

## TOLERANCE OF CLAY MINERALS BY CEMENT: EFFECT OF SIDE-CHAIN DENSITY IN POLYETHYLENE OXIDE (PEO) SUPERPLASTICIZER ADDITIVES

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**Abstract**—Polycarboxylate superplasticizer (PCE) is a widely used water-reducing agent that can reduce significantly the water demand of concrete, which reduces the porosity and enhances the strength and durability of the concrete. (The PCE consists of a single backbone with many long PEO side chains.) Generally, aggregate occupies >70 wt.% of concrete; clay minerals are ubiquitous in nature and are difficult to avoid in mined aggregates. Clay minerals in aggregate often render the PCE ineffective and give rise to rapid loss of the fluidity of the concrete; this phenomenon is referred to as ‘poor clay tolerance of PCE.’ Though the poor clay tolerance of PCE is known widely, the relationship between the clay tolerance and the molecular structure of the PCE, in particular the effect of the side-chain structures, on clay tolerance is not understood completely. The objective of the present study was to determine the effect of different grafting densities of polyethylene oxide (PEO) side chains on the clay tolerance of PCE. The raw materials included mainly PCE, which was synthesized using acrylic acid and isopentenol polyoxyethylene ether, and a natural montmorillonite (Mnt), one of the most common clay minerals. The loss of fluidity of the cement paste was tested to assess the clay tolerance; total organic carbon was used to measure the amount of PCE adsorbed; X-ray diffraction, transmission electron microscopy, Fourier-transform infrared spectroscopy, and thermogravimetric analysis were used to investigate the microstructure of the intercalated Mnt. The results showed that preventing the superficially adsorbed PCE from being intercalated into Mnt was of great importance in terms of the improvement in clay tolerance of PCE, which increased with greater grafting density of PEO in the side chain of the PCE. The results also suggested the possibility that polymers which intercalate preferentially into the Mnt could improve significantly the clay tolerance of the PCE system.

**Key Words**—Intercalation, Interlayer Adsorption, Interlayer Spacing, Montmorillonite, Superficial Adsorption.

### INTRODUCTION

At present, in cement-based materials, polycarboxylate superplasticizer (PCE) is a very popular water-reducing agent (reduces the water demand in cement-based materials to ensure consistent workability) (Li and Kwan, 2015; Yun *et al.*, 2015; Plank *et al.*, 2015), due to its excellent dispersing ability and dispersion retention ability (Houst *et al.*, 2008; Fan *et al.*, 2012; Zhang *et al.*, 2016). The presence of clay minerals in aggregate can reduce the water-reducing effects of PCE and often lead to rapid loss of the fluidity in concrete (Fernandes *et al.*, 2007; Tregger *et al.*, 2010); this is referred to as poor ‘‘clay tolerance of PCE’’ (Xu *et al.*, 2015; Tan *et al.*, 2015b). With rapid loss of fluidity, the concrete cannot be cast normally and the fluidity loss is, therefore, a good parameter to use in the assessment of the workability in engineering practice. Montmorillonite (Mnt), the most harmful clay mineral in this sense, reduces significantly the dispersing ability and dispersion retention ability of PCE (Sakai *et al.*, 2006; Konan *et al.*, 2008; Wang *et al.*, 2012). The large consumption of PCE

(Lei and Plank, 2012; Tan *et al.*, 2015b) has been reported as the main reason for this poor clay tolerance of PCE. The mechanism behind the large consumption of PCE is associated with the intercalation of PCE into the multilayer structure of Mnt, which consists of two silica-oxygen tetrahedral sheets sandwiching an alumina-oxygen octahedral sheet (Nehdi, 2014; Lei and Plank, 2014a). When Mnt encounters water, the interlayer space is enlarged (swollen) by the water, and the interlayer cations can be exchanged with the cations in solution. Simultaneously, PCE can be inserted into the Mnt interlayer space which results in the poor clay tolerance (Ait-Akbour *et al.*, 2015; Tan *et al.*, 2016).

Generally, the superficially adsorbed PCE (S-PCE) on the surface of the cement particle is most efficient in dispersing the cement particles because of the steric hindrance effect offered by the polyethylene oxide (PEO) side chain (Yamada *et al.*, 2001; Li *et al.*, 2012; Bey *et al.*, 2014). If intercalation of the S-PCE were to be prevented, then the dispersing ability of PCE would be maintained and the cement suspension would be kept stable. If the S-PCE were to be consumed by the Mnt particles, the cement particles would start to reunite and considerable reduction in fluidity would be observed. In cement-Mnt paste, the Mnt particles compete with the cement particles to adsorb PCE which results in less PCE adsorbing onto the surface of the cement particles

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DOI: 10.1346/CCMN.2016.064037

to form the S-PCE. Simultaneously, the S-PCE will probably be consumed over time by the Mnt which has not been intercalated; hence, the poor clay tolerance of PCE. Protecting S-PCE from being intercalated is, therefore, of great importance to the stability of the cement-Mnt suspension.

The modified molecular structure of PCE, which was impossible to intercalate into Mnt, is reported here; the clay tolerance of the modified PCE was enhanced because interlayer adsorption was avoided. For example, a structurally modified PCE synthesized with methacrylic acid and hydroxyethyl methacrylate esters showed excellent performance in terms of clay tolerance because the polymer was unlikely to be inserted into the interlayer space of Mnt (Lei and Plank, 2014b); the presence of beta-cyclodextrin as pendant groups in the side chain of PCE could impede significantly the intercalation of PCE into Mnt, thus enhancing clay tolerance (Xu *et al.*, 2015). The goal of modifying the molecular structure was to avoid the intercalation of PCE, or to reduce the intercalation of S-PCE into Mnt, which could provide enough S-PCE to stabilize the cement-Mnt suspension.

