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Interaction mechanisms between Na montmorillonite clay and MPEG-based polycarboxylate superplasticizers

S. Ng, J. Plank *

Technische Universität München, Chair for Construction Chemicals, 85747 Garching, Lichtenbergstraße 4, Germany

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ABSTRACT

Sodium montmorillonite clay is shown to negatively impact the dispersion force of two methacrylate based polycarboxylates (PCEs) in cement paste. The PCEs tested consist of methacrylic acid/MPEG methacrylate-ester with molar ratios of 6:1 and 1.5:1. It was found that the PCEs sorb both chemically and physically onto clay. The sorbed amounts are ~100 times more than on cement. Chemisorption occurs via intercalation of the poly(ethylene oxide) side chains into the interlayer region between the alumosilicate layers, while physisorption occurs on clay surfaces which are positively charged through uptake of Ca^{2+}. PCEs possessing high grafting density predominantly intercalate and show less surface adsorption, and vice versa. Also, the type of sorption is dosage dependent, whereby side chain intercalation dominates at higher PCE dosages, while electrostatic attraction via the anionic backbone prevails at lower dosages. Polyglycols can be utilised as sacrificial agents when highly grafted PCEs are employed at high dosages.

1. Introduction

Montmorillonite is a 2:1 smectite clay mineral, consisting of stacked octahedral aluminate layers sandwiched between two tetrahedral silicate layers (Fig. 1). The resulting alumosilicate layers measure about 1 nm in thickness [1]. The general composition of montmorillonite can be expressed as $M_x(Mg,Al,Fe)_2(OH)_2[Si_4O_{10}] \cdot nH_2O$, with $M^+ = Na^+$, K^+, 0.5 Mg^{2+} or 0.5 Ca^{2+}. Partial substitution of Si^{4+} by Al^{3+} generates an overall negative charge of the basal surfaces. This charge is balanced by intercalation of cations (M^+; hydrated or non-hydrated) in between the alumosilicate layers [2].

When clay is dispersed in electrolyte containing fluids such as cement pore solution, cations can also adsorb onto the permanently negatively charged basal surfaces of the clay platelets. Other anchoring sites for cations are the crystal edges where terminal –OH groups from aluminates and silicates are present [3,4]. Under high pH conditions, these terminal –OH groups are deprotonated and develop a negative charge (Fig. 2).

Montmorillonite is among the most researched clay minerals because of its natural abundance and its viscosifying property. Over the last two decades, novel nanocomposites comprising of polymer layered silicates (PLS) were developed whereby a wide range of monomers and polymers including glycols and polyimides intercalates into the galleries of montmorillonite clay. Such PLS nanocomposites, when compared to conventional materials based on glass or mineral fibre enforced polymers showed enhanced mechanical stiffness, strength and barrier properties [5–9]. Specifically, PLS nanocomposites provide enhanced thermal stability to the materials. In the construction field, applicators have observed that presence of certain clays may affect and can be detrimental to the initial workability of concrete [10–12]. Montmorillonite was found to be more harmful than other clays due to its expanding lattices which promote intercalation, swelling and cation exchange [13,14]. The extent of these interactions is dependent on many factors including pH and the type of polyelectrolyte present in the medium. The ability of this clay to sorb water and swell causes an increase in viscosity of the cement paste (a loss in workability) or a higher water demand to produce the same workability as before. This is detrimental for the mechanical properties and durability of concretes [15].

Some studies have shown that polymers can sorb on clay particles [16]. The impact of this process in the construction field is dependent on the type of admixtures used. For superplasticizers, polycondensates were shown to be less affected by the presence of clay than polycarboxylates [10,11,17,18]. This indicates that when concrete is contaminated by a significant quantity of montmorillonite, competing demands by different components (cement and clay) for the polycarboxylate can occur, thus reducing its availability for dispersion. In contrast to PCEs, polycondensates do not show this effect.

In the present study, the effect of clay addition to cement (dosage: 1% by weight of cement) on the behaviour of two polycarboxylate based superplasticizers was investigated. A naturally occurring sodium montmorillonite clay was employed. First, the influence of clay on the workability of cement pastes containing two different

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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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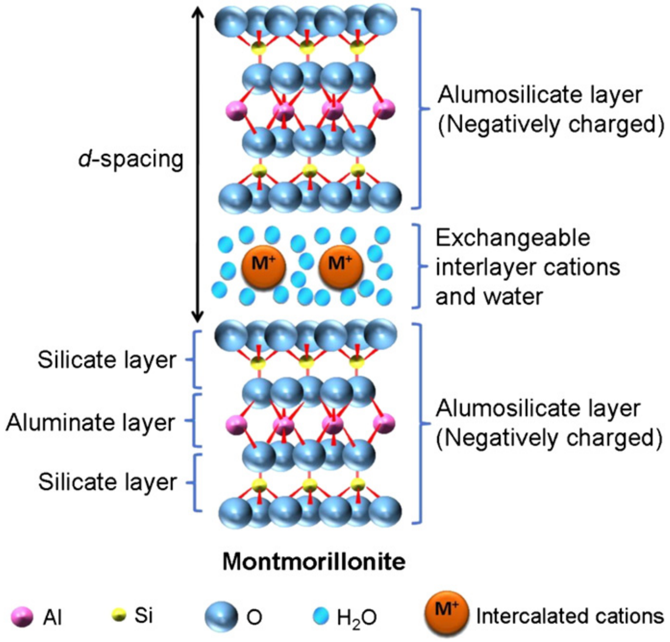

