median grain size [µm]	Particle size at 10% throughput [µm]	Particle size at 90% throughput [µm]
CEM I 32.5 R	29.18	18.57	1.40	69.68
CEM I 42.5 R	13.98	10.44	0.81	33.32

Table 5 Statistical evalution of lasergranulometric measurements

Average grain size	modal	median	Particle size at 10% passage	Particle size at 90% passage
[µm]	[µm]	[µm]	[µm]	[µm]
0,074	0,073	0,071	0,053	0,092

chemical constitution of the serum[1] is dominated by components of the surfactant compounds, especially potassium (10 mmol/l), sodium (253 mmol/l) and silicon (182 mmol/l).

For the determination of the particle charge 10 ml of a 1:40 diluted sample of the SA dispersion was titrated against the isoelectric point, using the titrant PolyDADMAC (0.001 N). It was necessary to dilute the SA dispersion, because the measuring cell of the Particle Charge Detector (Fa. Mütek) can only take up a limited amount of titrant. From the titrants consumption, the total charge of the dispersed SA particles was calculated based on a three-fold determination.

The infrared spectrum of the filmed styrene acrylate copolymer dispersion (stored for two days under laboratory conditions) is pictured in Fig. 1. It was recorded with the Fourier transform infrared spectrometer iZ10 from Thermo Scientific using ATR technology (ATR—attenuated total reflection). The sample was directly applied to a crystal with a high refractive index, in this case diamond. The infrared radiation passing the crystal under one or more total reflections is weakened depending on the wavelength, depending on the substance applied. This kind of measurement creates a spectrum that is very similar to the absorption curve that arises during the transmission measurement.

The following vibrational bands characterize the infrared spectrum of the SA copolymer:

[1] Fluid phase of the latex dispersion, extracted by dialysis.

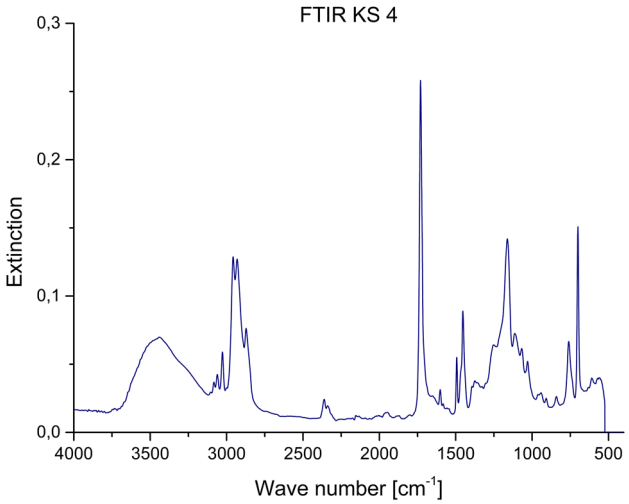

Fig. 1 Infrared spectrum of the filmed styrene acrylate

- The stretching vibration of O–H compounds at $\nu = 3340\ cm^{-1}$
- The antisymmetric and the symmetrical C–H stretching vibration of CH_2 compounds at $\nu = 2957\ cm^{-1}$ and $\nu = 2872\ cm^{-1}$, or the antisymmetric stretching vibration of the CH_3 compounds
- The stretching vibration of carboxyl groups at $\nu = 1731\ cm^{-1}$ and
- The framework vibrations of the C–C compounds of the aromatic ring at 1602 cm^{-1}, 1585 cm^{-1} and 1493 cm^{-1}.

2.1.3 Characterization of the polymer-modified cement pastes—Influence of styrene acrylate copolymers on hydration kinetics

The influence of the SA particles on the cement hydration was determined by calorimetric investigations with the MC CAL (C3 Prozess- und Analysentechnik). The

