



## Research paper

# Mechanism of intercalation of polycarboxylate superplasticizer into montmorillonite



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## ABSTRACT

It is well known that polycarboxylate superplasticizer (PC) has a poor clay tolerance, due to huge adsorption amount caused by clay minerals, especially by montmorillonite (Mt). The aim of the paper is to study the mechanism of the interaction of Mt and PC. AA-MA was synthesized by acrylic acid (AA) and methyl acrylate (MA), and PC was synthesized by AA and isopentenol polyoxyethylene ether (TPEG). X-ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Fourier-transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and Nuclear Magnetic Resonance (NMR) were used to discuss the structure of the Mt intercalated by polymers including TPEG, AA-MA and PC. The results show that: AA-MA, which is the main chain of PC without long side chain of polyethylene oxide (PEO), only adsorbs on the surface of Mt particles, and it cannot be intercalated into interlayer space of Mt. TPEG containing PEO, the long side chain of PC, can be easily inserted into the interlayer space. Furthermore, it is proved that not the whole molecular but only the long side chain PEO of PC is intercalated into interlayer space, which is the main reason for its huge adsorption amount and less efficient dispersing ability in cement-Mt paste. The results suggest a possibility that those salts or polymers that can preferentially insert into interlayer space of Mt can be utilized to impede the intercalation of the long side chain of PC and improve the clay tolerance of PC.

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## 1. Introduction

In recent year, comb-like copolymers (Ran et al., 2010) with long side chains of lateral polyethylene oxide (PEO) and short side-chains of anionic groups, such as carboxyl groups (COO<sup>-</sup>) (Alonso et al., 2007; Janowska-Renkas, 2013; Yamada et al., 2000), have been widely employed as the superplasticizer in high fluidity cement paste and concrete (Felekoglu and Sarikahya, 2008; Lv et al., 2013; Pfeifer et al., 2010), because of its high efficient dispersing ability and workability retention performance (Winnefeld et al., 2007; Liu et al., 2012; Singh et al., 2012). However, it is argued that polycarboxylate superplasticizer (PC) has poor compatibility to those concretes with aggregates containing clays (Fernandes et al., 2007; Burgos-Montes et al., 2012). It is also very hard to control the fluidity loss that is caused by clay minerals (Sakai et al., 2006; Tan et al., 2015a; Xu et al., 2015). According to current researches, it is found that montmorillonite (Mt) is more harmful to workability than any other clay minerals such as kaolinites, muscovite (Tan et al., 2015b; Konan et al., 2009; Konan et al., 2008; Wang et al., 2012). Mt in aggregates can substantially decrease dispersing ability of PC and lead to a quick fluidity loss of the fresh concrete (Lei and Plank, 2012a; Lei and Plank, 2012b). As far as we know, Mt is a multi-layer structure of silicon, aluminum and oxygen, which is built up from

two silica-oxygen tetrahedral sheets sandwiching an alumina-oxygen octahedral sheet; cations and water exist in interlayer space (Nehdi, 2014). When it meets water, the water enters the interlayer space, thereby increasing the interlayer spacing, and then the cations in solution can be exchanged with the interlayer cations easily. Meanwhile, PC can be intercalated into interlayer space and lose its high efficient dispersing ability (Lei and Plank, 2014). It also has been illustrated that there are two adsorption mechanisms between PC and Mt (Ait-Akbour et al., 2015): (1) superficial adsorption via electrostatic interaction; (2) intercalation of PC into interlayer space. Those researches will help us to understand the reaction between PC and Mt.