Fig. 1. Schematic illustration of the layer structure present in montmorillonite clay.

methacrylic acid–methacrylate ester based PCEs was determined by 'mini slump' test. The two PCEs varied by their grafting densities and correspondently anionic charge amounts. To ascertain the interaction of these PCEs with clay, their adsorption on the cement/clay mixture was measured via total organic carbon (TOC) method. A simplified system comprising only clay, PCE and synthetic cement pore solution was subsequently utilised to identify the sole effect of clay on PCE. First, the amount of PCE sorbed by clay was determined. XRD analysis was performed to probe a potential chemisorption of PCE by clay. For clarification of the specific interaction of individual PCE building blocks with clay, adsorption of the polymethacrylate backbone and of the poly(ethylene oxide) side chain were studied separately. This investigation was performed by using poly(methacrylic acid) (PMA) and polyethylene glycol (PEG). The individual amounts of side chain or backbone sorbed were used to calculate the idealised amount of PCE sorbed by clay. This way, the mechanism of interaction between PCE and clay in the cementitious system was sought to be clarified.

2. Materials and methods

2.1. Cement

A CEM I 52.5 R HS/NA (Holcim, Lägerdorf/Germany) was used. Its phase composition as obtained by quantitative X-ray diffraction (Bruker D8 advance instrument, software Topas 4.0) is presented in Table 1. The specific surface area of 4300 cm^2/g was measured using a *Blaine* instrument (Toni Technik, Berlin/Germany). The particle size (d_{50} value) of 8.33 μm was obtained on a laser granulometer CILAS 1064 (Cilas, Marseille/France), while the density was 3.22 g/cm^2 measured by ultrapycnometry (Quantachrome, Odelzhausen/Germany).

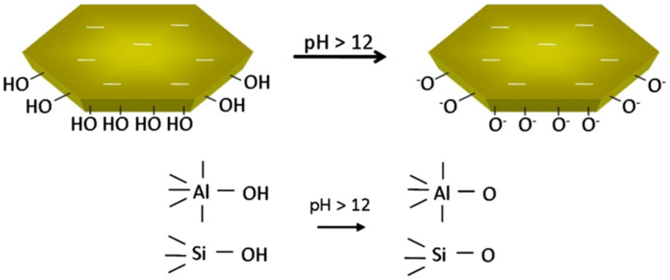

Fig. 2. Schematic illustration of charge distribution and deprotonation of terminal – OH groups present along crystal edges of a montmorillonite particle at high pH.

Table 1
Phase composition of CEM I 52.5 R HS/NA sample as determined by XRD using *Rietveld* refinement.

Phase	[wt.%]
C_3S, monoclinic	60.1
C_2S, monoclinic	19.0
C_3A, cubic	1.2
C_3A, orthorhombic	0.4
C_4AF, orthorhombic	14.5
Calcite	1.3
$CaSO_4 \cdot 1/2\ H_2O$[a]	2.2
$CaSO_4 \cdot 2\ H_2O$[a]	1.0
$CaSO_4$	0.4

[a] Determined by thermogravimetry.

2.2. Sodium montmorillonite clay

A commercial sodium montmorillonite clay sample (RXM 6020 supplied by Rockwood, Moosburg/Germany) was used as per obtained. This clay is a naturally occurring sodium montmorillonite clay. Its oxide composition is presented in Table 2. It develops a pH of ~9 when prepared as a 2 wt.% aqueous suspension. The XRD pattern of the dry clay reveals a *d*-spacing of 1.07 nm (Fig. 3).

2.3. Polycarboxylate samples

Two PCE superplasticizers and two polymers representing the poly(methacrylic acid) backbone and poly(ethylene oxide) side chain of the PCEs were utilised. The PCEs were synthesized according to a literature description by aqueous free radical copolymerization of methacrylic acid (MAA) and methoxy terminated poly(ethylene oxide) methacrylate (MPEG-MA) ester at molar ratios of 1.5 and 6 respectively [19]. Methallylsulfonic acid was used as chain transfer agent. Both copolymers have side chains made up of 45 ethylene oxide units (EOUs). They are denoted by 45PCx, where 45 refers to the number of EOUs in the side chain, and x corresponds to the molar ratio of MAA:MPEG-MA. The chemical formula of the PCEs is presented in Fig. 4. PMA was synthesized by aqueous free radical polymerization of MAA [20], while PEG-2000 was used as per obtained (Clariant, Frankfurt am Main/Germany).

For polymer characterisation, size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn/Germany) equipped with RI detector 2414 (Waters, Eschborn/Germany) and a 3 angle dynamic light scattering detector (mini Dawn from Wyatt Technologies, Santa Barbara, CA/USA) was used. Prior to application on the columns, the polymer solutions were filtered through a 0.2 μm filter. The polymers were separated on an Ultrahydrogel™ precolumn and three Ultrahydrogel™ (120, 250 and 500) columns (Waters, Eschborn/Germany) using 0.1 M aqueous $NaNO_3$ solution (adjusted to pH 12.0 with NaOH) as an eluant at a flow rate of 1.0 mL/min. From this separation, the molar masses (M_w and M_n), the polydispersity index (PDI) and the hydrodynamic radius ($R_{h(z)}$) of the polymers were

Table 2
Oxide composition of sodium montmorillonite clay sample, RXM 6020 as determined by X-ray fluorescence.