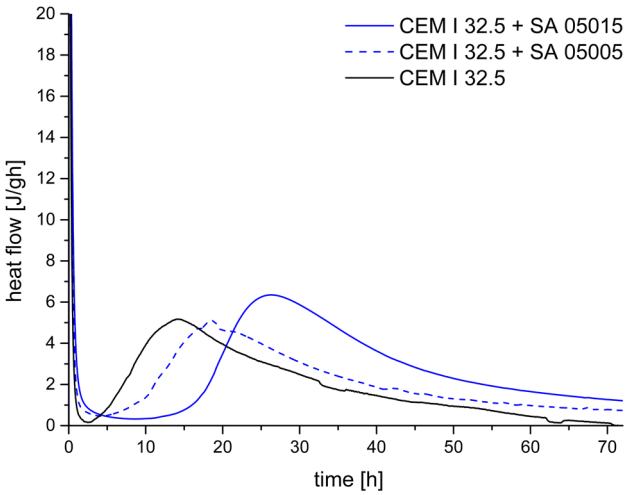

Fig. 2 Heat flow curves for CEM I 32.5 R with w/c = 0.5 and polymer-modified pastes with p/c = 0.05 und p/c = 0.15

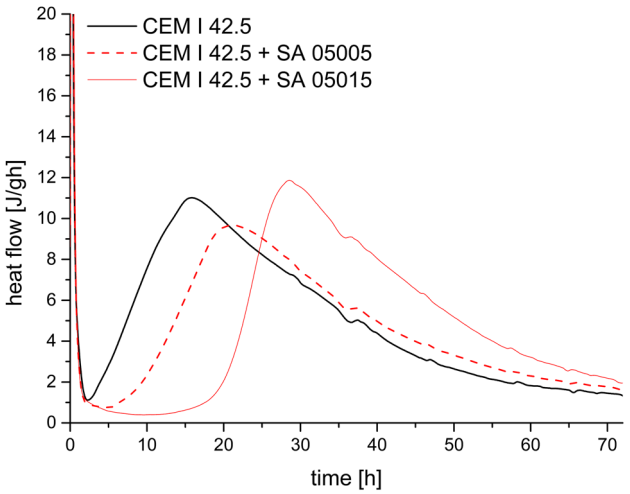

Fig. 3 Heat flow curves for CEM I 42.5 R with w/c = 0.5 and polymer-modified pastes with p/c = 0.05 und p/c = 0.15

polymer-modified cement pastes were produced with a water to cement ratio w/c = 0.5 and polymer contents of p/c = 0.05 (indication: 05005) respectively p/c = 0.15 (indication: 05015). After conditioning the raw materials at 20 °C inside of the calorimeter, the components were externally homogenized by using a laboratory mixer with a disperser unit. The measurements started after 5 min of hydration and were carried out at 20 °C as well. The results of the isothermal differential calorimetry are shown in Figs.2,3 and indicate an expectable retardation of the cement hydration with increasing polymer content. Because of their different specific surface, the reactivity of the cements varies, effecting in a lower heat flow maximum of the unmodified reference samples of CEM I 32.5 in comparison to the CEM I 42.5.

In the presence of the polymers a slowed down hydration can be observed, caused by a shift of the solution/precipitation equilibrium. The reasons for this shift are interactions of functional groups on the SA particle surface or of stabilizing additives that come from the fluid phase of the SA dispersion with ions of the cement paste pore solution. Furthermore nucleation areas occupied with adsorbed SA particles retard the hydrate phase growth.

However, once this threshold has been overcome and the saturation concentrations for hydrate phase formation have been reached, the reactions take place at a comparable intensity or, in the case of CEM I 32.5 with a p/c value of 0.15, even with an increased heat release.

2.2 Adsorption measurements—methodical approaches

2.2.1 Direct determination of styrene acrylate copolymers—Depletion method and thermo-gravimetric analysis coupled with mass spectrometry

The application of both direct methods for the quantification of polymer adsorption was proceeded for the same sample, following the preparation steps below. By centrifugation, the cementitious particles, with and without the adsorbed SA particles, settle due to the greater density, while the still freely mobile, not adsorbed SA particles remained suspended in the supernatant. Up to step 4, procedure corresponds to the description in [10] the sample preparation for the depletion method.

Preparation steps:

Supernatant

1. Mixing of polymer-modified cement paste with w/c = 0.5 and p/c = 0.05 respectively p/c = 0.15
2. Centrifugation of the polymer-modified cement paste after 7 min, 30 min, 60 min and 120 min[2] at 4000 rpm for 5 min
3. Removal of the supernatant with syringe, short term capping until gravimetric analysis
4. Extraction of a representative sample from inside of the sediment

Sediment

5. Immediately interruption of further hydration processes by cooling down the sediment with liquid nitro-

[2] Examination times were set, well before the solidification of the unmodified cement pastes started ($t_{setting,32.5}$ = 3 h, $t_{setting,42.5}$ = 3,25 h).

gen, complete hydration stoppage of the sediment by freeze drying till constant weight
6. Subsequent storage in the refrigerator at −5 °C until TG-MS-analysis

Using the centrifuge SIGMA 3K30 with the rotor 12155_H, the centrifugation regime corresponds to a relative centrifugal force of 1628 g.