Theoretically, if the S-PCE were increased, the clay tolerance would be improved. The grafting density of carboxyl group in side chain, *i.e.* the mole ratio of carboxyl group and PEO, determines the adsorption ability of PCE. A greater density of carboxyl groups, therefore, leads to greater adsorption ability of the PCE. A PCE with appropriate adsorbing ability can be obtained by adjusting the side-chain grafting density, therefore; the competitive absorption of PCE between the cement particles and Mnt particles can be balanced to increase the amount of S-PCE and increase in the amount of S-PCE would obviously enhance the clay tolerance of PCE. The objective here was to study the clay tolerance of PCE with the different side-chain grafting densities which were synthesized using acrylic acid (AA) and isopentenol polyoxyethylene ether (IPEG, which has PEO as its main part). Specifically, the loss of fluidity of cement-Mnt paste was studied to assess the clay tolerance of PCE under the same initial fluidity conditions. The adsorption behavior of PCE in cement and Mnt suspensions was studied, and the microstructure of Mnt intercalated by PCE was characterized to propose an adsorption model to explain the mechanism behind the improvement in clay tolerance. The effect of the

side-chain grafting density on clay tolerance of PCE was confirmed, and the results suggested a new method for enhancing the clay tolerance of superplasticizer systems.

## EXPERIMENTAL METHODS

### Materials

**Cement and montmorillonite (Mnt).** An ordinary Portland cement (42.5, Wuhan Yadong Cement Co., Ltd., Wuhan, Hubei Province, China), meeting the requirements of the 'GB175-2007' Chinese standard (China Building Materials Academy, 2007) was used in the present study. The CaSO<sub>4</sub> content in the cement was 4.2%, and the specific surface area was 350 m<sup>2</sup>/kg (obtained from the specifications supplied by Wuhan Yadong company).

Dry-ground powder of Mnt (Natural Mnt), which could pass through a 200-mesh sieve, was prepared. X-ray fluorescence (XRF) measurements (Table 1) revealed the chemical composition of the cement and the Mnt.

**Synthesis of copolymers.** The PCE was synthesized with acrylic acid (AA, reagent grade, from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and isopentenol polyoxyethylene ether (IPEG, from Wuhan Oxiranchem Co., Ltd., Wuhan, Hubei Province, China); it was >99.0% pure, and the degree of polymerization was ~48–52%, with various mole ratios of AA/IPEG (PCE1: 6:1, PCE2: 4:1, PCE3: 2:1, and PCE4: 1.5:1). The solid content of PCE was ~40%, and the pH value was ~7.0. A schematic diagram of the molecular structure of PCE is given in Figure 1.

Experimental measurement of gel permeation chromatography (GPC, 1260-RID instrument from Agilent, Santa Clara, California USA) (shown in Table 2), a technique which separates analytes on the basis of size, revealed the weight average molecular weight ( $M_w$ ), 'number-average' molecular weight ( $M_n$ ), ((total weight of the sample divided by the number of molecules in the sample), and polydispersity index (PDI) of the PCE samples. The eluent (liquid solvent) had a molar concentration of 0.1 mol/L NaNO<sub>3</sub> and the rate of addition was 1.0 mL/min. The concentration of sample was 0.5 wt.%.

The mole ratio of the carboxyl group and the PEO in the side chain could be inferred from the mole ratio of

Table 1. Chemical composition (wt.%) of cement and Mnt.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
Cement	24.08	4.72	2.46	2.31	58.24	1.95	1.02	0.27	3.82
Mnt	63.78	15.19	2.91	0.021	2.17	4.33	0.6	0.14	10.53

LOI: loss on ignition.

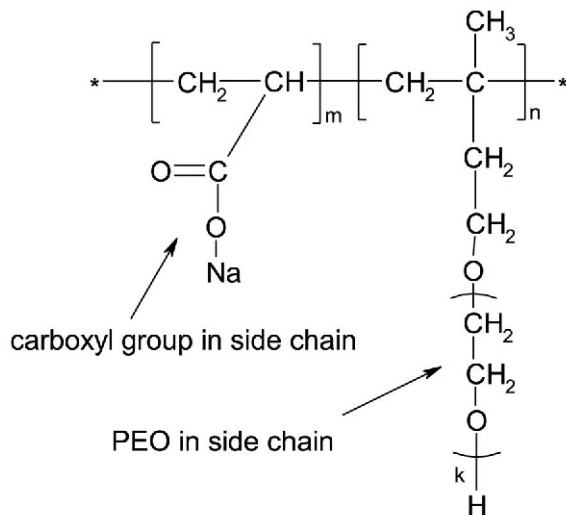


Figure 1. Schematic diagram of the chemical structure of PCE ( $k = 48-52$ ).

AA/IPEG which was used in the process of synthesizing PCE because almost all of the monomers (*i.e.* AA and IPEG) would be polymerized. The grafting density of the carboxyl group or the PEO could be illustrated from the  $m/n$  ratio (*i.e.* the ratio of carboxyl group: PEO in the side chain), therefore, as shown in Table 2. The polymer PCE1 had the greatest density of carboxyl group and the lowest density of PEO. PCE4 had the highest density of PEO and the lowest density of the carboxyl group.

#### Measurements

**Fluidity of cement and cement-Mnt paste.** A flow cone (60 mm tall, 36 mm top diameter, 60 mm bottom diameter) specified in the Chinese standard GB 8077-2000 (National Building Materials Industry Bureau of Suzhou Concrete Cement Products Academy, 2007), placed on a glass plate, was filled with a sample. After the cone had been removed from the sample, the maximum diameter of the sample spread and the maximum width perpendicular to that diameter were measured. The average of these two values was defined as the fluidity value.

Dosages of PCE were added to water in advance. Cement-Mnt paste was then prepared with a water/

cement weight ratio of 0.29:1 (87 g of water, 300 g of cement; or mixture of 29.5 g of cement and 4.5 g of Mnt) in accordance with the requirements of Chinese standard GB 8077-2008 (Standardization Administration of China, 2008). The cement-Mnt paste was tested immediately after preparation, giving the initial fluidity. Next, the cement-Mnt paste was stored in a container and tested again after 60 min, giving the '60 min' fluidity value. All measurements were made at 25°C.