Oxide	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI	Total
[wt.%]	59.7	18.4	0.8	2.3	4.0	2.3	0.1	0.1	12.1	99.8

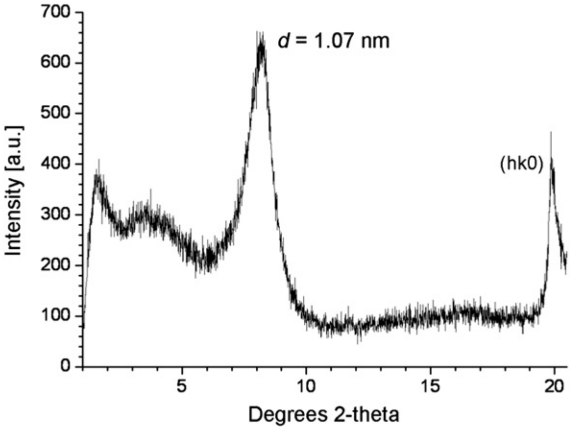

Fig. 3. X-ray diffraction pattern of dry sodium montmorillonite clay sample, RXM 6020.

determined. The value of dn/dc used to calculate M_w and M_n for all polymers was 0.135 mL/g (value for polyethylene oxide) [21].

Specific anionic charge amounts of the polymers were analysed by a particle charge detector (PCD 03 pH from Mütek Analytic Company, Herrsching/Germany). Solutions containing 0.02 wt.% of anionic polymer dissolved in synthetic cement pore solution were prepared and titrated against a 0.001 N solution of cationic polydiallyl dimethyl ammonium chloride (polyDADMAC) until charge neutralization was attained. The amount of negative charge per gram of polymer was calculated from the consumption of the cationic polyelectrolyte.

Purity of PEG-2000 was confirmed by ^{1}H NMR analysis using a Bruker DPX250 250 MHz instrument (Bruker, Ettlingen/Germany).

2.4. Zeta potential measurements

Zeta potentials of montmorillonite suspensions were determined as a function of pH in millipore water adjusted with 37 wt.% aqueous HCl and 19.5 wt.% aqueous NaOH, and in synthetic cement pore solution using a model DT 1200 Electroacoustic Spectrometer from Dispersion Technology, Inc. (Bedford Hills, NY/USA). The synthetic cement pore solution exhibited a pH of 12.8 and was prepared by dissolving 1.72 g $CaSO_4 \cdot 2H_2O$, 7.119 g KOH, 4.76 g K_2SO_4 and 6.956 g of Na_2SO_4 in 1 L of millipore water respectively. The ionic composition (mmol/L) of this synthetic cement pore solution ($Ca^{2+} = 10$; $Na^+ = 100$; $K^+ = 180$; $OH^- = 127$; $SO_4^{2-} = 86$) is typical for normal Portland cement dispersed in water at a w/c ratio of ~0.4 [22]. Particle size of clay was measured using a ZetaSizer from Malvern Instruments Ltd (Worcestershire/United Kingdom). The w/clay ratio was 53 to actualise the conditions in the 'mini slump' test where the w/c ratio was 0.53 and 1% by weight of cement of clay were present.

2.5. 'Mini slump' test

For determination of the paste flow, a "mini slump" test according to DIN EN 1015 was utilised and carried out as follows:

At first, the w/c ratio needed to attain a spread of 18 ± 0.5 cm for the neat cement paste was determined, and the dosage of PCE superplasticizer required to reach a spread of 26 ± 0.5 cm at this specific w/c ratio was established. The PCE solution was generally added to the mixing water placed in a porcelain cup and the amount of water introduced with the PCE solution was subtracted from the amount of mixing water required for a w/c ratio of 0.53. In a typical experiment, 300 g of solids (pure cement or cement blended with 1 wt.% of clay) were added to the mixing water, agitated for 1 min and left to stand for another minute. The cement paste was next stirred for 2 min before transferring into a Vicat cone placed on a glass plate. The dimensions of the Vicat cone were: height 40 mm, top diameter 70 mm, and bottom diameter 80 mm. The cement paste was filled to the brim of the cone and levelled before it was vertically lifted from the surface of the glass plate. The resulting spread of the paste was measured twice; the second measurement being perpendicular to the first. The final spread value was taken as the average of the two measured ones.

2.6. XRD analysis of clay hydrated in presence of PCE

0.025 g clay was added to 1.34 g of 0.93 wt.% polymer solution (w/clay ratio of 53). The suspension was manually mixed for 1 min, sonicated for 10 min and centrifuged at 14,600 rpm for another 10 min. The solid residue obtained was dried at 80 °C overnight before it was ground and analysed. XRD scans of all samples were taken at room temperature on a D8 Advance, Bruker AXS instrument (Bruker, Karlsruhe/Germany) utilising a Bragg–Bretano geometry. Samples were placed in a front mounted plastic sample holder. Step size was 0.15 s per step, and spin of sample during scanning was set at a revolution time of 4 s. Nickel filter was used for incident beam with an aperture slit of 0.3°. The scan range was set from 0.6° to 20° 2θ.