The depletion method, is aiming at the detection of not adsorbed SA particles in the supernatant by the determination of weight losses on drying ($m_{\text{physically bound water}}$) and annealing ($m_{\text{polymer}}$). Following the description in [10] drying takes place at 100 °C for 2 h in a drying oven and annealing at 600 °C for 1 h in a muffle furnace. Knowing the current polymer concentration of the sample c_{max} and the polymer concentration of the supernatant $c_{\text{supernatant}}$ (Eq. 1a and 1b, the adsorption degree is calculated by solving Eq. 2. When calculating the concentration of $c_{\text{supernatant}}$, the loss of water due to freeze drying of the sediment was considered as physically bound water as well.

$$c_{\text{supernatant}} = \frac{m_{\text{Polymer}}}{V_{\text{physically bound water}}}\left[\frac{g}{l}\right] \tag{1a}$$

$$V_{\text{physically bound water}} = \frac{m_{\text{physically bound water}}}{\rho_{\text{water}}}[l] \tag{1b}$$

$$\alpha_{\text{A}} = \frac{\left(c_{\text{max}} - c_{\text{supernatant}}\right)}{c_{\text{max}}} \times 100[\%] \tag{2}$$

The potential source of error is reasoned in interfacial forces between the sediment and the supernatant, which are favored by centrifugal forces. These may cause an increased accumulation of polymer particles in this area, which mistakenly get included in the calculation as "adsorbed".

To address the aforementioned preparative problem, not the supernatant but the sediment of the same samples were directly examined in a combination of thermogravimetry and mass spectroscopic analysis.

The use of the thermo-gravimetric analysis coupled with mass spectrometry (TG–MS) enabled the investigation of the sediment with regard to the contained polymer amount, whereby the calculation of the adsorption degree based on the evaluation of pyrolysis product signatures. Furthermore, the weight loss during the polymer pyrolysis is evaluated.

To the best of our knowledge, this method was not applied to quantify polymer adsorption yet.

Using the simultaneous thermal analysis equipment STA 449 F3 Jupiter (NETZSCH) coupled with the mass spectrometer QMS 403 D Aëolos$^{\text{Ò}}$, the investigations were carried out. Boundary conditions of the measurements were a temperature range from 35 to 1000 °C, a heating rate of 10 K/min, a controlled inert atmosphere under argon and a nearly constant sample weight of 45 mg. Before starting the measurement, three times repeated vacuum was drawn. The conditions are listed in Table 6.

Before the experiments were started, the temperature was calibrated with the help of calibration substances with sufficiently well-known transition temperatures. The calibration takes place under the same conditions as the subsequent measurements. (Table 7).

2.2.2 Analysis algorithm – evaluation of pyrolysis product signatures

Using the example of an evaporated, 7 min hydrated CEM 32.5 paste with a SA content of 15%, Fig. 5 shows the mass losses (red curve), which result from the dehydration of hydrate phases and the pyrolysis of the styrene acrylate copolymer. Due to the overlap of the temperature areas in which these processes takes place, the associated weight loss cannot be clearly assigned. By identifying the ion current, which is associated with the pyrolysis of the polymer using quasi multiple ion detection (QMID—green curve), a quantitative determination of the fragments is possible. The fragmentation patterns of the styrene acrylate copolymer were detected in a temperature range in between 200 and 500 °C. The concentration of ions with mz = 104 is assigned to styrene (Fig. 4). To quantify these signals the appropriate integral $F(X)_{104,\ \text{CEM+Pol}}$ between 200 and 500 °C was calculated (green hatched area in Fig. 5). The same procedure was performed for defined silica/polymer samples with exactly known polymer contents w_{Pol} between 0.5 and 15 wt% based on silica, for getting a calibration line (Fig. 6), in which the integral $F(X)_{104,\ \text{Silica+Pol}}$ is assigned to the corresponding polymer concentration.

