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A novel method for solving the impact of clay on concrete workability: dimensional design and mechanism analysis

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Abstract

Clay often has severe detrimental impacts on cement-based materials. Therefore, it is necessary to investigate the mechanism causing the deterioration to improve the service life of cement-based materials. Based on accurate dimensional analysis, a mechanism that influences clay is proposed: the intercalation of the side chains of superplasticizer molecules in the interlayer space of the clay. To lessen this harmful effect, a new clay-resistant admixture (CRA) possessing cationic groups of small molecular size was synthesized through a novel dimensional design. The length and width of the side chains of this superplasticizer molecule were 9.50–17.50 and 0.25–0.40 nm, respectively, with a radius of ~3.74 nm in solvent, which is larger than the interlayer spacing of montmorillonite (*i.e.* 1.09–2.14 nm). The longitudinal and latitudinal lengths of the CRA molecule were 0.468 and 9.456 nm, respectively, ensuring intercalation in the interlayer of montmorillonite. The increase in interlayer spacing of the clay was 0.364 nm following addition of polycarboxylate superplasticizer (PCE) plus CRA and 0.632 nm following addition of PCE, which suggests that the CRA plays the role of a ‘sacrificial agent’ that is preferentially intercalated into the interlayer space of clay to further prevent the side chains of the superplasticizer molecules from entering the interlayer. The aim of this study was to propose a suitable means of synthesizing a new CRA to address the impact of clay through dimensional design and mechanism analysis, which contributes to the theoretical study and technological improvement of cement-based materials.

Keywords: admixture, adsorption, clay, dimensional design, workability

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The polycarboxylate superplasticizer (PCE) has become a key material in the preparation of high-performance concrete, self-compacting concrete and high-flowing pump concrete because it is added in small proportions and has a large dispersing capability, significant slump retention and adjustable molecular structure (Cerulli *et al.*, 2003; Sakai *et al.*, 2006). However, an increasing number of studies have reported that PCE shows poor adaptability to concrete containing large amounts of clay, especially montmorillonite, attached around aggregates (Kuder & Shah, 2007; Tregger *et al.*, 2010; Tan *et al.*, 2016). Many engineering practices showed a strong sensitivity of PCE to clay minerals, manifested as reductions in fluidity, slump retention and later strength of the concrete (Kroyer *et al.*, 2003).

Previous work has shown the detrimental impacts of clay on the dispersing capacity of PCE (Jeknavorian *et al.*, 2003; Lei & Plank, 2012, 2014; Plank & Winter, 2012). The adverse influence of clay has been attributed to total or partial adsorption of PCE in the clay interlayers such that the amount of PCE available to the concrete mix is reduced and the dispersing efficiency decreased, resulting in the loss of workability (Ng *et al.*, 2012). However, there are still many questions that need to be answered. For example, it is not known whether whole superplasticizer macromolecules intercalate between clay interlayers; neither do we know the number of chains

that might intercalate between the interlayers. Mechanistic investigations need to be performed based on the dimensional analysis of superplasticizer molecules and the interlayer space of clay, but to date few studies have been carried out on these topics.

Atarashi *et al.* (2004) suggested that PCE may be adsorbed mainly between the interlayers of montmorillonite, but interlayer intercalation occurs rarely in naphthalene superplasticizers. Consequently, various approaches to overcoming the problem of PCE being adsorbed in montmorillonite interlayers have been proposed. Typically, a type of cycloaliphatic polycondensate prepared from cyclohexanone, formaldehyde and sulfite is used to inhibit the unwanted effects of clay when it has a large molecular weight, and this polymer also behaves like an admixture that may enhance the fluidity performance of cement paste (Lei & Plank, 2012). A concrete admixture possessing strong dispersing ability was prepared and showed better robustness towards clay than common admixtures (Lei & Plank, 2014). Improvements in clay tolerance may be accomplished with modification of the molecular structure of PCE. Terminal carboxylic group (Chen *et al.*, 2017), polymeric ferric sulfate (Tan *et al.*, 2018) or β -cyclodextrin (Xu *et al.*, 2015) used as pendant groups in the long side chains of PCE or as additives, may hinder intercalation completely.

In the oil industry, the incorporation of inhibitors may significantly impede the swelling of clay minerals (Nehdi, 2014). In addition, polyethylene glycol might be intercalated preferentially into the interlayer to hinder the intercalation of PCE (Tan *et al.*, 2017). Furthermore, the influence of the polymer structure of PCE (Borralleras *et al.*, 2019b), adsorption conformations (Borralleras

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et al., 2020) and experimental procedures (Borralleras *et al.*, 2019a) on intercalation behaviour in montmorillonite clays has also been investigated systematically. However, these methods always weakened the side chains of the superplasticizer, which may lead to a loss of dispersing capacity. In addition, various layered structures of clay minerals, including a variety of combinations of tetrahedral and octahedral sheets, will lead to various levels of reduction of the dispersing capacity of the superplasticizer. It is thus necessary to investigate systematically the impacts of each type of clay mineral (rather than simply referring to “clay” as a whole) on the rheological properties of cement-based materials and the adsorption behaviour of the superplasticizer in the presence of clay. There have been few systematic studies on these aspects. In the present approach, the use of a novel clay-resistant admixture (CRA) possessing short linear architecture may ensure that it enters preferentially the montmorillonite interlayer, and thus may solve the problem of the workability of PCE. As previous studies have not addressed adequately the negative effects of clay on the workability of concrete based on the molecular dimensions of the superplasticizer, studies of the molecular design, chemical synthesis and mechanism analysis of a novel CRA are needed.

In this study, four clays were selected and their detrimental effects on the fluidity of cement paste, the slump of concrete and the adsorption behaviour of the superplasticizer were examined to study systematically the mechanism of impact of clay type on the workability of concrete. Then, the action mode of the superplasticizer in the presence of clay was probed based on molecular dimensional analysis. After calculating accurately and comparing the molecular dimension of the superplasticizer and the spacing between the clay interlayers, the question was answered of whether the whole superplasticizer molecule may intercalate in the interlayer space. Based on this study, a new type of concrete admixture possessing linear molecular chains for minimizing the negative impacts of clay was proposed as an effective solution. These novel polymers with various molecular weights were synthesized, and improvements in the workability of concrete in the presence of clay were evaluated. The working mechanism of this CRA was studied using X-ray diffraction (XRD). The innovation of this study is that the mechanism of the interaction between the clay and superplasticizer was investigated in detail from the perspective of dimensional analysis, which gives a further assessment of the amount of improvement, depending on innovative design and synthesis. This finding offers not only a new direction for exploring a clay-resistant type of admixture, but also a theoretical basis for chemically researching the mechanism of the resistance of the admixture.