2.7. Sorption experiments

PCE sorption on clay or cement was determined by the depletion method, i.e. it was assumed that removal of PCE from the pore solution solely was the result of interaction with clay and/ or cement and that no precipitation had occurred. In sample preparation, 300 g of pure cement or cement blended with 1 wt.% of clay were added to 2.0 wt.% 45PC1.5 or 0.17 wt.% 45PC6 solutions over 1 min in a porcelain cup (PCE dosages and w/c ratio as determined in 'mini slump' test). The mixture was allowed to rest for another minute before it was stirred for 2 min. Thereafter, the paste was centrifuged at 8500 rpm for 15 min. The filtrate was recovered, diluted and acidified

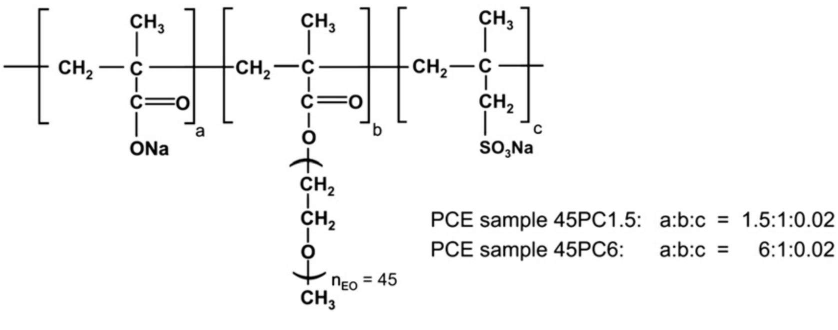

Fig. 4. Chemical structure of the PCE samples employed in the study.

with conc. HCl solution in a TOC sample flask. This final solution was then analysed by combustion at 890 °C on a HIGH TOC II instrument (Elementar Analysensysteme, Hanau/Germany). The sorbed amount of PCE was calculated from the difference between the TOC content in the stock solution and that left in the filtrate. In a separate experiment, 20 g/L of PCE was dissolved in the filtrate of clay suspended in synthetic cement pore solution and left to stand overnight. No precipitation was found, thus signifying that PCE depletion was solely a result of sorption by the cement or clay.

Sorption experiments of PCE, PMA and PEG-2000 on clay in synthetic cement pore solution were performed by using polymer solutions with concentrations ranging from 12.5 to 200% by weight of (bwo) clay. These polymer solutions were added to 0.025 g of clay, manually homogenized and sonicated for 10 min to achieve maximum dispersion of the clay particles and thus interaction with polymers. The mixture was then centrifuged at 14,600 rpm for 10 min. Thereafter, the filtrate was collected, diluted and acidified prior to further analysis by TOC measurement as before.

2.8. Theoretical calculation of PCE sorption

45PC1.5 consists of 11.6 wt.% PMA (backbone) and 88.4 wt.% PEG (side chain), while 45PC6 consists of 26.8 wt.% of PMA (backbone) and 73.2 wt.% PEG (side chain). From the experimental individual sorbed amounts of PEG-2000 and PMA, and from the relative percentage of each structural element present in the PCE, idealised amounts of 45PC1.5 and 45PC6 sorbed by clay were calculated as presented in Eqs. (1) and (2) and compared. Potential effects of different molecular architectures or sorbed conformations of the polymers were assumed to be negligible.

$$\text{PMA : Calculated amount of PCE sorbed} = \frac{\text{Exp.sorbed amount of PMA}}{\text{wt.\% of PMA present in PCE sample}}[\text{mg/g}] \qquad (1)$$

$$\text{PEG : calculated amount of PCE sorbed} = \frac{\text{Exp.sorbed amount of PEG}}{\text{w.\% of PEG sample}}[\text{mg/g clay}] \qquad (2)$$

Eqs. (1) and (2). Calculation of the sorbed amounts of PCEs based on the sorption profile of individual PMA and PEG respectively.

3. Results and discussion

3.1. Surface charge of montmorillonite

To assess the potential for electrostatic interaction between clay and PCE, its approximate overall surface charge as expressed by the zeta potential was measured. In deionised water, the zeta potential of the montmorillonite sample was found to be consistently negative due to its innate negative basal surface charge (Fig. 5). Till ~pH 5, the zeta potential of the clay suspension remained relatively constant at ~ −15 mV, but decreased sharply to ~−35 mV at pH 8 and stabilized thereafter. The transition in surface charge from pH 5 to 8 can be attributed to deprotonation of terminal silanol and aluminol groups present along the crystal edges of the clay platelets [23,24].

In synthetic cement pore solution (0.4 g/L Ca^{2+}), however, the clay suspension exhibited a zeta potential value of +15.1 mV, implying that cations such as Ca^{2+} adsorbed onto the clay surfaces. Through this mechanism, clay attains a positive surface charge and potential anchoring sites for incoming anionic polymers are formed.

3.2. Properties of PCE samples

The molecular characteristics and anionic charge amounts of the polymers are shown in Table 3. According to this data, the synthesized poly(methacrylate) backbone on average consists of 33 methacrylate units while the PCE copolymers 45PC1.5 and 45PC6 contain 23 and 17 methacrylate functionalities respectively. The anionic charge amounts increase by the order as follows: PEG<45PC1.5<45PC6<PMA. ^{1}H NMR analysis (spectrum not shown here) confirmed purity of >99% for PEG-2000.

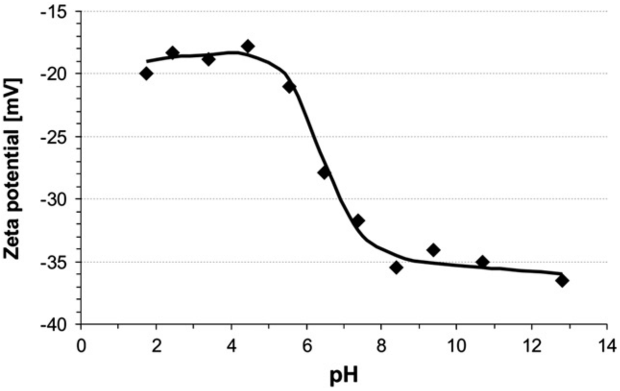

Fig. 5. Zeta potential of aqueous RXM 6020 montmorillonite suspension as a function of pH (w/clay ratio = 53).

