

The Clay-tolerance of Amide-modified Polycarboxylate Superplasticizer and Its Performance with Clay-Bearing Aggregates

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Abstract. Amide-modified polycarboxylate superplasticizer (PCE) has shown many advantages compared with conventional polycarboxylate superplasticizer due to its unique molecular structure. In this study, we introduced three types of clay, montmorillonite, kaolinite and muscovite into cement and their influence on the dispersion ability of conventional PCE and amide-modified PCE was compared. It was found that conventional PCE is negatively affected by all three types of clay especially for montmorillonite where as amide-modified PCE was less affected. The concrete application performance showed that amide-modified PCE was more robust than conventional PCE when clay-bearing aggregate was utilized.

Introduction

Polycarboxylate superplasticizers were introduced as a new generation of concrete admixture due to its high water-reducing ability and slump-retaining ability [1-3]. However, its drawback was unveiled when it was utilized under certain aggressive condition [4]. It is very sensitive to different cement and it exhibited great absorbing ability on clay minerals which could occur as an impurity in aggregates. As a result, concrete often suffered great workability-loss when using clay-containing aggregates.

Clay particles presented in aggregates are very small, resulting in very high specific surface areas and potentially increasing water demand and PCE dosage. When dispersed in concrete, clay particles will absorb more water into its layered structure, increasing water demand moreover [5]. The swelling capacity of clay depends on its structure so different types of clay and their performance on cement paste fluidity should be compared [6-7].

In this study, we employed three types of clay, montmorillonite, kaolinite and muscovite to examine the difference on the absorbing behavior between our previously synthesized amide-modified PCE and conventional PCE. Additionally, concrete application test was carried out by using clay-containing aggregate in order to determine the amide-modified PCE's practical performance.

Materials and methods

PCE samples. Two PCE were used in this study, the one is amide-modified PCE which aforementioned in our previous study [8] and the other is conventional PCE supplied by our own admixture department. The chemical structure of both PCE was shown in Figure 1.

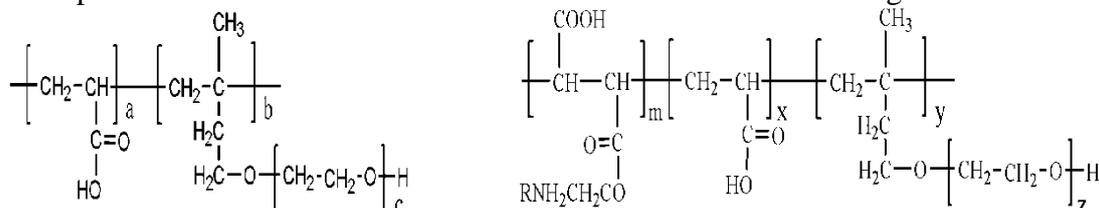


Fig.1 Molecular structure of conventional PCE (left) and amide-modified PCE(right)

Clay minerals. All clay minerals are commercially available product and their chemical composition is listed in Table 1.

Table.1 Chemical composition for clay minerals

| Clay type | Oxide contents (wt %) | | | | | | | | |
|-----------------|-----------------------|--------------------------------|------|------|--------------------------------|-------------------|------------------|-----------------|-------|
| | SiO ₂ | Al ₂ O ₃ | CaO | MgO | Fe ₂ O ₃ | Na ₂ O | K ₂ O | SO ₃ | LOSS |
| Kaolin | 44.37 | 39.77 | 0.21 | 0.37 | 1.15 | 0.21 | 1.87 | 0.07 | 11.03 |
| Muscovite | 45.56 | 27.21 | 0.71 | 1.98 | 2.52 | 0.32 | 9.33 | 0.12 | 9.89 |
| Montmorillonite | 62.21 | 19.62 | 1.32 | 1.08 | 2.21 | 1.55 | 1.04 | 0.03 | 6.53 |

Measurements. Depletion method was used to determine the PCE absorption amount on clays. Firstly, 1g powder (cement, montmorillonite, kaolinite or muscovite) was added in a beaker which contained 50ml PCE solution with a concentration of 4g/L and stirred for 3min. After 4min, 5ml sample was drawn from the beaker and diluted with nine volumes of water and centrifuged for 20min at 10000 rpm. At last, the total organic carbon (TOC) content of the final sample was determined using a Liqui TOC analyzer (Elementar, Germany). The absorption amount of PCE was calculated from the difference between the TOC content in the final sample and the original TOC content.

Generally, test of the fluidity of cement pastes added with superplasticizer was under the Chinese National Standard (GB 8077-2000) and the cement used for the test was HUAXIN P·O 42.5, the w/c ratio was 0.29 and the dosage of the PCE was 0.13% (by percent Weight based on solids cement). For the clay samples, 1wt% cement was substituted with clay.

Concrete performance was measured following the Chinese National Standard (GB 8077-2008) “Concrete admixtures”. The material proportion was shown in Table 2.