To get defined samples as accurately as possible the preparation procedure of silica/polymer samples was as follows:

1. Freeze-drying of the SA dispersion

Table 6 Test conditions of TG-MS measurements

Heating rate	10 K/min
Purge gas	Argon
Purge gas rate (balance / sample)	20 / 50 mL/min
Initial temperature of the samples	Ambient
Final temperature of the samples	1000 °C
Sample weight	45 mg
Pan	Pt/Rh (80/20), 190 µl

Table 7 Details of the temperature and sensitivity calibration

Calibration substances	Nominally temperature	Experimentally determined temperature	Corrected temperature
Biphenyl	67.7	66.8	67.9
Benzoic acid	121.5	120.4	121.5
Rubidium nitrate	164.2	163.4	164.5
Potassium perchlorate	299.3	298.0	299.1
Silver sulphate	425.6	424.4	425.4
Cesium chloride	473.3	472.7	473.7
Potassium chromate	670.0	668.5	669.5
Barium carbonate	801.4	799.5	800.5

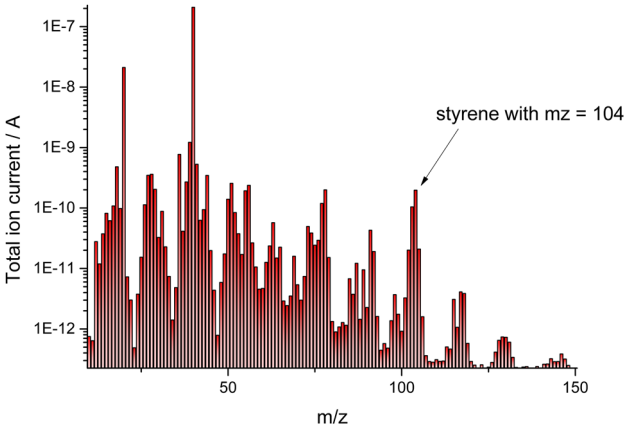

Fig. 4 Mass spectrum of fragmented styrene acrylate copolymer at a temperature of 320 °C; red circle: styrene with mz = 104

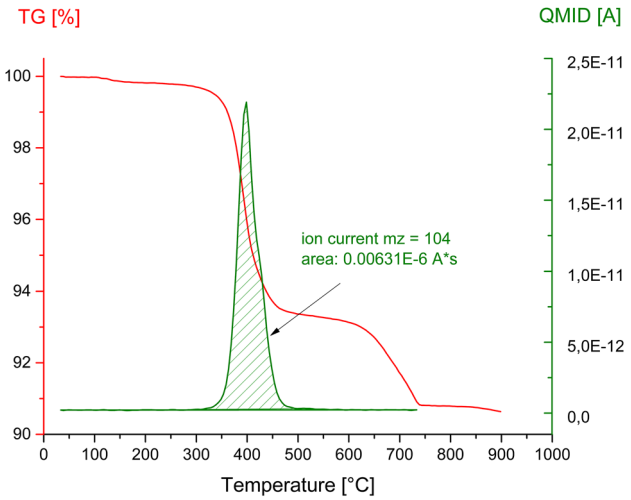

Fig. 5 TG-curve (red) of the CEM I 32.5, p/c 0.15 after 7 min of hydration overlayed with the ion concentration of ions with mz = 104 (green); green hatchen: line integral in between 200 °C und 500 °C for mz = 104 (styrene)

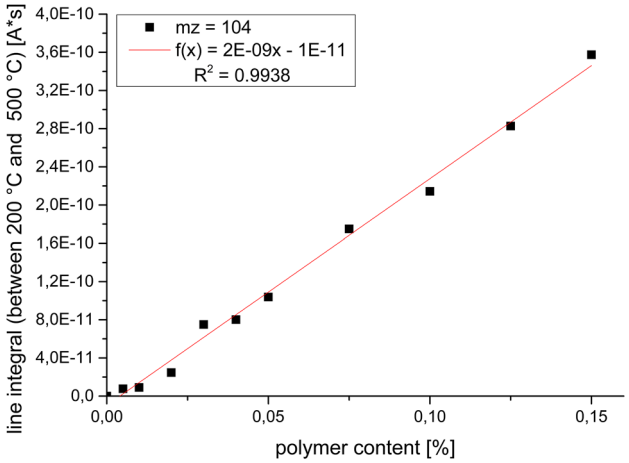

Fig. 6 Calibration line for mz = 104, received by TG–MS analysis of silica/polymer samples, with known polymer contents ($0.5\% \leq w_{Pol} \geq 15\%$), normalized to 1 mg