3.3. Dispersing performance of PCE in presence of clay

The w/c ratio of the neat cement paste for a spread of 18 ± 0.5 cm was determined to be 0.53. When 1 wt.% of clay was added, availability of water decreased due to consumption by hydration and swelling of the clay. Thus, the spread of the cement paste decreased to 15.3 cm (~−15%) as a result of increased viscosity.

In the absence of clay, the dosages of 45PC1.5 and 45PC6 required to obtain a spread of 26 ± 0.5 cm were 1.07 and 0.09% bwoc respectively. Obviously, PCE polymer 45PC6 is a much more effective dispersant due to its significantly higher anionic charge.

However, when 1 wt.% of clay was added, the spreads decreased by 41% and 58% to 22.3 cm and 21.3 cm for cement pastes with added 45PC1.5 and 45PC6 respectively (Fig. 6). These reductions in paste fluidity much exceed that observed in the absence of PCE which was 15% only. Thus, it indicates that besides water sorption, interaction of PCE with clay may also affect its dispersing effectiveness.

3.4. PCE sorption in cement/clay system

To ascertain the effect of clay on PCE, the sorbed amounts of 45PC1.5 and 45PC6 in cement paste with and without 1 wt.% of clay were investigated. Table 4 shows the sorbed amounts of the PCEs in presence or absence of clay.

When clay was present, then the sorbed amounts of the PCEs increased greatly. The effect was particularly strong with 45PC1.5 possessing high grafting density (sorbed amount increased from 25% to 55% of dosage added). Considering the small amount of clay present, this presents a huge increase in PCE sorption. Thus, it confirms strong interaction between this PCE and clay, plausibly higher

Table 3
Molecular properties and anionic charge amounts of 45PC1.5, 45PC6, PMA and PEG respectively, measured in synthetic cement pore solution.

Property	45PC1.5	45PC6	PMA	PEG
Molar mass M_w [g/mol]	196,300	156,400	26,200	2080
Molar mass M_n [g/mol]	51,900	43,680	7511	2090
Polydispersity index (PDI)	3.8	3.6	2.7	1.0
Molar ratio MAA : MPEG-MAA	1.5:1	6:1	–	–
Specific anionic charge amount $_{PS}$ [μeq/g]	175	1100	7900	0

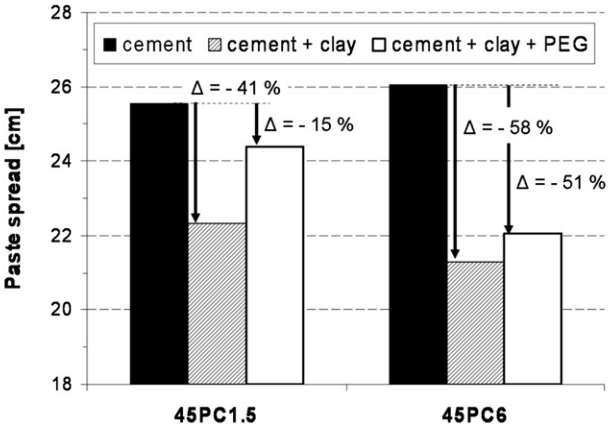

Fig. 6. Paste spread of cement slurries with and without 1 wt.% of clay added, in the presence of 1.07% bwoc of 45PC1.5 and 0.09% bwoc of 45PC6, with or without PEG-2000 added in equivalence to the PCE dosages (w/clay = 0.53).

than with cement. This result instigates that in a cementitious system, a considerable amount of PCE can be consumed by a relatively minor amount of clay contaminant.

To examine the effect of clay only on PCE and to eliminate the effect from cement, a simplified system consisting of only clay and PCE in synthetic cement pore solution was utilised next.

3.5. PCE sorption by montmorillonite

The sorption isotherms of 45PC1.5 and 45C6 on clay in synthetic cement pore solution are displayed in Fig. 7. The isotherms are *Langmuirian* L type as characterised by the steep initial increase of the adsorbed amounts. This montmorillonite exhibits an extremely high affinity for both PCE polymers, showing maximum sorbed amounts of 415 mg/g and 380 mg/g for 45PC1.5 and 45PC6 respectively. Such sorbed amounts are ~100 times higher than for an ordinary Portland cement (OPC), thus confirming the high affinity of PCE for clay [25–27].

3.6. Interaction of PEO side chain with clay

PCE consists of two main structural elements, the polymethacrylate backbone and the poly(ethylene oxide) side chain. The main question is thus which one interacts with clay, and to which extent.

Theoretically, two possibilities exist: first, in synthetic cement pore solution, due to the uptake of Ca^{2+} cations by the clay surface, electrostatic interaction between cationic clay surfaces sites and the anionic PCE backbone may occur. Second, the poly(ethylene oxide) side chains present in PCE have similar chemical composition as polyglycols. Polyglycols, especially those possessing high molecular weight, are known to be readily sorbed by this clay in large amounts [28]. The mechanism behind glycol sorption is intercalation between the alumosilicate layers occurring via H-bonding of the partially polarized oxygen atoms present in the polyethylene oxide chains and water molecules anchored by the silanol groups present on the surfaces of the alumosilicate layers (Fig. 8) [29,30]. Thus, a side chain interaction of PCE with clay is plausible. To discern between these two possibilities, the PCEs were studied in two portions, first the poly(ethylene glycol) side chain made up of 45 ethylene oxide units and second, the anionic backbone consisting of repeating units of methacrylic acid. Each building block can be represented by PEG and PMA respectively, and sorption studies of these two polymers were performed.