Materials and methods

Materials

Acrylic acid (AA), ammonium persulfate (APS), allyltrimethylammonium bromide (AMAB) and sodium methallyl sulfonate (SMAS) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China; all $\geq 99\%$ purity). Vitamin C (Vc) and sodium hydroxide (NaOH) were obtained from Beijing Chemical Works (Beijing, China; all $\geq 99\%$ purity). Commercial PCE as a concrete superplasticizer was purchased from Liaoning Kelong Fine Chemical Co., Ltd (Liaoyang, China). Reference cement P.I.42.5, fly ash, slag sand and gravel with particle sizes of 3–32 μm , 10–30 μm , <10 mm, 0.15–4.00 mm and 5.0–40.0 mm, respectively, were supplied by China United Cement Corporation (Qufu, China). The bentonite, kaolinite and

Table 1. Chemical compositions of reference cement and clay minerals (wt.%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI
Reference cement	21.65	4.36	3.06	63.32	1.84	2.85	1.40	–	1.86
Montmorillonite	60.67	18.27	3.08	0.79	3.24	0.02	2.11	0.12	10.98
Kaolinite	52.11	37.85	0.97	0.05	0.32	0.13	0.11	2.83	6.36
Mica	48.54	32.16	2.87	0.10	1.82	0.12	0.26	9.02	4.52

LOI = loss on ignition.

Table 2. Mixing proportion of concrete (kg m⁻³).

Cement	Fly ash	Slag	Sand	Gravel	Water	PCE
220	85	85	850	995	185	1.1

mica were purchased from Hebei Zhenxin Clay Technology Co., Ltd (Zhangjiakou, China). The bentonite had an average particle size (D50 value) of 0.9 μm , specific surface area of 41.6 m² g⁻¹ and moisture content of $\sim 5.5\%$. For kaolinite and mica, their D50 values, specific surface areas and moisture contents were 1.2 and 2.4 μm , 8.6 and 3.4 m² g⁻¹ and 0.7% and 0.4%, respectively. The water used in this experiment was deionized water. The chemical compositions of the reference cement and clay minerals are illustrated in Table 1.

Synthesis

The AA (57.60 g), SMAS (101.12 g) and AMAB (144.00 g) were dissolved in water, added to a four-neck round-bottomed flask and heated at constant temperature (65°C) for 10 min under stirring. Thereafter, an aqueous solution of Vc (8.45 g) was added to the flask, followed by dropwise addition of an aqueous solution of APS (21.91 g) to the mixture within 3 h. Finally, the synthesized product was cooled to room temperature and the pH value was adjusted to 6–7 with 30 wt.% NaOH aqueous solution. The final product in the form of an aqueous solution was designated as CRA.

Mixing proportions

The mixing proportions of the constituents of the prepared concrete are illustrated in Table 2. The coarse and fine aggregates employed in this experiment were washed and oven dried to be free of impurities.

Characterization and measurements

The molecular properties of the synthesized polymer products were determined at 30°C using a Waters PL-GPC50 chromatograph (Polymer Laboratories, UK) equipped with a PL aquaqel-OH MIXED 8 μm chromatographic column and fitted with differential refractive index (RI), laser light scattering and capillary viscometer detectors. The mobile phase was aqueous sodium azide solution with an injection volume of 100 μL and a flow rate of 1 mL min⁻¹. Polyethylene glycol narrow standards were used for calibration. The determination of molecular weight was carried out according to standard method GB/T 31816-2015 (2015) described in the National Standards of the People's Republic of China.

The amounts of the polymer samples adsorbed on clays or cement grains were evaluated using the depletion method (Plank *et al.*, 2010). The non-adsorbed portion of polymer