**Amount adsorbed.** Cement or Mnt (1.0 g) was mixed with PCE solutions (20 mL, 0.4 g/L) and stirred for 5 min, and the mixture was then separated, with solution in the upper layer and precipitation in the bottom layer, by centrifugation at  $2650 \times g$  for a period of 4 min. Analysis of the total organic carbon (using a Multi N/C 2100 instrument, Analytik, Jena, Germany) was used to measure the solution (and not the separated precipitate) of PCE, and the TOC results were used to calculate the amounts of PCE adsorbed. Measurements were generally repeated three times to assess deviation, and the average is given as the result. All measurements were done at a temperature of 25°C. The amount of cement or Mnt (mg/g of cement or Mnt) adsorbed was calculated based on the following equation:

$$\text{Amount adsorbed} = V(C_0 - C)/m$$

where  $C_0$  is the initial concentration (g/L) of PCE before any adsorption;  $C$  is the residual concentration (g/L) after adsorption;  $V$  is volume of the solution (mL); and  $m$  is the mass of the cement or Mnt (g).

**Preparation of intercalated Mnt samples.** Water (100.0 g) and PCE (5.0 g) were mixed first and then Mnt (5.0 g) was added to the solution and stirred by hand for 10 min. The solid was then filtered and washed with distilled water several times until the TOC result of the filtrate was constant, indicating that the superficially adsorbed polymer had been cleaned thoroughly. Next, the solid was dried in a vacuum drier (using a DZF6020 instrument, Shaoxin Subo, China) at  $\sim 105^\circ\text{C}$ , and ground to powder by hand to pass through a 200-mesh sieve. Finally, the powder was prepared for analysis by X-ray diffraction (XRD), transmission electron microscopy

Table 2. Structural parameters and properties of PCE.

Polymer sample	Carboxyl group: PEO in side chain ( $m/n$ )	$M_w$ (g/mol)	$M_n$ (g/mol)	PDI ( $M_w/M_n$ )
PCE1	6:1	60200	41700	1.44
PCE2	4:1	65400	42500	1.54
PCE3	2:1	62900	40100	1.57
PCE4	1.5:1	62200	40100	1.55

$M_w$ : weight average molecular weight;  $M_n$ : number average molecular weight; PDI: polydispersity index;  $m/n$  is the mole ratio of carboxyl group and PEO in the side chain.

(TEM), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

**XRD.** The powder samples were tested by XRD (D/Max-RB instrument, Rigaku, Japan) using  $\text{CuK}\alpha$  radiation, a current of 40 mA, voltage of 40 kV, at a scan speed of  $4^\circ/2\theta/\text{min}$ , and a step size of  $0.02^\circ/2\theta$  in the range from  $4$  to  $60^\circ/2\theta$ . The interlayer spacing was calculated using  $2d\sin\theta = n\lambda$  (Lei and Plank, 2014b).

**TEM.** The powder samples were dispersed in ether by ultrasonic waves for 30 min and then examined by TEM (JEM-2100F STEM/EDS instrument, Jeol, Japan). The TEM point resolution was 0.23 nm; the lattice resolution was 0.102 nm; the lattice resolution on the TEM image was 0.20 nm; the minimum spot size was 0.5 nm; the accelerating voltage was 160–200 kV; the magnification was  $\sim 50,000$ – $1,100,000$ . The TEM images were used to analyze the interlayer spacing of Mnt.

**FTIR and TGA.** 1–2 mg of Mnt was ground and mixed with 200 mg of pure KBr; the powder was then placed in a mold and pressed into a transparent sheet using  $(5\text{--}10) \times 10^7$  Pa of pressure in a hydraulic device. The transparent sheet was prepared for measurement by FTIR spectroscopy, which was performed using a Nexus instrument (Thermo Nicolet, USA) over the spectral range  $4000\text{--}400\text{ cm}^{-1}$ .

Powder samples were analyzed by TGA using a STA449c/3/G instrument (Netzsch, Selb, Germany), in

the temperature range  $\sim 298\text{--}1000^\circ\text{C}$  under an atmosphere of flowing air and a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### *Fluidity of cement-Mnt paste with PCE*

Increasing the dosage of polymers may reduce the loss of fluidity in fresh concrete, if it is made from a low-quality aggregate which contains clay minerals. With a greater amount of polymers, however, the initial fluidity can also be increased, which may bring about bleeding and segregation (bleeding and segregation mean that the stone in concrete is separated from the mortar; this phenomenon is to be avoided). In the present study, the loss of fluidity was assessed using the same initial fluidity level. An appropriate dosage of PCE was used to fix the initial fluidity at a certain level (260 mm), and the fluidity of the cement or cement-Mnt paste at '60 min' was tested.

Experimental measurement of the fluidity (Figure 2) revealed that in the cement paste, to reach the initial fluidity level, a dosage of PCE1 of 0.6 g was needed, and for PCE2, PCE3, and PCE4, dosages of 0.65 g, 1.0 g, and 1.8 g, respectively, were needed, illustrating that the dispersing ability of PCE was reduced with decreasing grafting density of the carboxyl group in the side chain, in agreement with previous studies (Jun *et al.*, 2015; Ran *et al.*, 2010). At 60 min, the fluidity of the cement paste with PCE1 and PCE4 was decreased to 62% and 94%, respectively, of the initial fluidity. Fewer carboxyl groups in the side chain could enhance the dispersion