It is clear that PC can be intercalated into the layers in hydration process of Mt. However, the microstructure of the intercalated Mt is uncertain, and especially it is still unclear that whether the whole molecular or part of PC is intercalated into interlayer space. To discuss this, AA-MA, the main chain of PC without long side chain of PEO, was synthesized by acrylic acid (AA) and methyl acrylate (MA); PC was synthesized by AA and isopentenol polyoxyethylene ether (TPEG). Mt that was respectively intercalated by TPEG, AA-MA and PC was prepared for the measurements. The interlayer spacing was investigated by X-ray Diffractometry (XRD) and Transmission Electron Microscopy (TEM). Fourier-transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and Nuclear Magnetic Resonance (NMR) were used to analyze the microstructure of the intercalated Mt. From those studies, it is expected

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to obtain an explanation for the mechanism of PC's intercalation into Mt in the hydration process and suggest a new method to enhance the clay tolerance of PC.

## 2. Experimental methods

### 2.1. Materials

#### 2.1.1. Montmorillonite (Mt)

Natural Mt, which was purchased from Shenyang Yiyao Technology Co., Ltd (China), was used. Its cation exchange capacity (CEC) is 73.6 mmol/100 g. The Mt was grinded into powder and dried at 105 °C. The powder that could pass through the 200-mesh sieve was prepared for the experiment.

#### 2.1.2. Synthesis of copolymers

TPEG (solid) was made by Wuhan Oxiranchem Co., Ltd. (China), and its purity is >99.0%; the degree of polymerization is about 48–52. Solution (40 wt%) of TPEG was prepared for the experiment.

PC was synthesized by AA (reagent grade, made by Sinopharm Chemical Reagent Co., Ltd., China) and TPEG. AA-MA was synthesized by AA and MA (reagent grade, made by Sinopharm Chemical Reagent Co., Ltd., China). NaOH (reagent grade, made by Sinopharm Chemical Reagent Co., Ltd., China) was used to balance the pH value of PC and neutralize AA-MA solution. The solution (40 wt%) of PC and AA-MA was prepared for the experiment.

Schematic illustration of molecular structure PC and AA-MA is shown in Figs. 1 and 2.

### 2.2. Measurements

#### 2.2.1. Preparation for intercalated Mt samples

Water (100 g) and different polymers (AA-MA, 5 g, 40 wt%; TPEG, 5 g, 40 wt%; PC, 5 g, 40 wt%) were mixed together in advance, respectively. Mt (5.0 g) were mixed with the solution and stirred by a magnetic stirrer for 30 min. After that, the solid was sifted by filter paper. Next, the solid was cleaned by distilled water and separated by filter paper three times. Afterwards, the solid was dried in a vacuum drier at 105 °C; then the solid was grinded into powder. Finally, the powders, which could pass through 200-mesh, were prepared for the measurements of XRD, FTIR, TGA, TEM, XPS and NMR.

#### 2.2.2. XRD

The powder samples were tested by XRD (D/Max-RB, made by Rigaku, Japan) with Cu (K $\alpha$ ) radiation and a current of (40 mA, 40 kV), at a speed of 4°/min and a step of 0.02° in the range from 4 to 60°. From the results, the interlayer spacing of Mt can be calculated.

#### 2.2.3. TEM

The powder sample was dispersed in ether by ultrasonic wave for 30 min. The powder samples were then tested by TEM (JEM-2100F STEM/EDS, made by JEOL, Japan). TEM Point Resolution was 0.23 nm;

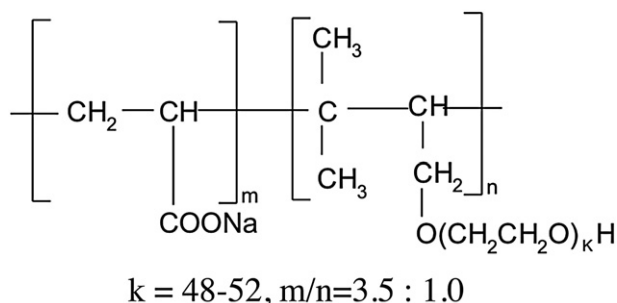


Fig. 1. Schematic illustration of molecular structure of PC.