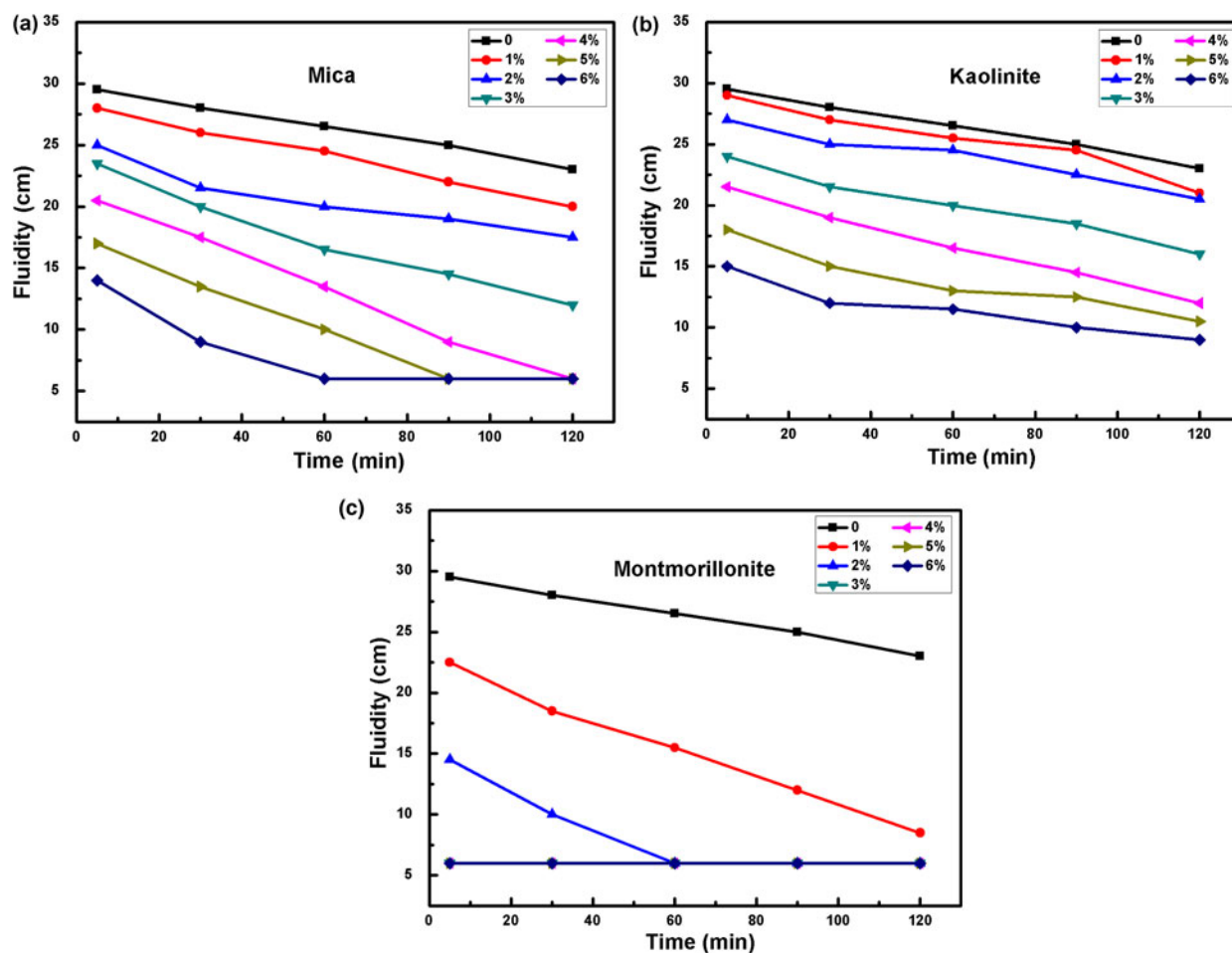


Fig. 1. Fluidity of the cement pastes at different clay dosages in the absence and presence of various clay minerals: (a) mica, (b) kaolinite, (c) montmorillonite.

remaining in solution at equilibrium conditions was analysed using the total organic carbon (TOC) content of the solution, determined using a Vario TOC Cube instrument (Elementar Analysensysteme GmbH, Germany). In the experiment, after various stirring times, the sample solution was loaded into a 50 mL centrifuge tube and then centrifuged for 5 min at 6000 rpm in a TGL-16C high-speed bench centrifuge (Shanghai Anting Scientific Instrument Factory, Shanghai, China). The supernatant was diluted with deionized water. From the difference between the TOC content of the polymer reference sample and that of the supernatant of the slurry suspension, the amount of the admixture polymer adsorbed was calculated (Li *et al.*, 2017; Ilg & Plank, 2020).

The interlayer spacings of all of the samples (in powder state) were measured using XRD traces recorded at room temperature on a Shimadzu XRD-6000 diffractometer (Shimadzu Corporation, Japan) with Cu- $K\alpha$ radiation. The X-ray tube was operated at 40 kV and 100 mA. The scanning step used was $0.01^\circ 2\theta$ (Ng & Plank, 2012).

The Marsh cone times of the cement pastes containing the synthesized admixture samples were examined using the Marsh cone method (Roussel & Roy, 2005). The fluidities of the cement pastes containing superplasticizer and the synthesized admixture samples in the presence of clay were tested at a water:cement ratio (W/C) of 0.29 according to standard method GB/T 8077-2012 (2012) described in the National Standards of the People's Republic of China. The slump and slump flow of

the concretes containing superplasticizer and the synthesized admixture samples in the presence of clay were tested according to standard method GB/T 50080-2016 (2016) described in the National Standards of the People's Republic of China.

Results and discussion

Effects of clay minerals on the rheological fluidities of cement paste and concrete

Effects on fluidities of cement pastes

The main constituent of bentonite is montmorillonite (Ray & Okamoto, 2003), which has been studied thoroughly because of its natural abundance and its high viscosity (Ng & Plank, 2012). Thus, montmorillonite mica and kaolinite were considered in the present study. The effects of the three clay minerals (the clay dosage was by weight of cement) on the fluidities of cement pastes are illustrated in Fig. 1.

Mica and kaolinite had similar effects on the fluidity of the cement pastes (Fig. 1). The fluidity decreases with increasing clay dosage, with the decrease becoming noticeable when the clay dosage exceeds 4%. In comparison, montmorillonite has a significant impact on the fluidity of the cement pastes at dosages as low as 1%. Fluidity is lost at montmorillonite dosage 2%. These results confirm that montmorillonite weakens the effectiveness of the superplasticizer used in the cement paste (Chen *et al.*, 2017).

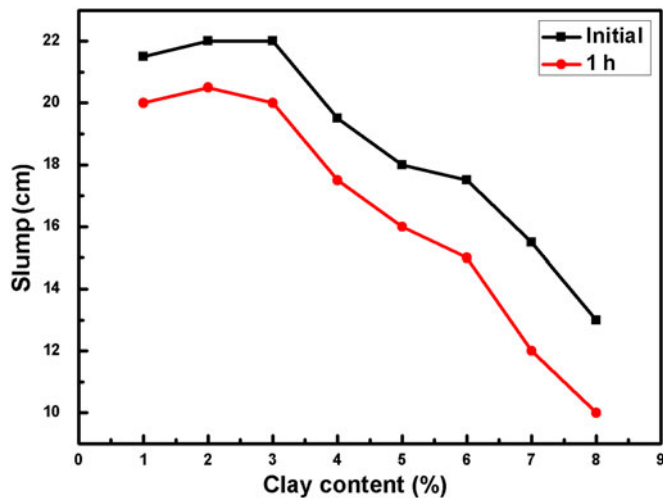


Fig. 2. Slumps of concretes containing various montmorillonite contents at 0 and 1 h.

Effects on slumps of concretes

The initial slumps (at 0 h) and slumps at 1 h of the concretes prepared according to Table 2 at montmorillonite dosages of 1–8% are shown in Fig. 2.

For montmorillonite dosages below 3%, the fresh concrete mixtures present good workability and <9% loss of slumps after 1 h, which meets the requirements of construction engineering. For montmorillonite dosages of 4–5%, the slump loss increases and the workability deteriorates, manifested as an increase in viscosity and a reduction in flow rate. At montmorillonite dosages of >6%, the slumps at 0 and 1 h decline sharply, even to <100 mm (a loss of almost half of the slump), showing poor workability and a strong sensitivity to the presence of montmorillonite. This may also demonstrate a more severe impact of montmorillonite on the rheological flowability of the concrete than other clay minerals, which is in good accordance with the fluidity results of the cement pastes (Cornelis *et al.*, 2012). This behaviour might be attributed to the strong adsorption of montmorillonite to the workable polymer admixture that exists in concrete (Ng & Plank, 2012), which will be discussed further below.

Adsorption behaviour of the superplasticizer on clay

Amounts adsorbed on clay

The amounts of superplasticizer adsorbed on cement and various clay minerals were determined, and the ratios of 'superplasticizer adsorbed on clay' to 'adsorbed on cement' (0.13 mg g^{-1}) are shown in Table 3. The ratios of the adsorption amount of superplasticizer on kaolinite and montmorillonite to those on cement are 1.70 and 2.74, respectively, demonstrating that these clay minerals exhibit greater adsorption to superplasticizer than cement. In addition, the amount of superplasticizer adsorbed on montmorillonite is much greater than that adsorbed on cement, and among these clay minerals, montmorillonite shows the greatest adsorption capacity. Therefore, the presence of clay may

Table 3. Amounts of superplasticizer adsorbed on cement and clay minerals.