2. Finely grounding of the remaining residues with a pestle and mortar (agate) under fluid nitrogen
3. Weighing of silica and SA to five places of decimals

The determination of the adsorption degree follows the three steps below:

1. Calculation $F(X)_{104,\,CEM+Pol}$ for the sediment of cement/polymer samples
2. Assignment of $F(X)_{104,\,CEM+Pol}$ to polymer content w_{Pol} based on the calibration curve
3. Calculation of the adsorption degree by putting the polymer content of the sediment $w_{Pol,centrate}$ in relation to the maximum polymer content of the whole sample $w_{Pol,max}$ (according to Eq. 3)

$$\alpha_A = \frac{w_{Pol,centrate}}{w_{Pol,max}} \times 100 \quad (3)$$

Uncertainties are given by sample inhomogeneity due to centrifugally pressed in SA particles in the sediment and their top down grading distribution in vertical direction. Answering this, all samples, analyzed by TG–MS were taken from the lower third of the sediment, assuming that this area is least distorted. Not adsorbed but convicted SA particles in the sediment are not registered.

2.2.3 Indirect determination of styrene acrylate copolymers—VIS-photometry

Another methodical approach to quantify the adsorption of SA particles on cementitious surfaces is the determination of the turbidity, caused by not adsorbed SA particles in the fluid phase using the spectral photometry in the VIS range.

The analyzes were carried out with a stray-light-reduced two-beam spectrophotometer, the SPECORD® 250 from Analytik Jena, at a wavelength of 546 nm in the visible range of the light spectrum.

Due to the method inherent inaccuracy at high turbidities, carrying out these measurements requires the dilution of polymer-modified cement paste samples. With the help of dilution series, considering the varying equilibrium of adsorption and desorption at different dilution stages, the adsorption degree for an undiluted system is calculated.

Preparation steps for dilution series:

1. Mixing of polymer-modified cement pastes with w/c = 0.5 and p/c = 0.05 respectively pc = 0.15
2. Subsequently, at fixed times, 1 g of the polymer-modified cement paste was diluted with a certain amount of deionized water.
3. The different dilution stages were prepared from the same polymer-modified cement paste lot and then centrifuged for 3 min at 2000 min^{-1}.

Using the centrifuge SIGMA 3K30 with the rotor 11,390 (insert 13,097), the centrifugation regime corresponds to a relative centrifugal force of 604 g.

To assign the turbidity of the fluid phase to a polymer concentration $c_{t,i}$ in g/l, calibration curves were prepared for the styrene acrylate copolymer dispersion. Low dilution levels during the later sample preparation result in polymer concentrations, which are nonlinear to the turbidity they cause. For this reason, when determining the calibration curves for the polymer dispersions, it was necessary to consider the evolution of turbidity as a function of the concentration even for relatively high solids contents. The result is the nonlinear curve shown in Fig. 7.

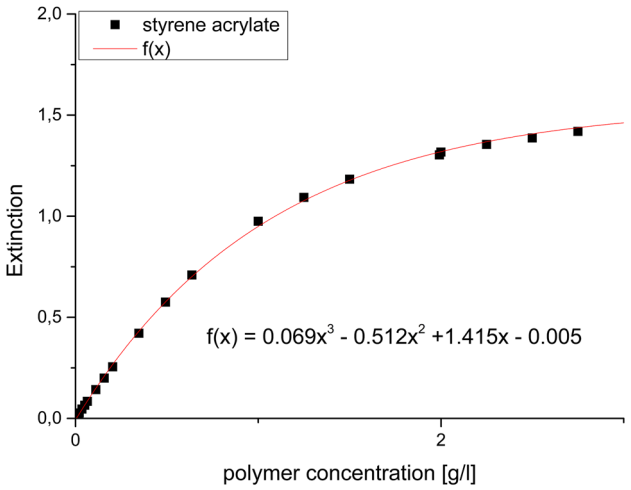

Fig. 7 Calibration curve of styrene acrylate copolymer dispersion – data fitted trend line, After 5 iterations the fit converged. Final sum of squares of residuals: 0.000517317, relative change during last iteration: -1.93649e^{-10}