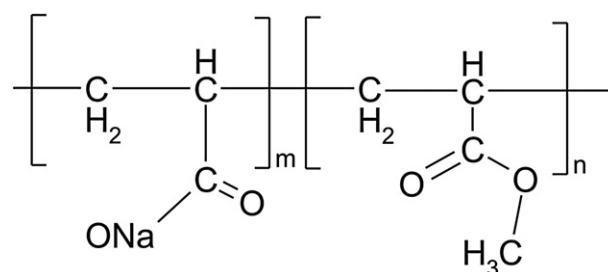


Fig. 2. Schematic illustration of molecular structure of AA-MA.

lattice resolution was 0.102 nm; lattice resolution on TEM Image was 0.20 nm; minimum spot size was 0.5 nm; accelerating voltage was 160–200 kV; magnification was 50–1100 k. The TEM images can be used to analyze interlayer spacing of Mt.

#### 2.2.4. FTIR and TGA

The 1–2 mg of Mt was grinded together with 200 mg of pure KBr to be uniform; then the powder was placed in a mold and pressed into a transparent sheet with  $(5-10) \times 10^7$  Pa pressure in the hydraulic machine. The transparent sheet was prepared for FTIR measurement. The FTIR spectra of the samples were recorded with a FTIR spectrometer (Nexus, made by Thermo Nicolet, USA). In order to determine the hydrophobic aliphatic groups ( $-\text{CH}-$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ) and ester groups ( $-\text{COOCH}_2\text{CH}_2-$ ), FTIR spectra for the intercalated Mt were taken over the whole spectral range ( $4000-400 \text{ cm}^{-1}$ ).

Synchronous thermal analyzer (STA449c/3/G, made by NETZSCH, Germany) is used to analyze the weight loss of the powder samples. Temperature range was RT ~ 1000 °C under an atmosphere of flowing air, and heating rate was 0.7 K/min.

If the polymers had been intercalated into the layer, there would have been an obvious difference from the blank Mt in FTIR spectra and TGA curve. Therefore, from the results of FTIR and TGA, it can be inferred whether the polymers have been intercalated into the layer structure of Mt.

#### 2.2.5. NMR and XPS

The silicon and aluminum of the powder samples were tested by X-ray photoelectron spectrometer (XSAM 800, made by KRATOS, England); aluminum was used as an anode target ( $h\nu = 1486.6 \text{ eV}$ ); energy resolution was 0.100 eV; the experimental pressure was  $6 \times 10^{-7}$  Pa; XPSPEAK 4.1 was used to deal with the data of XPS. The  $^{29}\text{Si}$  NMR and  $^{27}\text{Al}$  spectra of the powder samples were obtained by Solid State Nuclear Magnetic Resonance (AVANCE III 400WB, made by Bruker, Germany). All operations were made at 25 °C.

The results of XPS and NMR can indicate the change of the structure of silica-oxygen tetrahedral sheet and alumina-oxygen octahedral sheet.

## 3. Results and discussion

### 3.1. X-ray diffraction and TEM analysis

It is well known that Mt is the multi-layer structure, and cations in solution can easily be exchanged with the interlayer cations; after Mt is dried, cations are left in the interlayer space, and the interlayer spacing is altered. In order to verify whether polymers could be intercalated into its layer structure, XRD and TEM were used to analyze the interlayer spacing of Mt.

The results of XRD have been shown in Fig. 3. As shown in the figure, interlayer spacing of the blank Mt is about 1.50 nm ( $2\theta = 5.89^\circ$ ), and that of Mt with PC is about 1.77 nm ( $2\theta = 4.97^\circ$ ), which is the same result as others (Lei and Plank, 2012a). With TPEG, it is 1.62 nm ( $2\theta = 5.46^\circ$ ); with AA-MA, it is 1.25 nm ( $2\theta = 7.08^\circ$ ). Meanwhile, it has been proved that interlayer spacing can be calculated from TEM image (Plank and Yu, 2010). From Fig. 4, it is easy to find out the

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