Clay	Kaolinite	Mica	Montmorillonite
Ratio of 'superplasticizer adsorbed on clay' to 'superplasticizer adsorbed on cement'	1.70	0.94	2.74

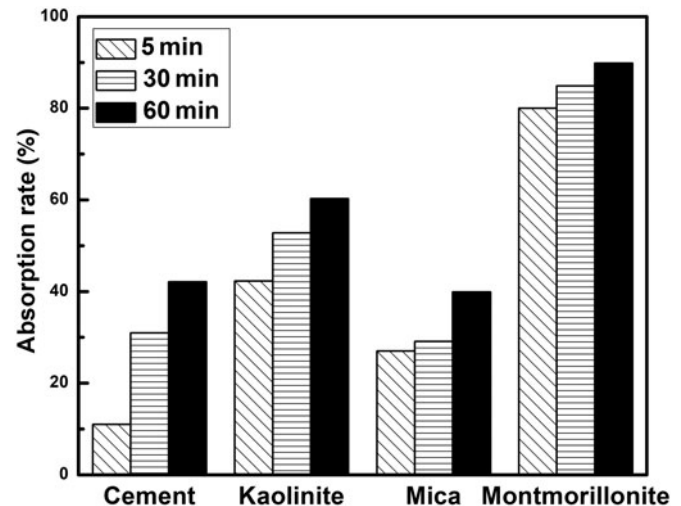


Fig. 3. Time-dependent adsorption rates of the superplasticizer on cement and clay minerals.

reduce the effectiveness of the superplasticizer, with montmorillonite showing the most severe negative effects (Kong *et al.*, 2016).

Time-dependent adsorption rates on cement and clay

The time-dependent adsorption rates (the percentage of the adsorbed PCE) of the superplasticizer on cement and clay minerals are shown in Fig. 3.

The initial adsorption rates of the superplasticizer on each clay mineral within 5 min are far higher than those on cement; on the other hand, the adsorption rate of the superplasticizer on cement increases more rapidly than those on each clay mineral over time. This is mainly related to the surface-charge characteristics of the cement particles. Indeed, the cement particles have significant hydration activity, and thus the hydration process is accelerated upon mixing with water, resulting in the creation of initial hydration products with positive charges, which leads to the spontaneous adsorption of negative $-\text{COO}^-$ groups of superplasticizer on cement particles (Wu *et al.*, 2012). Subsequently, the amount of superplasticizer adsorbed on hydration products increased significantly with the growing number of hydration products and was manifested as a faster adsorption rate after 5 min. In contrast, the surface potential of the studied clay minerals that bear negative charge remained unchanged, and new hydration products did not form due to the absence of hydration reaction. Thus, the adsorption rate of the superplasticizer on clay minerals increased slowly over time. Interestingly, montmorillonite showed the greatest adsorption rate at each time, which is in good accordance with the data in Table 3.

Interaction mode based on molecular dimensional analysis

Adsorption mode of the superplasticizer on clay

To further probe the adsorption mode of the superplasticizer on clay, the d_{001} basal spacing of montmorillonite, which was selected as a representative clay mineral due to it having the most detrimental effect on the workability of concrete, was measured after the various treatments. The results are shown in Fig. 4.

Without any treatment, montmorillonite exhibits a d_{001} spacing of 1.443 nm, which is comparable to that of montmorillonite washed by deionized water (1.487 nm). After treatment of montmorillonite with 0.68% superplasticizer solution, the 001 peak shifted to 1.863 nm (Fig. 4). This increase in spacing by 0.42

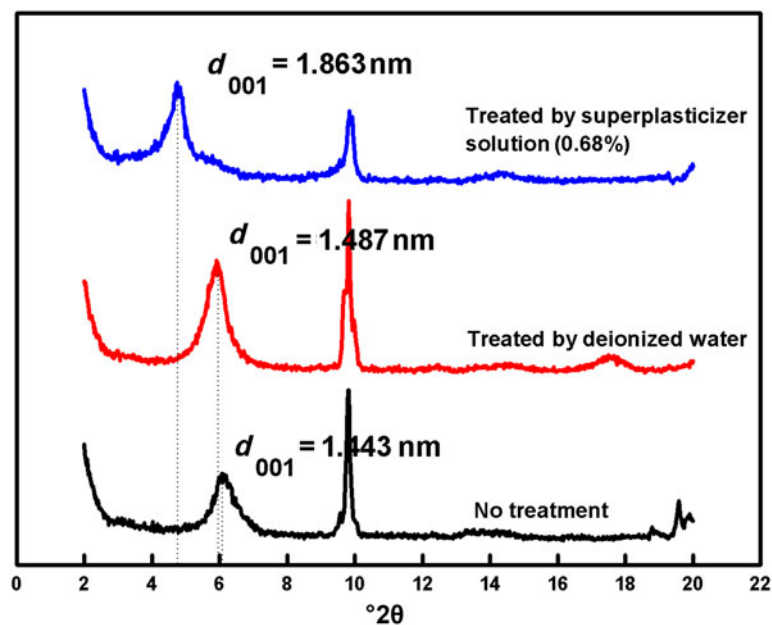


Fig. 4. Basal spacings (d_{001}) of montmorillonite after the various treatments.

nm is extremely close to the width of the side chain of the superplasticizer macromolecule, which has a comb-shaped structure, implying intercalation of the side chains of the superplasticizer macromolecule into the interlayer of montmorillonite.

The details of the adsorption of the superplasticizer on montmorillonite were also investigated. The basal spacings of montmorillonite treated with superplasticizer solutions at various concentrations were measured (Fig. 5).

The d_{001} spacing of montmorillonite treated with superplasticizer solutions at various concentrations was not affected by the concentration of the solution, suggesting that a dimensional equilibrium may be achieved after the side chains of the superplasticizer macromolecules intercalate into the interlayer space of montmorillonite. This is an interesting conclusion based on the above experimental results and the reported dimensional data of Stechemesser & Dobias (2005).