The calculation of the adsorption degrees $\alpha_{a,i}$ for all dilution stages i follows Eq. 4 and 5:

$$c_{a,i} = c_{max} - c_{t,i}\left[\frac{g}{l}\right] \tag{4}$$

$$\alpha_{a,i} = \frac{c_{a,i}}{c_{max}} \times 100[\%] \tag{5}$$

where $c_{t,i}$ Polymer concentration c, determined from the turbidity measurement (index: t) at the dilution state i., c_{max} Maximal polymer concentration c contained in a polymer-modified cement paste sample., $c_{a,i}$ Concentration of adsorbed polymer particles at the dilution state i., $\alpha_{a,i}$ Adsorption degree at the dilution state i.

Finally the adsorption degrees plotted against the water content were fitted to linear functions (samples with p/c = 0.05) or rather second grade polynomial functions (samples with p/c = 0.15). The continuation of these functions to the intercept tags the theoretical adsorption degree in an undiluted system. The data for this approximation based on two measurements at every dilution stage. Figs. 8,9.

Especially at a high polymer content, there are methodological limitations to be considered. The influence of colloidal cementitious particles stabilized by agents, originated from the polymer dispersion, remain unconsidered and may effect in negative adsorption degrees for highly diluted samples. Interfacial forces between the sediment and the supernatant that cause an increased accumulation of polymer particles in this area are less effective

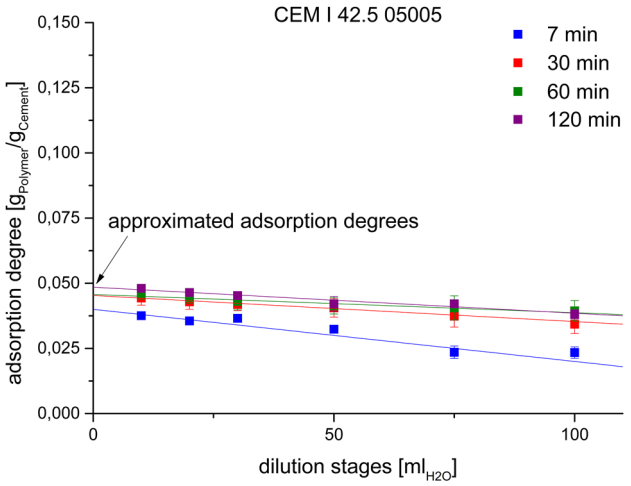

Fig. 8 Linear relation between adsorption degree [$g_{polymer}/g_{cement}$] and amount of water [ml] for dilution for polymer-modified cement pastes with a p/c ratio of 0.05

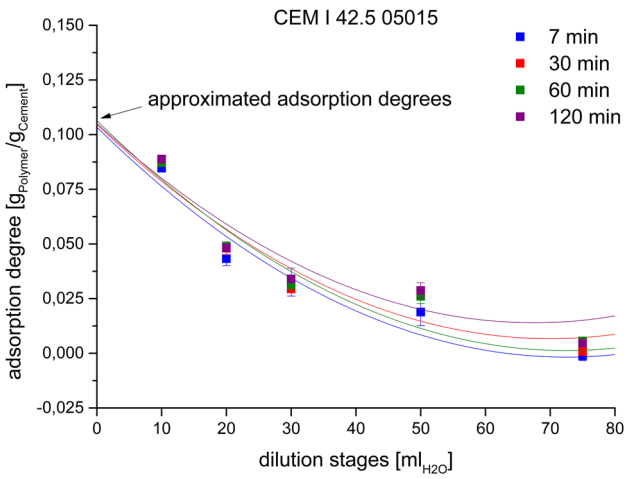

Fig. 9 Relation between adsorption degree [$g_{polymer}/g_{cement}$] and amount of water [mL] for dilution for polymer-modified cement pastes with a p/c ratio of 0.15 data fitting on second grade polynomial functions

than in undiluted samples, nevertheless an influence is not excluded.

For pastes with a high polymer content the adsorptions/desorption equilibrium results in nonlinear functions. If second grade as well as third grade polynomial fitting curves exhibit comparable regressions but lead to different approximated adsorption degrees, the method is inapplicable to quantify the adsorption degree.