Table 2 Material proportion for the concrete test

| Water (kg/m ³) | Cement (kg/m ³) | Fly ash (kg/m ³) | Slag (kg/m ³) | Sand (kg/m ³) | Gravel (kg/m ³) |
|----------------------------|-----------------------------|------------------------------|---------------------------|---------------------------|-----------------------------|
| 155 | 210 | 90 | 80 | 760 | 1080 |

Results and discussion

Absorption amount of PCE on clay. Figure 2 displays huge difference in absorption amount between montmorillonite and the two other clay minerals (kaolin and muscovite) for both conventional PCE and amide-modified PCE. Montmorillonite exhibits strongest absorption behavior than the other two clays which suggest montmorillonite has particular negative effect on PCE, as a result, less PCE was left to disperse the cement. On the other hand, it can be seen that the amide-modified PCE was less affected by all types of clay, indicates weaker interaction between amide-modified PCE and clays. This is probably because when the polymer chain was modified by the amine, cationic unit was employed to the side chain and it could neutralize the charges on the clay which prevents the clay from swelling.

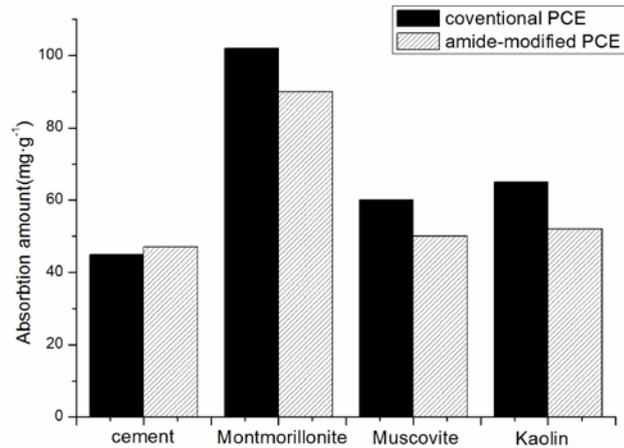


Fig.2 Adsorption amount of two PCE on cement and three types of clay

Performance of PCE on the cement paste in the presence of clay. To get a better understand on the dispersion ability of PCE in the presence of clay, cement paste test was carried out by using 1wt% of clay in substitution of cement and the result was shown in Figure 3.

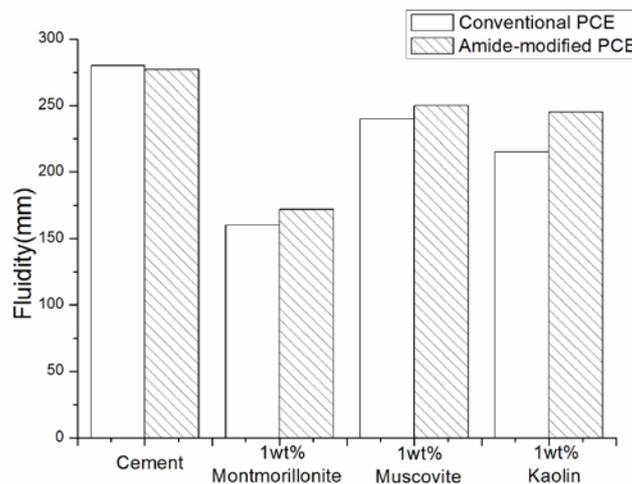


Fig.3 Fluidity of cement paste containing different PCE measured in the absence and presence of 1wt% of clay

The cement paste test results were in well accord with the absorption amount ones. It can be seen that the presence of montmorillonite can strongly reduce the dispersion ability for both PCE as the cement paste lost almost half of the spread flow. In comparison, muscovite and kaolin showed a similar trend in flow reduction but the degree is much less. It has to be noted that the dispersion ability of amide-modified PCE was much steadier in the presence of muscovite and kaolin than conventional PCE, as the spread flow decreased less than 15%.

Concrete application test. Gravel containing around 5wt% clay minerals (measured by the methylene blue test according to the national standard GB/T 14685-2011) was used in the concrete test as a comparison and the results were shown in Table 3.

Table 3 Performance of PCE in concrete with or without clays

| sample | (slump/spread)/mm | Compressive strength (MPa) | PCE dosage(%) |
|--------|-------------------|-------------------------------|---------------|
| | | 28d | |
| 1 | 230/570 | 39.5 | 1.8 |
| 2* | 230/565 | 40.1 | 1.8 |
| 3 | 235/420 | - | 1.8 |
| 4 | 230/575 | 37.1 | 2.1 |
| 5* | 240/555 | 37.5 | 1.8 |

*Sample 1 and 2 used clean gravel with a clay-mineral content less than 2wt% while sample 3,4,5 used gravel with a clay-mineral content of 5wt%.

*Conventional PCE was added in sample 1,3 and 4 while amide-modified PCE was added in sample 2 and 5.

According to Table.3, by using conventional PCE, the concrete suffered great workability loss at the same admixture dosage when clay mineral-containing gravel was used. It has to add approximately 3% of PCE to achieve a similar workability which will cause remarkable fluctuation on PCE dosage in practical concrete production. On the contrary, when amide-modified PCE was added in the concrete (compare the sample 1, 2* and 5*), the workability was minor affected. Unfortunately, the amide-modified PCE can't alleviate the strength reduction cause by clay-mineral which is fatal problem in concrete plant.

Conclusions

The influence of three types of clay, montmorillonite, kaolinite or muscovite on the performance of amide-modified PCE and conventional PCE was studied. The absorption of both PCE on montmorillonite was strong which will lower the dispersion effectiveness of PCE. However, the dispersion power amide-modified PCE was less affected by kaolinite and muscovite. Furthermore, concrete test proved the amide-modified PCE to be the more robust than conventional PCE as its capacity remain steady when the property of the aggregates changed. This behavior would benefit to practical concrete application because it reduces the sensitiveness of PCE used on very harsh, poor quality aggregates.

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