Dimensional analysis of the superplasticizer molecules between clay interlayers

Good fluidity of cement paste or fresh concrete is achieved due to the strong dispersing and fluidity capacities of the superplasticizer, which has a comb-like macromolecule. The long side chains of polyethylene oxide and the backbone of anionic groups have the functions of steric hindrance and electrostatic repulsion, respectively. In the presence of montmorillonite, the state of the superplasticizer macromolecules will change due to the strong adsorption ability and structure of montmorillonite (Plank, 2011). To confirm the role of montmorillonite, the interaction between the superplasticizer and montmorillonite was analysed by means of dimensional calculation.

The basal spacing of montmorillonite is 0.96 nm under complete dehydration, reaching ~ 1.95 nm under saturated water absorption (Theng, 1982). According to the bond lengths and the bond angles of the C–C bond and the C–O bond, the length and

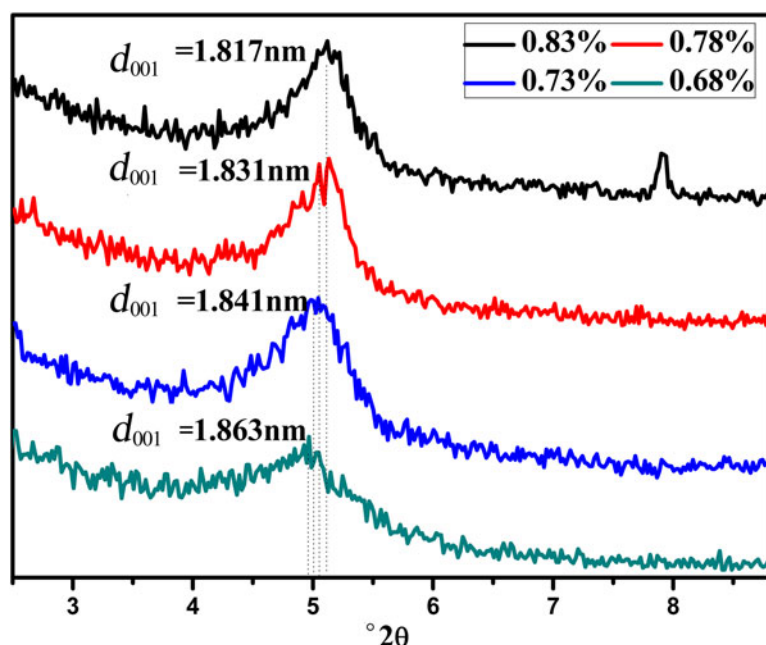


Fig. 5. Basal spacings of montmorillonite treated with superplasticizer solutions at various concentrations.

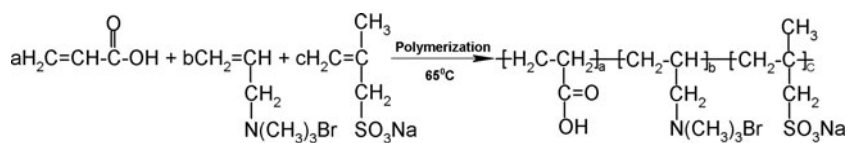


Fig. 6. Structural diagram of the synthesis of CRA.

Table 4. Bond lengths (nm) of the covalent bonds used for the dimensional analysis of CRA (Lyle, 1986).

Covalent bond	C–C	C–O	C–N	C–S
Bond length	0.154	0.143	0.147	0.181

width of the ethylene oxide (EO) unit on the side chain of the superplasticizer molecule are typically 0.19–0.35 and 0.25–0.40 nm, respectively. Assuming that the polymerization degree of the side chain of the superplasticizer molecule is 50, the maximum extension length and the minimum folding length of a side chain of the superplasticizer molecule are 17.5 and 9.5 nm, respectively. In addition, the radius of the side chain of the superplasticizer molecule presenting a free coil-like conformation in water is ~ 3.74 nm, calculated according to the Flory equation (He *et al.*, 2007). These calculations imply that the spatial size of the whole superplasticizer molecule should be considerably larger than the maximum interlayer spacing of montmorillonite under water-saturation conditions. Thus, it can be concluded that the superplasticizer molecule cannot be wholly adsorbed within the interlayer of montmorillonite. Although a side chain of the superplasticizer molecule is far longer than the interlayer spacing of montmorillonite, its width is sufficient to allow accommodation in the interlayer space, as was confirmed from by XRD data. Hydrogen bonds may form between the O atoms of EO units of the superplasticizer molecules and the H atoms of H₂O in interlayer spaces, or between the O atoms of H₂O in interlayer spaces and the H atoms of silanol groups on the layers of montmorillonite (Ng & Plank, 2012). As a result, the side chains of the superplasticizer molecules are fixed in the spaces between the interlayers of montmorillonite *via* bridging of H₂O in interlayer spaces (Burchill *et al.*, 1983; Amarasinghe *et al.*, 2009).

Synthesis and application of CRA

Design and synthesis of CRA based on dimensional analysis

Montmorillonite has detrimental effects on the efficacy of the superplasticizer through its reduction of the fluidity and workability of the fresh cement-based materials. Due to the intercalation of the side chains of the superplasticizer molecules in the interlayer space of montmorillonite, its function of providing steric hindrance, which enhances the dispersion of cement particles will be reduced or even lost. To avoid this negative effect, it is necessary to prepare an admixture that will resist the adverse effects of the clay. Using a novel design, a CRA possessing a linearly shaped molecular structure and positive charge (due to the negative charge of clay) will perform well in the cement-based materials containing the superplasticizer in the presence of montmorillonite. A structural diagram of the synthesis of CRA is shown in Fig. 6.

This polymer, which has a smaller size and contains numerous trimethylammonium cationic groups, is apt to be adsorbed between the electronegative interlayers of montmorillonite and so block the interlayer spaces and further prevent the side chains of the

superplasticizer molecules from entering the interlayers. During practical application as a ‘sacrificial agent’, this CRA is added to the cement-based materials in the presence of clay and is mixed together with the superplasticizer. Thereafter, the polymer will be adsorbed preferentially on the surfaces or into the interlayers of montmorillonite, thereby preventing the superplasticizer molecules from being adsorbed (Giraudeau *et al.*, 2009; Li *et al.*, 2017).

Based on this design, the synthesized CRA should be small enough to enter freely into the interlayer spaces. Therefore, the dimensional analysis of CRA can be performed in detail. The bond lengths of the covalent bonds used for this dimensional analysis are listed in Table 4. Based on these data, the molecular dimensions of CRA were calculated and marked in the structural formula of CRA (Fig. 7).