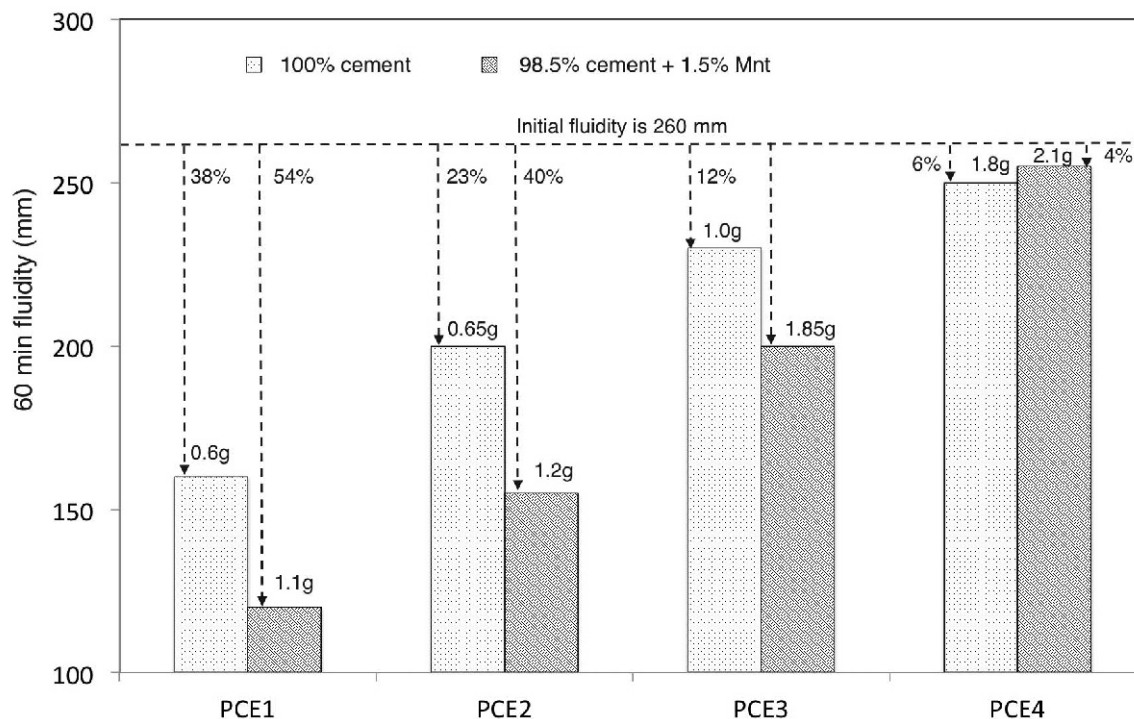


Figure 2. 60 min fluidity of the cement and the cement-Mnt paste with PCE.

retention ability, also corroborated by other studies (Winnefeld *et al.*, 2007; Liu *et al.*, 2012). The main reason for the improvement in fluidity loss was the increased dosage of PCE used to achieve the initial fluidity; this allowed for more polymers in solution preparing for later adsorption to provide dispersion continuously over time.

To reach the same initial fluidity of 260 mm in a cement-Mnt paste, 1.1 g of PCE1 was added and for PCE2, PCE3, and PCE4, 1.2 g, 1.85 g, and 2.1 g, were added, respectively. Obviously, the presence of Mnt increased the dosage of PCE needed to reach the initial fluidity level, and this was due to the large amount of PCE adsorbed and the significant water demand of Mnt. As for pure cement paste, the '60 min' fluidity of the cement-Mnt paste was increased with a decrease in the grafting density of carboxyl groups on the side chain; PCE4 had the best clay tolerance. Having enough polymers in solution was, therefore, the main factor in maintaining the balance of the suspension system.

#### Amount adsorbed

Experimental measurement of the amount of PCE in Mnt suspension or cement suspension (Figure 3) adsorbed revealed the adsorbing behavior of PCE with various side-chain grafting densities. In the cement suspension, the superficial adsorption was responsible for the initial amount of PCE adsorbed, and that depended on the grafting density of the carboxyl groups in the side chain (Liu *et al.*, 2011). Because the grafting density of the carboxyl groups of PCE1 was greater than that of PCE4, the amount of PCE1 adsorbed should be greater than that of PCE4, which was, in fact, the observation here (Figure 3).

By contrast, with the decreasing grafting density of the carboxyl groups in the side chain, the amount of PCE adsorbed on Mnt was increased rather than decreased, unlike that of PCE in the cement suspension. If most of the PCE had adsorbed superficially in the Mnt suspension, the amount adsorbed would have been reduced with the decreasing grafting density of the carboxyl groups in the side chain, consistent with the result of the PCE in the cement suspension. As a consequence, the assumption was confirmed that the amount of superficial adsorption was not responsible, in the main, for the large amount of PCE in Mnt suspension adsorbed.

In the Mnt suspension, the adsorbing behavior includes not only superficial adsorption *via* electrostatic attraction but also interlayer adsorption *via* intercalation of PCE (Ait-Akbour *et al.*, 2015). The PCE can adsorb onto the surface of Mnt particles, and can also be intercalated into the interlayer structure of Mnt; a greater grafting density of PEO side chains resulted in greater interlayer adsorbing ability (Ait-Akbour *et al.*, 2015; Ng and Plank, 2012). From the discussion above, decrease in the grafting density of the carboxyl groups, or increase in the grafting density of PEO, should lead to increased interlayer adsorption, in agreement with the results shown in Figure 3. Interlayer adsorption was largely responsible, therefore, for the large amount of PCE in Mnt suspension adsorbed.