Table 4
Sorption of 45PC1.5 and 45PC6 on cement in presence or absence of clay (w/c = 0.53).

System	PCE dosages [% bwoc][a]	Sorbed amount of PCE [mg/g of solid]	Sorption [% of PCE dosage added]
CEM I 52.5 R + 45PC1.5	1.07	2.63	24.6
CEM I 52.5 R + 45PC1.5 + 1 wt.% clay	1.07	5.84	54.6
CEM I 52.5 R + 45PC6	0.09	0.42	46.4
CEM I 52.5 R + 45PC6 + 1 wt.% clay	0.09	0.59	65.0

[a] bwoc = by weight of cement.

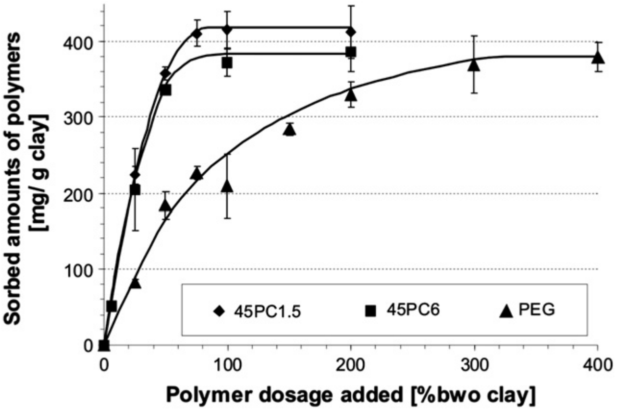

Fig. 7. Sorption isotherms of PCE polymers 45PC1.5, 45PC6 and PEG-2000 on montmorillonite dispersed in synthetic cement pore solution (Ca^{2+} concentration = 0.4 g/L, w/clay = 53).

First, it was found that a very high amount of PEG-2000 (at saturated equilibrium condition: 380 mg/g clay) was sorbed due to the high affinity of the PEO chain to clay (Fig. 7). Comparing the PEG and PCE sorbed amounts, it can be observed that the maximum sorbed amounts of the PCE polymers are in the same order (380–420 mg/g clay). The only difference being that the PCEs reach the point of saturated adsorption at lower addition. Therefore, it can be concluded that side chain interaction plays a significant role in the interaction between PCE and clay.

To confirm the mechanistic role of the side chain in the uptake of PCE by clay, XRD analysis was performed. Here, clay was mixed with PCE, PEG and PMA at a w/clay ratio of 53 and polymer dosages of 50% bwo clay respectively. According to Fig. 9, when hydrated, pure clay shows a *d*-spacing of 1.23 nm. A shift in the *d*-spacing from 1.23 nm to 1.77 nm was observed when PEG was added to the montmorillonite. This *d* value is characteristic for montmorillonite intercalated with polyglycols [31,32]. Likewise, when 45PC1.5 and 45PC6 were added to the clay, a shift in *d*-spacing from 1.23 nm to 1.77 nm was also detected. However, no significant change in *d*-value was observed when PMA was added to the clay. These results signify that intercalation of the PEO side chain of PCE in between the alumosilicate layers occurs. Whereas the polymethacrylate backbone does not incorporate into the interlayer region.

A second observation was the change in width of the reflection characteristic for the *d*-spacing of 1.77 nm. An increase in broadness of the characteristic reflections was observed as the side chain density of the polymers decreased, i.e. PEG < 45PC1.5 < 45PC6. This can be explained by their different ability to form ordered layers during intercalation. In the absence of a backbone, the pure polyglycol (PEG-2000) can intercalate in between the clay layers with ease and generate highly ordered layer structures, thus producing sharper reflections. On the other hand, when PCEs are incorporated into the clay, turbostratic disorderness due to electrostatic repulsion of the anionic backbone by the negatively charged alumosilicate layers occurs. The extent of the disruption is a function of the grafting

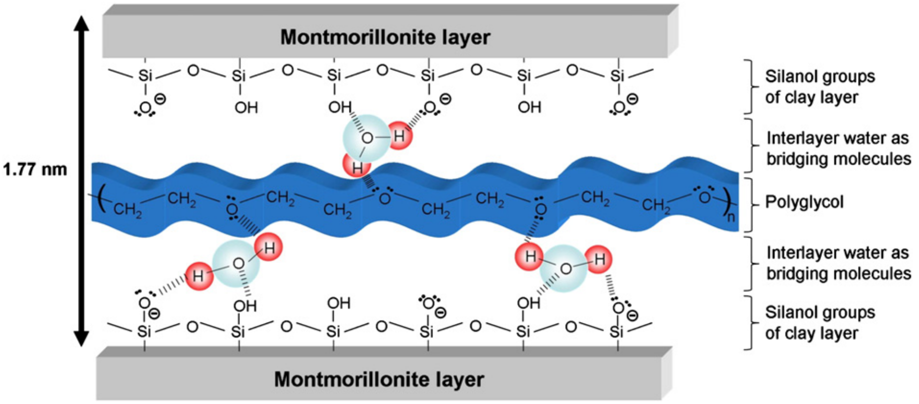

Fig. 8. Conceptual illustration of polyglycol intercalation between the alumosilicate layers of montmorillonite.

density; 45PC6 with its lower grafting density and higher anionic charge showed a more diffused reflection, thus greater disturbance in the layer structure. On the other hand, 45PC1.5, with its higher grafting density and lower anionic charge showed a more ordered intercalate product.