The lengths of the carboxyl, cationic and sulfo functional groups on the backbone of the admixture are 0.242, 0.245 and 0.273 nm, respectively. The longitudinal and latitudinal lengths of the molecule of this CRA are 0.468 and 9.456 nm, respectively (Table 4). Therefore, this longitudinal length is much shorter than the interlayer spacing of montmorillonite, and its overall size is also smaller than that of the superplasticizer molecule, which helps CRA enter into the interlayer space to ensure that the superplasticizer molecules work outside the interlayer space of montmorillonite.

Molecular properties of CRA

To investigate the effects of the molecular properties on the application performances of CRA, the monomer ratio and the initiator amount were varied during synthesis. The reactant ratios and the molecular weights of the final synthesized products (*i.e.* CRAs) are listed in Table 5.

It follows from Table 5 that with increasing initiator amount, the molecular weight of the synthesized products decreases gradually (Vojkovsky *et al.*, 2016). In addition, a decreasing trend in the molecular weight of the synthesized products is observed with decreasing amounts of AMAB (the amounts of AA and SMAS are constant).

Performance of CRA in cement paste

Marsh cone experiments were performed to examine the application performance of the polymers synthesized (*i.e.* CRAs) in cement pastes. The Marsh cone test method is used for the specification and quality control of cement pastes and grouts. The time needed for a certain amount of slurry to flow out of a cone is related to the ‘fluidity’ of the tested slurry. The shorter the flow time, the better the fluidity (Roussel & Roy, 2005). The Marsh cone tests of the cement pastes containing 0.2% (by weight of cement) superplasticizer and 0.5% (by weight of clay) synthesized CRA in the presence of 5% montmorillonite (by weight of cement) were carried out at a W/C ratio of 0.35. The Marsh cone test result times are listed in Table 6. Sample 0 signifies the cement paste in the absence of the synthesized CRA.

The molecular weight of CRA is related directly to the Marsh cone time of the cement paste (Table 6). With decreasing molecular weight

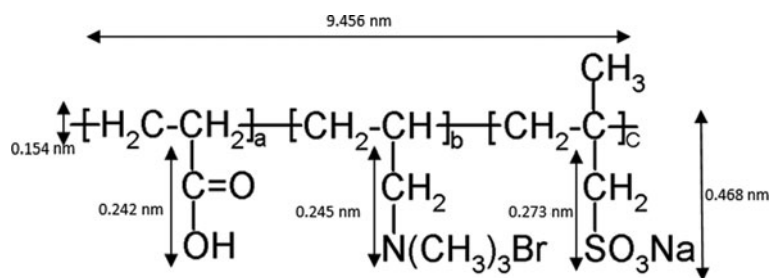


Fig. 7. Molecular dimensions of CRA.

Table 5. Reactant ratios and molecular weights of the synthesized products.

Sample	Monomer ratio			Initiator ratio		Molecular weight
	AA	AMAB	SMAS	APS	Vc	
1	1	2.0	0.8	0.090	0.045	13,100
2	1	1.5	0.8			12,000
3	1	1.0	0.8			11,300
4	1	0.5	0.8			9070
5	1	2.0	0.8	0.120	0.060	7500
6	1	1.5	0.8			6640
7	1	1.0	0.8			5670
8	1	0.5	0.8			4850

Table 6. Marsh cone times (s) of the cement pastes.

Sample	Marsh cone time	
	After 5 min of water addition	After 60 min of water addition
0	6.65	15.27
1	5.72	-
2	5.82	15.18
3	5.81	14.82
4	5.10	13.89
5	4.87	13.66
6	4.74	13.37
7	4.10	12.42
8	4.17	12.76

of CRA, the Marsh cone time of the cement paste reduces gradually, implying that the fluidity of the cement paste may be improved significantly by adjusting the molecular weight of the CRA. Samples 7 and 8, in which the molecular weight of CRA is as low as 4000–6000,

exhibit shorter Marsh cone times, being 2–3 s shorter than that of sample 0. These results show clearly that the addition of CRA increases the resistance towards montmorillonite and improves the stability of the cement paste. These effects are more evident when the molecular weight of CRA is small.

Improvements in concrete workability for CRA

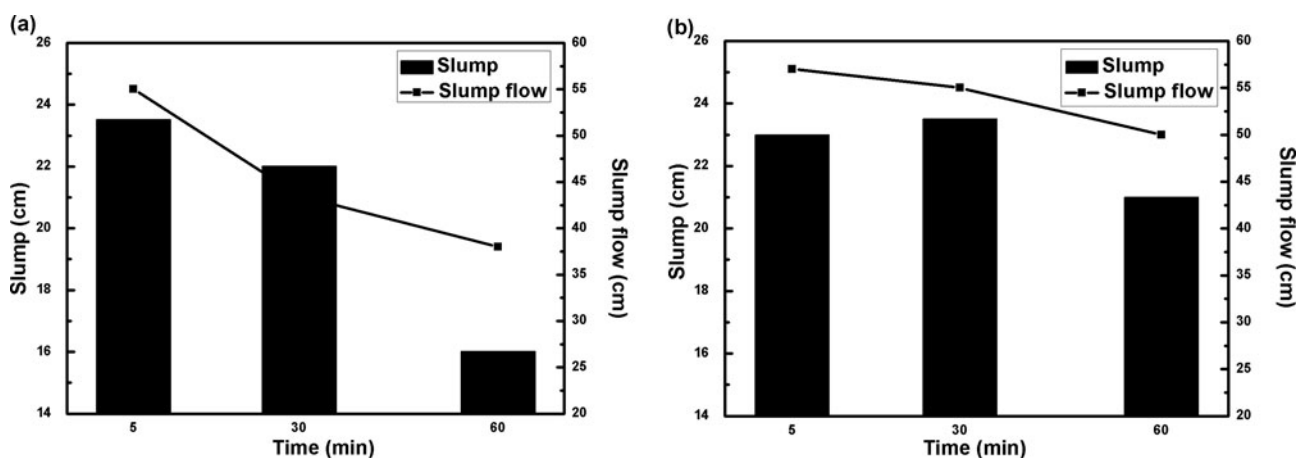
To evaluate the improvement in concrete workability of CRA, Sample 7, as a CRA, together with PCE (*i.e.* PCE + CRA), was used in comparison with PCE alone. PCE and PCE + CRA were added to the concretes prepared in the presence of 5% montmorillonite (by weight of cement). The slump test results are illustrated in Fig. 8.

The concrete containing PCE + CRA exhibits an initial slump close to that of the concrete containing PCE and a higher initial slump flow than that of the concrete containing PCE (Fig. 8). This trend is more pronounced after 30 min or even 60 min, showing that the polymer synthesized in this study exhibits better workability of concrete over time in the presence of montmorillonite. It follows that the synthesized CRA contributes to excellent resistance to montmorillonite and shows substantial improvements in concrete workability in the presence of montmorillonite.