#### Intercalation of PCE into Mnt

In Mnt, interlayer cations can be exchanged easily with cations in solution. If PCE enters the interlayer space, the interlayer structure of dried Mnt would be different from the blank Mnt, due to the existence of the polymers in the interlayer space. To discuss the effect of

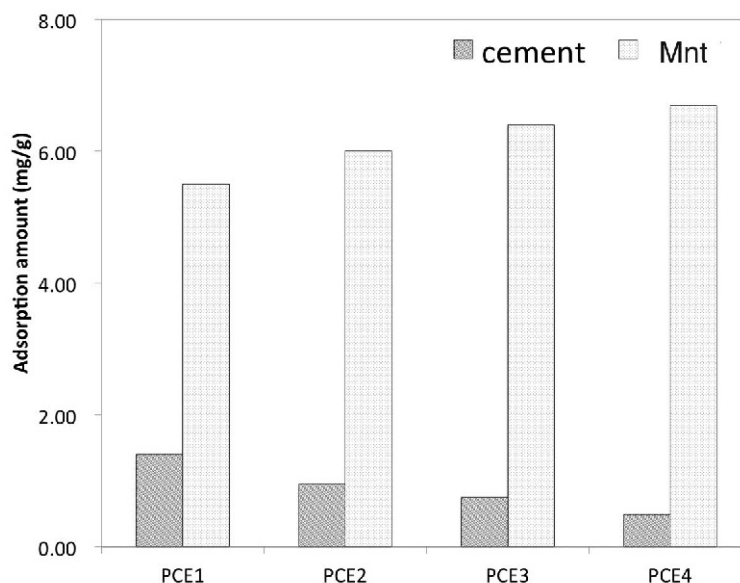


Figure 3. Amount of PCE adsorbed on the cement and on the Mnt.

side-chain grafting density on interlayer adsorption, XRD, TEM, TGA, and FTIR were used to verify the intercalation of PCE into Mnt.

X-ray diffraction (Figure 4) showed that the interlayer spacing of the hydrated Mnt without PCE was  $d_{001} = 1.50$  nm ( $5.89^\circ 2\theta$ ), while the interlayer spacing with PCE was  $d_{001} = 1.77$ – $1.78$  nm ( $4.95$ – $4.99^\circ 2\theta$ ). The presence of PCE increased the interlayer spacing by  $0.27$ – $0.28$  nm, indicating that PCE had been intercalated into Mnt. Examination of PCEs with different side-chain grafting densities indicated almost no appreciable differences in terms of preventing the intercalation.

Transmission electron microscopy (Figure 5) revealed that the interlayer spacing of hydrated Mnt without PCE was  $1.50$  nm which increased to  $1.77$ – $1.78$  nm in the presence of PCE. This result agreed with the XRD, and both suggested that the PCE had been intercalated into Mnt interlayer space; the same was true of all four of the PCEs examined, *i.e.* the same or a very similar increase in the interlayer space was observed.

The TGA weight loss at temperatures below  $250^\circ\text{C}$  was considered to have been caused by the loss of interlayer water and externally adsorbed water. Between  $250$  and  $600^\circ\text{C}$ , the weight loss was due to the loss of structural hydroxyl groups from the octahedral sheets. This temperature range is of more interest because the interlayer polymers can be decomposed and can cause noticeable weight loss. Thermogravimetric analysis (Figure 6) revealed that the weight loss of Mnt with PCE was considerably greater than that for Mnt without PCE over the  $250$ – $600^\circ\text{C}$  temperature range. Because distilled water was used to wash the samples carefully, the superficially adsorbed PCE should have been removed. Between  $250$  and  $600^\circ\text{C}$ , the polymers responsible for

weight loss should, therefore, exist in the interlayer space only; the TGA results illustrated only minor variations among the four different PCEs tested.

Fourier-transform infrared spectroscopy (Figure 7) also confirmed the intercalation of PCE. In the FTIR spectrum of Mnt without PCE, the presence of  $-\text{OH}$  ( $\sim 3650$ – $3600$   $\text{cm}^{-1}$ ),  $-\text{Si}-\text{O}-$  ( $\sim 1020$ – $1040$   $\text{cm}^{-1}$ ),  $400$ – $600$   $\text{cm}^{-1}$ , and  $-\text{Al}-\text{O}-$  ( $400$ – $600$   $\text{cm}^{-1}$ ) was noted. In contrast, in the FTIR spectrum of Mnt with PCE, alkyl peaks ( $-\text{CH}-$ ,  $-\text{CH}_2-$ , and  $-\text{CH}_3$ , at  $\sim 3000$ – $2800$   $\text{cm}^{-1}$ ) were also observed clearly. Because the superficially adsorbed PCE had been removed, the alkyl peaks definitely belonged to PCE intercalated into the interlayer space of the Mnt. This result was in agreement with those from the XRD, TEM, and TGA studies.

Clearly, PCE was intercalated easily into the interlayer space of Mnt, and various side-chain grafting densities of the four PCEs tested indicated no difference in terms of the intercalation into Mnt. Intercalation was responsible for most of the PCE adsorbed.

#### Mechanism

Adsorbing onto the surface of cement particles is the first step in the reaction between PCE and cement particles (Zhang and Kong, 2015), and the adsorption behavior is considered to be the most important characteristic in the dispersing ability of PCE (Yamada *et al.*, 2001; Ran *et al.*, 2010; Tan *et al.*, 2015a). Steric hindrance provided by the PEO long side chain of the S-PCE is largely responsible for the dispersing ability (Zhang *et al.*, 2015). In terms of the molecular structure, the initial dispersing ability of PCE depends on the grafting density of the carboxyl groups and the length of the PEO side chain (Winnefeld *et al.*, 2007; Ran *et al.*,

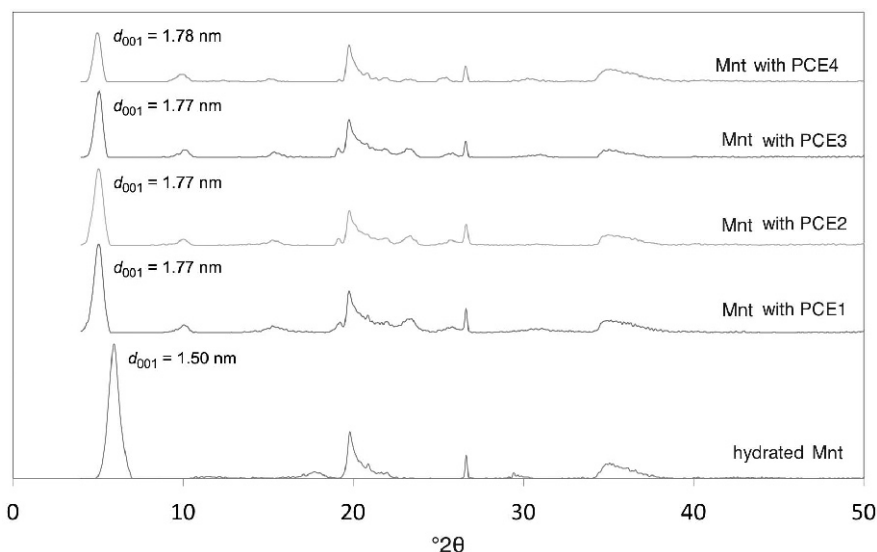


Figure 4. XRD patterns of the hydrated Mnt.