Above all, the potential of this method lies in the fact that the ratio of adsorption to desorption can be used for a relative assessment of the strength of effective attractive forces, as comparative studies in [19] showed.

3 Comparative discussion of experimental results

At a low polymer content (p/c = 0.05) qualitatively all presented results transport the same message (Fig. 10). The well-known fact that a high specific surface leads to an increasing polymer adsorption could be shown by every methodical approach. Focusing the "initial" adsorption at 7 min of hydration, quantitatively, the lowest adsorption degrees with $\alpha_{32.5,TG\text{-}MS} = 0.018\ g_{Polymer}/g_{Cement}$ (36%) and $\alpha_{42.5,TG\text{-}MS} = 0.029\ g_{Polymer}/g_{Cement}$ (58%) were determined using the TG-MS analyze. Substantially higher adsorption, $\alpha_{32.5,depl} = 0.036\ g_{Polymer}/g_{Cement}$ (68%) and $\alpha_{42.5,depl} = 0.044$ (88%), was registered with the depletion method. Spectralphotometrically generated values lying in between these extremes.

In [23] also the adsorption behavior of anionically stabilized SA particles on cementitious surfaces was studied. For a CEM I 32.5 paste (w/c = 0.3) with a p/c value of 0.057 a degree of adsorption of 0.039 g_{SA}/g_{cement} was determined using the filtration method, which is described in [24]. A CEM I 42.5 (w/c = 9) with p/c = 0.05 was examined in [7] using the sedimentation test. As a result 0.05 g_{SA}/g_{cement} adsorbed. Both values are well above the degrees of adsorption determined in this paper. In both cases the polymer-modified cement paste samples had to be diluted to determine the polymer particle adsorption.

Because numerous factors influence the final determined degree of polymer particle adsorption, the comparison of data that were not obtained in exactly the same way is generally questionable. In addition to the methodology and the type of preparation used, these factors obviously include the specific constitution of the raw materials and the paste as a whole.

For this reason, all data that enable a comparison of the three methods that are the subject of this article were determined independently and explicitly for the specific material systems.

The results of the investigations of the CEM I 32.5 with *high polymer content* (p/c = 0.15) showed the same order of the adsorption degrees—lowest values were generated with the TG–MS-analysis ($\alpha_{32.5,TG\text{–}MS} = 45\%$), highest with the depletion method ($\alpha_{32.5,depl} = 66\%$) and

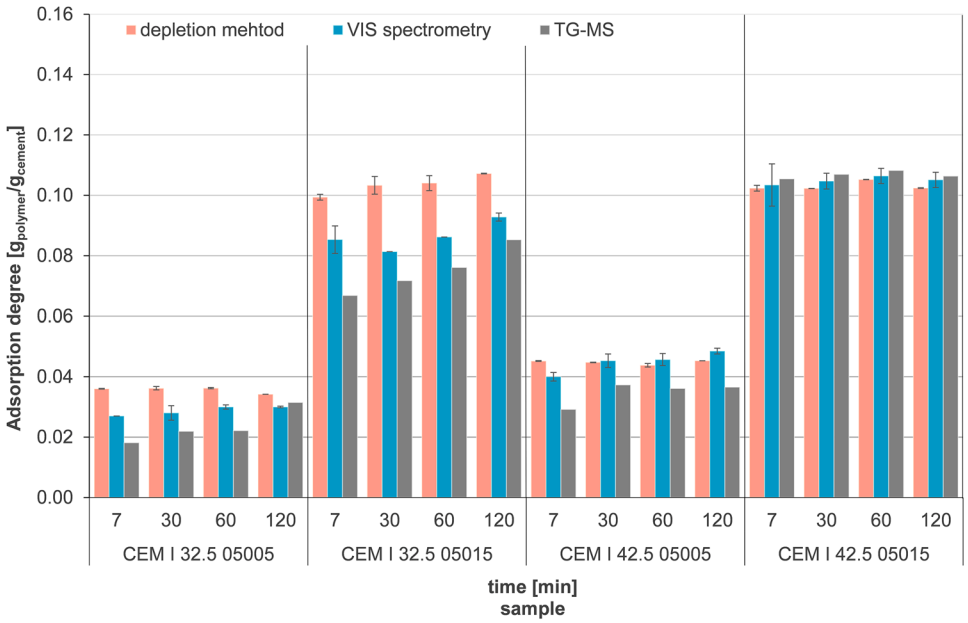

Fig. 10 Amount of adsorbed polymer relative to the cement [$g_{polymer}/g_{cement}$] – comparing depletion method (orange), VIS-spectrophotometry (blue) and TG–MS trials (grey)

in between the values of the turbidity measurements ($\alpha_{32.5,turb} = 54\%$) are situated.