Working mechanism of CRA

Adsorption behaviour of CRA

Sample 7 was also used to investigate the adsorption behaviour of CRA. Cement, kaolinite, mica and montmorillonite were selected as adsorbates. Due to the various functions of the PCE and CRA, the adsorption behaviours of PCE and CRA on various adsorbates were examined for comparison, although there is previous work

**Fig. 8.** Slumps and slump flows of the fresh concretes containing (a) PCE and (b) PCE + CRA.

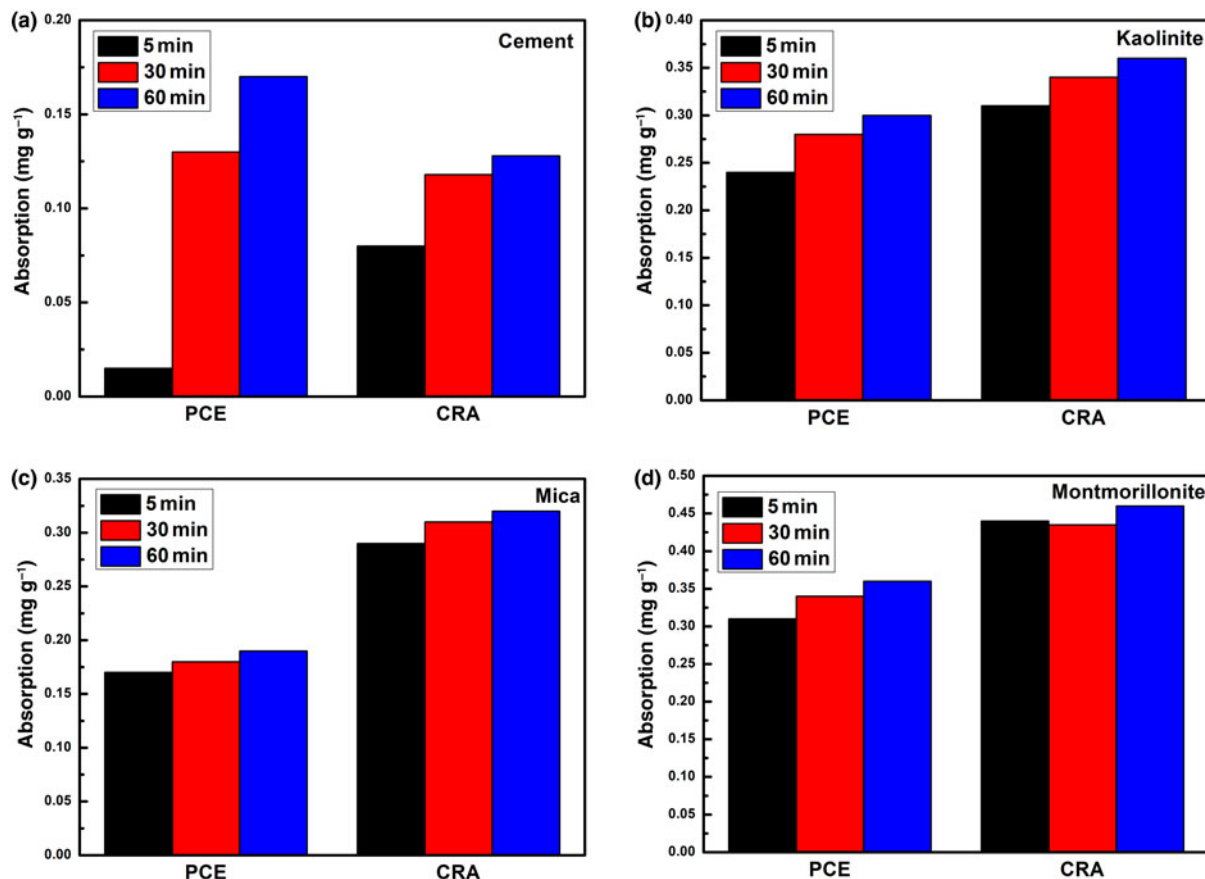


Fig. 9. Time-dependent adsorption amounts of PCE and CRA on (a) reference cement, (b) kaolinite, (c) mica and (d) montmorillonite.

on the adsorption behaviour of PCE (*e.g.* Wang *et al.*, 2012; Ait-akbour *et al.*, 2015). The time-dependent adsorption amounts of PCE and CRA on various adsorbates are shown in Fig. 9. The experiments were carried out at 25°C with a W/C (or clay mineral) ratio of 4:1.

The amount of CRA adsorbed is greater than that of PCE on a reference cement within 30 min, and then the opposite trend is observed after a further 30 min (Fig. 9). This is due to the continuous hydration of cement. The continuously formed hydration products tend to 'trap' free PCE macromolecules. In addition, the amount of CRA adsorbed on montmorillonite remains much greater than that of PCE; this trend is also observed in kaolinite and mica (Fig. 9) and is attributed to the fact that the CRA synthesized in this study, which has a positive charge, is apt to be adsorbed by the negatively charged clay layers (Hang & Brindley, 1970; Türköz & Tosun, 2011), which is controlled by the structural and charge characteristics of the clay minerals. The CRA synthesized in this study adsorbs quickly and readily on clay minerals. Consequently, if this CRA is mixed with PCE, which provides workability to concrete, reducing the adverse impact of clay may be achieved, which is consistent with the original design concept.

Interaction mode of CRA

To further investigate the interaction between CRA and clay, XRD analysis was performed on montmorillonite without treatment (blank), treated with PCE and treated with PCE + CRA. The samples were dried overnight at 80°C prior to grinding and then analysed. The XRD traces are shown in Fig. 10.