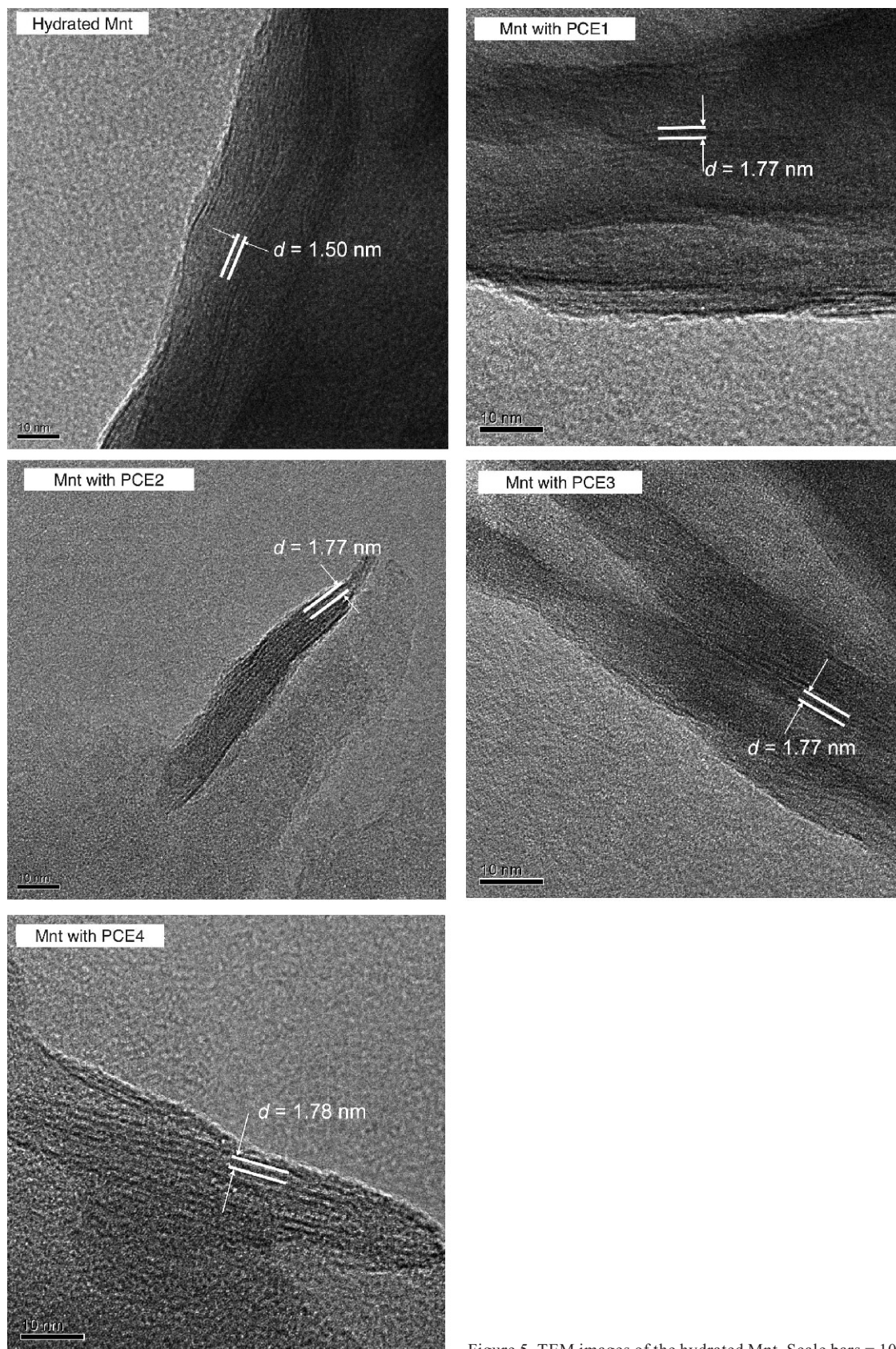


Figure 5. TEM images of the hydrated Mnt. Scale bars = 10 nm.