Against expectations each method delivers the same result for the polymer-modified cement paste with CEM I 42.5 and a p/c value of 0.15–70% adsorption of the SA particles over the entire observation period. The explanation for the fact that no higher values were determined using the depletion method, is probably due to the interactions in the interface between supernatant and sediment that cannot be clearly estimated. The interface enrichment apparently decreases when the actual degree of adsorption increases, since there are significantly fewer non-adsorbed SA particles in the supernatant getting attracted.

Regardless of whether the supernatant or the sediment is examined, an overestimation of the polymer adsorption can be assumed. According to the analysis of the sources of error in Sect. 2.2, the impact of preparation is higher when examining the supernatant. The investigation of the sediment therefore is generally regarded as more accurate. However, the experiments using TG–MS are initially a first feasibility study with a new method—a reliable error range cannot yet be specified based on the data determined. Further investigations are currently in progress.

4 Conclusions

The presented critical examination of methods for the quantitative determination of the adsorption degree of SA particles on cementitious surfaces and hydration products revealed the sampling by centrifugation as the decisive influencing factor.

Using the depletion method, there is a high impact of the centrifuging regime, because interfacial forces between sediment and supernatant causes an increased accumulation of polymer particles in this area, which mistakenly are considered in the calculation as "adsorbed". The results confirmed that the degree of adsorption is significantly higher when the polymer concentration of the supernatant is determined, as long as interfacial interaction cause a polymer particle enrichment in this area. This influence seems to decrease when the polymer concentration in the supernatant falls below critical value. Even qualitative statements cannot be made with certainty, since the equilibrium between sediment and supernatant is system-dependent – the degree of hydration, the chemical constitution, suspension-specific parameters and the degree of polymer adsorption itself result in the state, which arises in the supernatant.

In the case of diluted polymer-modified cement paste samples, also separated by centrifugation, the interface accumulation of polymer particles plays a lesser role. For this reason, the visible spectrophotometry was developed to determine the polymer concentration. Conclusions about the degree of adsorption are drawn by an approximation, extrapolating various dilution state turbidities to an undiluted stage. Uncertainties in the approximation arise in particular from colloidal mineral particles, stabilized by agents originated from the polymer dispersion that remain unconsidered. This influence of the stabilizing agents increases with an increasing polymer content.

Fitting nonlinear functions to the experiment data (at a high polymer content) may also lead to incorrect forecasts and absolute statements cannot be made with this method either. Qualitatively, when comparing different systems under the same conditions, the method is classified as suitable.

For the investigated samples, the same relation of adsorption was identified with all three methods, but due to the potential sources of error when examining the supernatant of diluted and undiluted systems, depletion method and turbidity measurements should be reconsidered for quantitative analysis of the polymer adsorption.

An obvious conclusion to avoid these problems is the investigation of the sediment for which the use of the thermogravimetry coupled with mass spectrometry turned out to be suitable. Uncertainties are given by not adsorbed but convicted polymers in the sediment and sample inhomogeneity due to centrifugally pressed in polymer particles, especially near the interface. To minimize the latter influence, sampling from the lower area of the sample is recommended.

In spite of the high expenditure in terms of equipment and time compared to the other methods, the first trials suggest that the results obtained have a high informative value.

A great advantage of TG–MS is the applicability on systems with more than one organic additive, as long as the pyrolysis product signatures are clearly distinguishable. Initial findings within application-orientated studies indicates that e.g. in the presence of PCE-plasticizer the styrene acrylate copolymer is faultless detectable and quantifiable by TG–MS.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Code availability The data fitting of the calibration curve of the styrene acrylate copolymer dispersion was done with the freeware gnuplot and the calculation of the polymer concentration from the turbidity was carried out with matlab using the custom code attached as file "calculation polymer concentration.pdf".

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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