3.7. Interaction of PMA backbone with clay

The data presented so far clearly indicate that the PEO side chain of PCE constitutes the one structural element which facilitates PCE intercalation into the clay layer structure. However, according to Fig. 7, it becomes evident that in addition to this side chain interaction, another mode of interaction between PCE and clay must prevail as the amount of PEG sorbed cannot account for the relatively small difference in the sorbed amounts of 45PC1.5 and 45PC6, which possess significantly different amounts of PEO side chains. Additionally, according to Fig. 7, PCEs were consumed by clay at a much faster rate than individual PEG. Therefore, another mechanism of different nature must be at play. To investigate, the sorption of pure PMA backbone by clay was studied next.

According to Fig. 10, clay also sorbed PMA via electrostatic attraction mediated by the monolayer of Ca^{2+} cations formed on the clay surface in synthetic cement pore solution. This mechanism was confirmed by a dosage dependent decrease of zeta potential of the clay suspension when PMA was added until an equilibrium value representing the state of saturated adsorption was reached (curve not shown here). The fact that PMA adsorbs on clay signifies that PCEs can also be consumed through mere surface adsorption. However, the maximum adsorbed amount of PMA is only 32.5 mg/g clay. This value is much lower than those for PEG and PCEs (see Fig. 7) and can be attributed to the absence of graft chains.

3.8. Comparison of experimental sorption data with theoretical calculations

From the experimental sorption isotherms of individual PMA and PEG, the total amounts of PCE sorbed can be calculated, considering the overall composition of the PCEs as presented in Section 2.8. These calculations were performed and the results obtained were compared with those attained in earlier experiments (see Fig. 7).

Fig. 11 displays the calculated sorbed amounts of 45PC1.5 and 45PC6 based on experimental data on PEG sorption. The maximum sorbed amounts of 510 mg/g clay and 420 mg/g clay for samples with added 45PC1.5 and 45PC6 were attained only after adding 300% bwo clay of PCE, indicating a much slower sorption rate than experimentally determined (Fig. 7). However, when the point of saturated sorbed amount (equilibrium state) was reached, the trend in the difference in sorbed amount of the PCEs (calculated versus actual) was comparable, suggesting that the poly(ethylene oxide) side chain steers the sorption process at higher PCE dosages.

Likewise, the same calculations were performed based on experimental sorption data of PMA presented in Fig. 10. From this, the

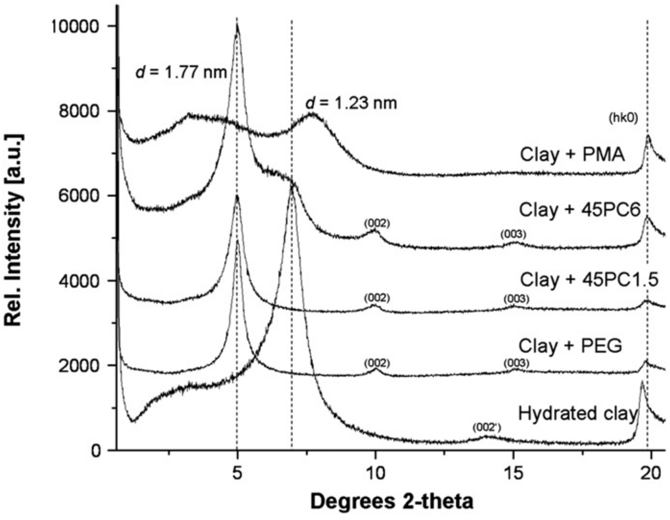

Fig. 9. XRD patterns of montmorillonite dispersed in synthetic cement pore solution, holding 50% bwo clay of PMA, PEG, 45PC1.5 and 45PC6 respectively (w/clay = 53).

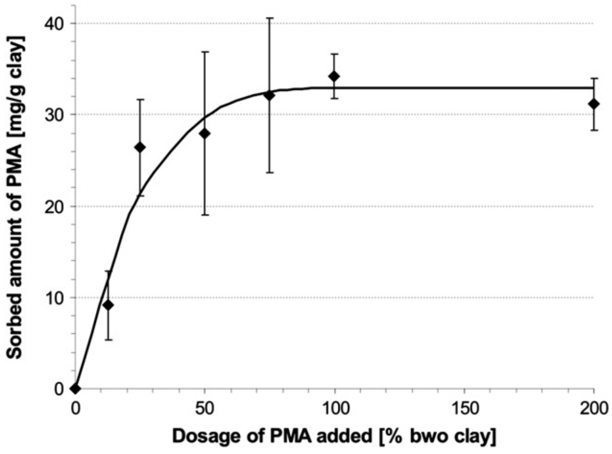

Fig. 10. Sorption isotherm of PMA on montmorillonite dispersed in synthetic cement pore solution as a function of PMA dosage ($Ca^{2+} = 0.4$ g/L, w/clay = 53).