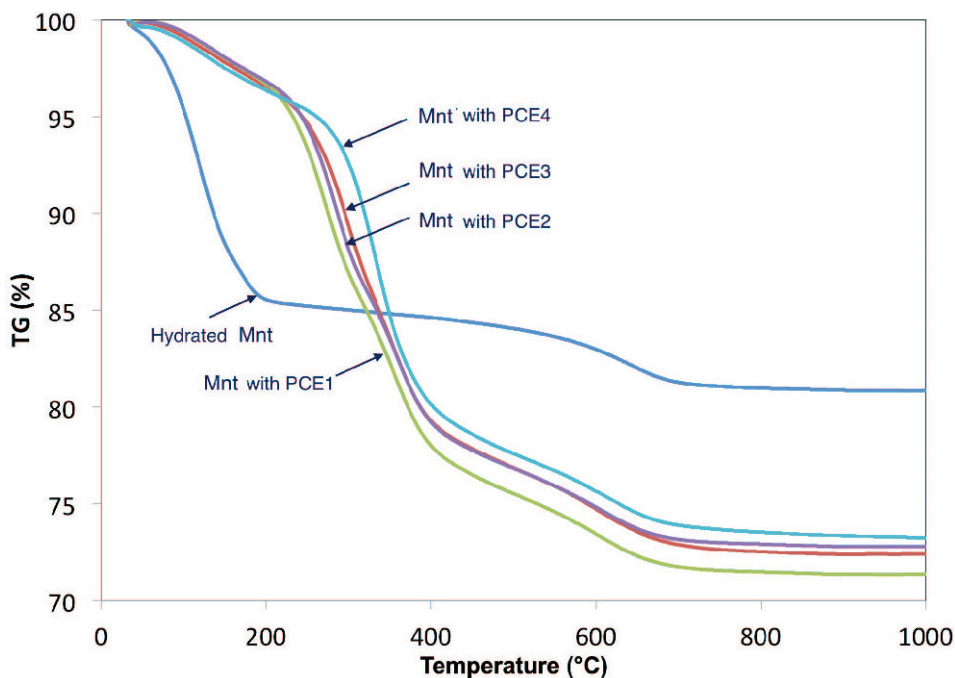


Figure 6. TG analysis of the hydrated Mnt.

2009). The lower grafting density of the carboxyl groups tends to reduce the initial adsorbing ability and the initial dispersing ability; more PCE with a lesser grafting density of the carboxyl groups is required to increase the amount of S-PCE to reach the initial dispersion level, as described in the previous discussion.

The dispersion retention ability depends on the balance of the superficially adsorbed PCE (S-PCE) and the amount of PCE in solution. The S-PCE can be enfolded within and consumed by cement hydration products over time, and the PCE in solution can continue to adsorb onto the adsorption sites to maintain the

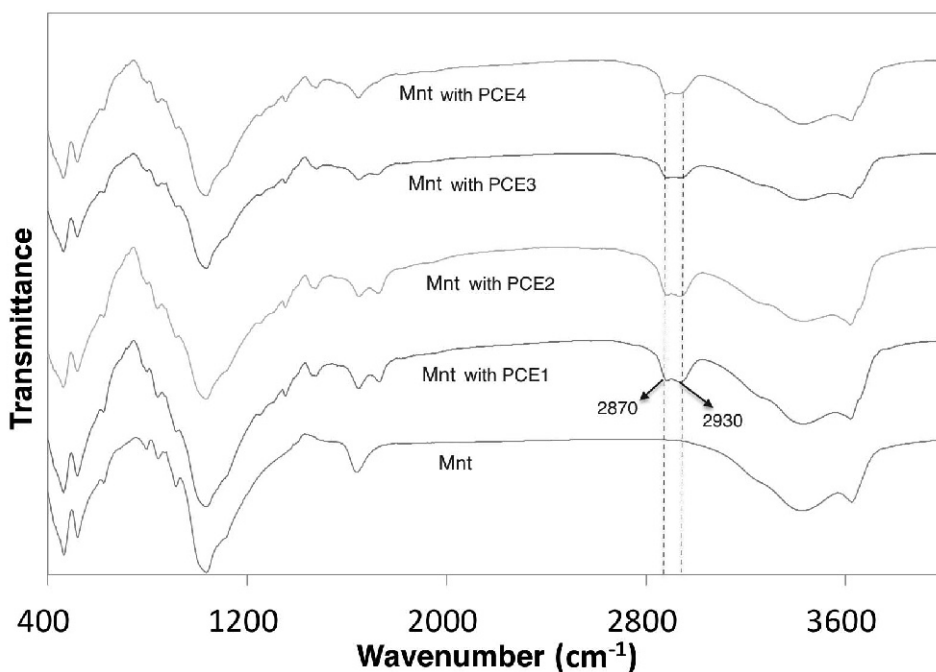


Figure 7. FTIR analysis of the hydrated Mnt.



dispersion and keep the suspension stable. If the PCE in solution were insufficient for later consumption, the balance of cement suspensions would not be maintained. The dispersed particles would start to reunite and loss of fluidity would be observed. The lower grafting density of the carboxyl groups not only increased the amounts of PCE needed to reach the initial dispersing level, but also decreased the adsorbing ability to avoid fast consumption. In that case, the PCE in solution was sufficient for later consumption, which was inferred to be the main reason for the improvement in the loss of fluidity of the cement paste containing PCE with lesser adsorbing ability.

The PCE found in the cement-Mnt suspension system can be divided into four categories as shown in Figure 8b: PCE adsorbed superficially on cement particles (S-PCE), PCE adsorbed superficially on Mnt particles, intercalated PCE, and PCE in solution. The S-PCE largely provided the dispersing ability to maintain the stability of the cement-Mnt suspension. If the

partly intercalated Mnt or unintercalated Mnt makes contact with S-PCE, the long side chain of S-PCE will be intercalated into the interlayer space. In this way, the steric hindrance provided by the long side chain of PEO would lose its effectiveness, reflected by the loss of dispersing ability. The particles in suspension would then tend to reunite and the paste would begin to lose its fluidity, as shown in Figure 8d. In addition, one Mnt particle might be intercalated by several S-PCE. Therefore, a valid way to protect S-PCE from rapid consumption by Mnt is of great importance in the prevention of fluidity loss by cement-Mnt paste.