The basal spacing of the original montmorillonite is 1.093 nm, which increased to 1.725 nm after treatment with PCE (Fig. 10) due to the intercalation of the side chains of PCE in the interlayer space of clay. Similarly, a shift of the basal spacing from 1.093 to 1.457 nm is observed after treatment with PCE + CRA. This increase in interlayer spacing of 0.364 nm is comparable to the longitudinal length of the molecule of CRA based on the calculation given above,

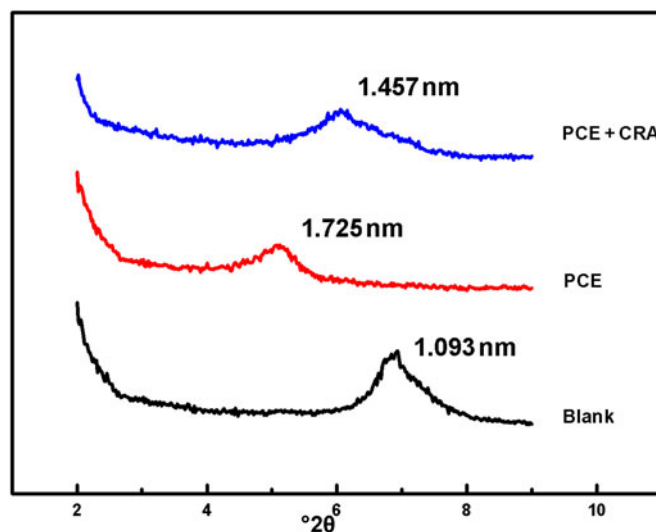


Fig. 10. XRD traces of montmorillonite treated using various methods.

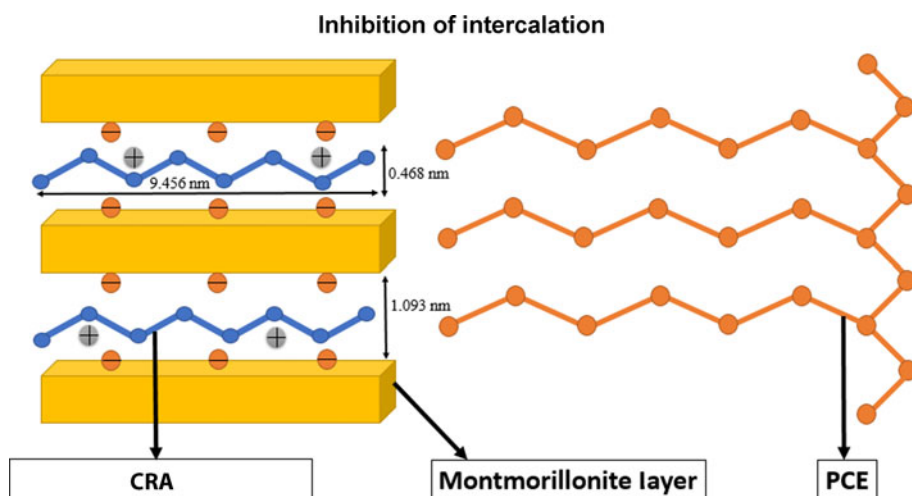


Fig. 11. Schematic illustration of the interaction between montmorillonite and PCE in the presence of CRA.

indicating intercalation of CRA in the interlayer space of clay. Comparatively, the increment in interlayer spacing for the intercalation of CRA is significantly shorter than that of the side chains of PCE. This result is consistent with the dimensional analysis. CRA has smaller molecular chains and a positive charge, and thus it will preferentially enter into the interlayer space of montmorillonite. The peaks at 1.725 and 1.457 nm (Fig. 10) correspond to the interlayer spacing of clay intercalated by PCE and by CRA, respectively. These results demonstrate that CRA prefers to enter into the interlayer space of montmorillonite when it mixes with PCE.

In addition, the interlayer spacing of montmorillonite intercalated with PCE + CRA is 0.268 nm smaller than that intercalated with PCE, implying the different molecular sizes of these polymers, which may affect the mode of intercalation. The longitudinal and latitudinal lengths of CRA are 9.456 and 0.468 nm, respectively. This molecular size is smaller than that of PCE and much smaller than the basal spacing of montmorillonite, leading to a more flexible molecular configuration (Borget *et al.*, 2005), so that it may easily be adsorbed in the interlayer space of montmorillonite and further protect other workable PCE. This also explains why the CRA exhibits preferential intercalation in the interlayer space of clay. The mechanism of interaction between montmorillonite and PCE in the presence of CRA is illustrated in Fig. 11.

These data allow us to conclude that this new CRA has some positively charged ammonium groups that may adsorb electrostatically on the negatively charged surfaces of montmorillonite and a small molecular size, which helps it to intercalate entirely into the interlayer space. When this CRA is mixed with PCE and then added to the concrete in the presence of montmorillonite, the surfaces and interlayers of montmorillonite are preferentially occupied by these admixtures due to their small size and positive charge (Fig. 11). Thereafter, the interlayer spaces of montmorillonite are too small to allow the PCE molecules to enter. Hence, the PCE is protected from intercalating in interlayer spaces blocked by CRA, thereby minimizing the detrimental effects of clay and allowing PCE to function.

Conclusion

Montmorillonite had a greater effect on the fluidity of the cement paste and the workability of concrete. The flowability of cement paste or concrete declined sharply with increasing clay dosage, and comparatively, quite poor fluidities were observed after addition of 2% montmorillonite and 4–5% mica and kaolinite.

All of the clay minerals showed faster initial adsorption rates of superplasticizer than the original cement. Montmorillonite also presented the greatest adsorption rate and adsorption amount, with the order being montmorillonite > kaolinite > mica. When montmorillonite was treated with a superplasticizer solution, a shift of basal spacing from 1.443 to 1.863 nm was observed, regardless of the concentration of superplasticizer solution.

The length and width of the side chain of the superplasticizer molecule were 9.5–17.5 and 0.25–0.40 nm, respectively, with a radius of ~3.74 nm in solvent, which was larger than the basal spacing of montmorillonite. Accordingly, the superplasticizer molecule could not completely intercalate into the interlayer of montmorillonite. Only the side chains of the superplasticizer molecule could intercalate into the interlayer space, thus explaining why clay weakens the effectiveness of the superplasticizer.

A series of CRAs with small molecular size and containing cationic groups was synthesized successfully using our novel design. The longitudinal and latitudinal lengths of the molecule of the CRA were 0.468 and 9.456 nm, respectively, ensuring the intercalation into the interlayer spaces of montmorillonite. Shorter Marsh cone times were obtained when the molecular weight of the admixture was 4000–6000 atomic mass units. The workability of concrete in the presence of clay was also improved significantly through addition of this admixture.

The increments in interlayer spacing of clay were 0.364 nm after addition of PCE + CRA and 0.632 nm after addition of PCE, suggesting that the CRA, in the role of a 'sacrificial agent', intercalated preferentially into the interlayer spaces of clay to further prevent the side chains of the superplasticizer molecules from entering.

This is the first report on the improvement of a new synthetic polymer to minimize the detrimental effects of clay, giving a useful insight into the mechanism of interaction between polymers and clays. Another benefit of this study has been the confirmation of the working efficacy of the superplasticizer in the presence of clay.

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