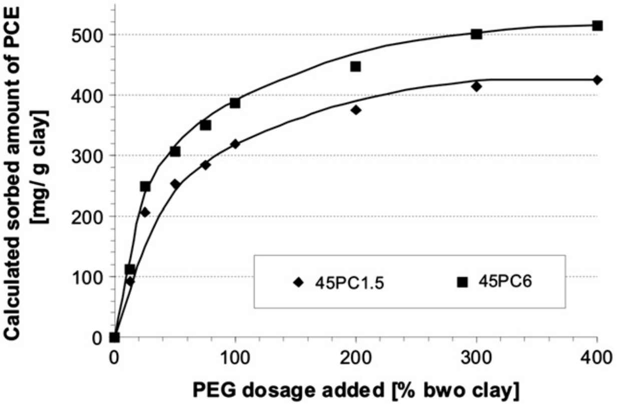

Fig. 11. Idealised sorption isotherms of the PCEs, calculated from sorption data of individual PEG on clay, assuming that PCE sorption solely occurs through PEO side chain interaction.

theoretical maximum amounts of PCE which can adsorb onto clay solely via electrostatic attraction were calculated as ~290 mg/g clay for 45PC1.5 and 120 mg/g clay for 45PC6 respectively (Fig. 12). These values do not fit the experimentally found sorbed amounts of 415 mg/g clay and 380 mg/g clay for 45PC1.5 and 45PC6 samples. However, the initial steep increase in sorbed amounts of PCE is similar to that obtained experimentally (Fig. 7). This signifies that at lower dosages, the PCE–clay interaction is mainly driven by electrostatic attraction.

To summarize, the mechanism of interaction between PCE and clay depends not only on the PEO content of PCE, but is also dosage dependent. At lower PCE dosages, backbone interaction with montmorillonite clay surfaces via electrostatic attraction dominates, while at higher dosages, intercalation of the poly(ethylene oxide) side chain prevails.

3.9. PEG as sacrificial agent

To confirm our concept of side chain interaction, pure PEG was added to cement/clay pastes holding both PCE polymers, and the paste spread was measured by 'mini slump' tests. The results are presented in Fig. 6. Both pastes incorporating pure PEG showed less decrease in workability than in the absence of this agent (spread value 24.4 cm instead of 22.3 cm for 45PC1.5, and 22.1 cm instead of 21.3 cm for 45PC6). This demonstrates that due to the similarity in chemical composition with the PCE side chain, polyglycols such as PEG can work as a sacrificial agent to reduce the amount of PCE consumed by clay, thus softening the negative impact on PCE performance in the presence of clay contaminants. Additionally, the higher regain in spread for 45PC1.5 confirms that for this PCE (employed at a higher dosage of 1.07% bwoc), interaction with clay is more driven by side chain interaction, which is a result of its higher grafting density. On the other hand, in 45PC6, the trunk plays a more important role in its consumption by clay, especially due to the lower dosage of 0.09% bwoc required to fluidize this cement.

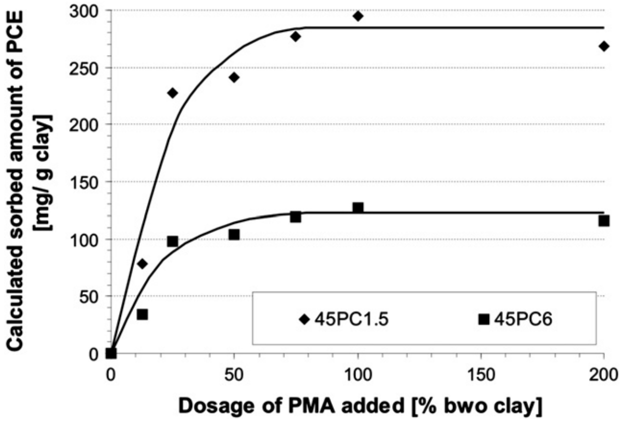

Fig. 12. Idealised adsorption isotherms of PCE samples, calculated from sorption data of PMA on clay, assuming that the PCE molecules only sorb via their backbone.

These results instigate that the usage of glycols as sacrificial agents generally is suitable for PCEs possessing higher side chain density such as 45PC1.5 (ready-mix type PCE) which in actual field applications are utilised at fairly high dosages (~0.3–0.5%). However, for PCEs with high anionic charge amounts (precast type) where added dosages are usually much less (~0.05–0.1%), the improvement in flow is not as desirable. Therefore, an alternative remedy, possibly interfering with their electrostatic preference for clay surfaces is required.

4. Conclusions

This work confirms that sodium montmorillonite clay exhibits a much higher affinity for PCE than cement. When only very minor amounts of montmorillonite clay are introduced into cement pastes, they reduce the availability and thus dispersing effectiveness of PCE superplasticizers. The effect on clay can be correlated to the specific molecular composition and the dosages of PCE employed. Generally, the affinity of PCE to clay originates from two different mechanisms: first, the intercalating ability of the poly(ethylene oxide) side chain of PCE into the interlayer space of the alumosilicate layers. Second, especially for PCEs possessing increased anionic charge density, electrostatic attraction mediated by surface adsorbed Ca^{2+} cations occurs. Theoretical calculations demonstrate that electrostatic attraction plays a more prevalent role at lower PCE dosages while side chain intercalation dominates at high PCE dosages. Therefore, the total amount of a PCE sorbed by clay is the result of a delicate balance between PCE dosage added, amount of PEO side chains available for intercalation, and anionic charge density of the PCE which promotes surface adsorption.

The failure of PCE to fluidize in concrete can have many reasons. It is known that SO_4^{2-} can greatly affect the performance of PCEs by competitive adsorption onto the surfaces of cement particles [33], or it may arise from incompatibility with other admixtures, or even the overall composition of cements. The latter influences are not well understood as of today. As shown here, another potential reason for failure is interaction with clays such as montmorillonite. Therefore, when a PCE fails during application, a methylene blue test for clay might help to identify the root cause (such as contamination from sand, gravel or limestone) for the problem, from which a suitable remedy such as addition of a glycol can thus be devised.

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