Among the four types of PCE, PCE4 performed best in terms of maintaining the fluidity of cement-Mnt paste, for the following reasons:

(1) Because it had the largest grafting density of PEO in the side chain, PCE4 had the greatest interlayer adsorbing ability. When the interlayer space was opened in solution, PCE4 could be inserted quickly into the space to form the fully intercalated Mnt in solution

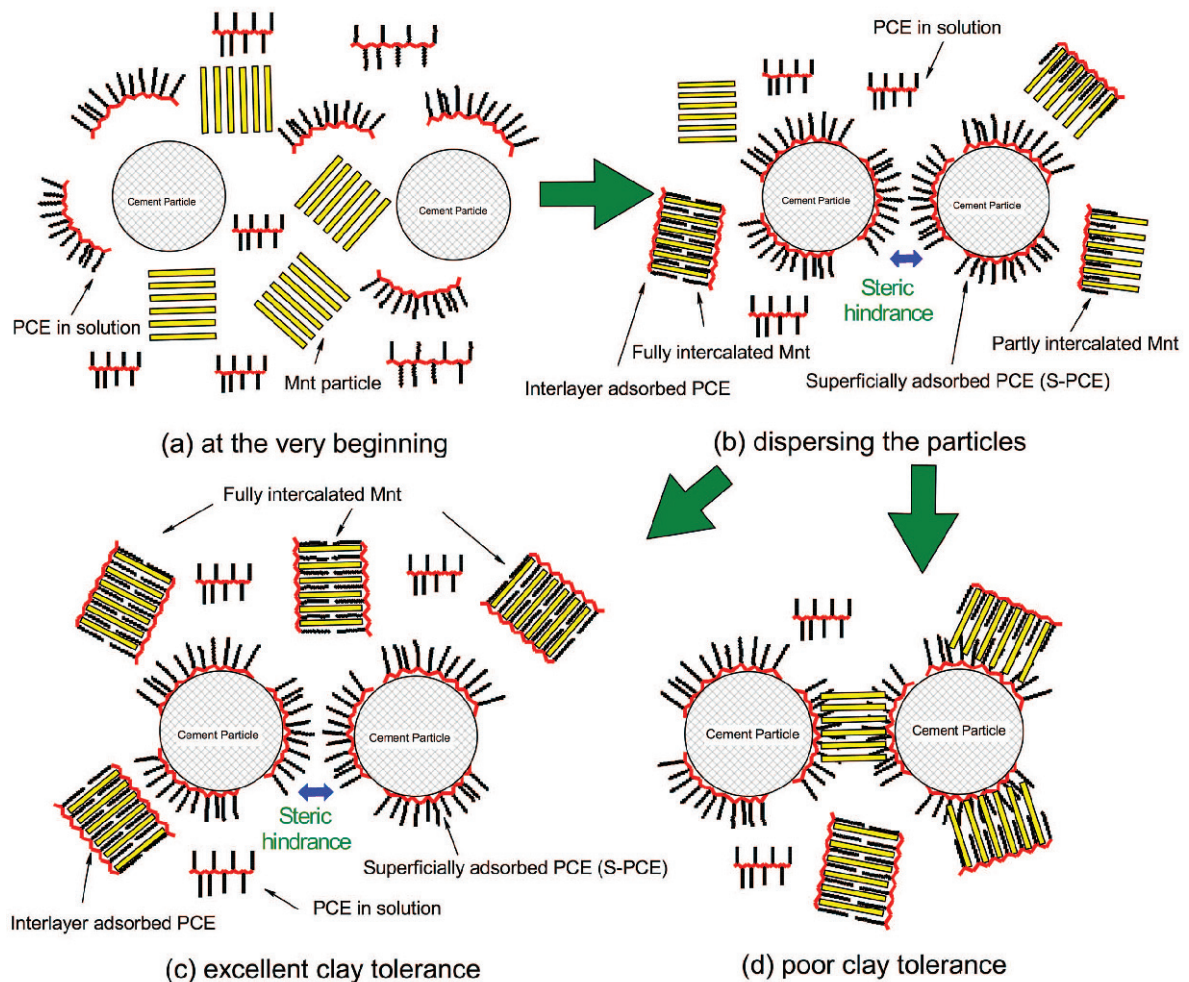


Figure 8. The process of intercalation of PCE into Mnt in cement-Mnt paste.

which could not be intercalated again by S-PCE. In that case, rare Mnt particles in suspension could react with the S-PCE to consume the superficial structure and break the balance of suspension, as shown in Figure 8c. As a result, the S-PCE was protected by preferential intercalation of PCE in solution.

(2) To achieve the initial fluidity level, the addition of PCE4 was much greater than that of other PCE and the superficial adsorbing ability of PCE4 on the surface of the cement particle was weaker than that of others, which could increase the amount of polymer in solution. As a result, more polymer in solution could be intercalated into the Mnt interlayer space to form the fully intercalated Mnt, and could also supplement the S-PCE which had been consumed by cement hydration or the intercalation of Mnt over time. As a consequence, the constant content of S-PCE was observed to maintain the dispersion.

From the aforementioned discussion, the loss of fluidity in cement and cement-Mnt pastes depends on the stability of S-PCE. To reach the same initial dispersing level, more PCE with a greater grafting density of PEO in the side chains was needed; this could provide more polymers in solution to form the fully intercalated Mnt to impede the intercalation of S-PCE and increase the clay tolerance.

### CONCLUSIONS

(1) In cement paste, with the decreasing grafting density of the carboxyl groups in the side chain, the adsorbing ability and initial dispersing ability of PCE were decreased, but the dispersion retention ability was improved significantly through increased dose of the polymers.

(2) The PEO long side chain could be intercalated easily into the interlayer space of Mnt, and increasing the grafting density of the PEO side chain could increase the interlayer adsorption of PCE. The intercalation of superficially adsorbed PCE into Mnt was the main reason for the loss of fluidity from the cement-Mnt paste.

(3) PCE with a lesser grafting density of the carboxyl groups in the side chain had better clay tolerance because of the better protection from intercalation of superficially adsorbed PCE through preferential intercalation of PCE in solution.

The results also suggested the possibility that polymers which can be intercalated preferentially into the interlayer space of Mnt in solution could improve significantly the clay tolerance of the PCE system.

### ACKNOWLEDGMENTS

The present study was supported by grants from the National Natural Science Foundation of China (51408448) and from the Science and Technology Support of Hubei Province, China (2015BAA084).

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(Received 25 May 2016; revised 10 October 2016; Ms. 1111; AE: P.B. Malla)