

Functionalization of Metakaolin with Non-Ionic Surfactants: Swelling and Pozzolanic Reactivity

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ABSTRACT

Metakaolin (MK) has been widely used in modifying cement and designing high-performance concrete, while the role of this aluminosilicate mineral has not been fully exploited due to its low reaction degree, especially at high-volume incorporations. To enhance the pozzolanic reactivity, functionalization of MK particles with two non-ionic surfactants, namely polyoxyethylene (9) nonylphenylether (PONPE9) and t-octyl phenoxy poly ethoxyethanol (TX100), are investigated in this study under a hypothesis that the intercalations of the surfactants into MK's interlayer space can trigger changes in structure and properties. The dry MK particles were mixed with aqueous solutions with two surfactant concentrations to reach two surfactant loadings in MK at its 1.0 and 6.0 cation exchange capacity (CEC). The surfactant uptake behavior of MK and its influence on the hygroscopic swelling, pozzolanic reactivity, and dissolution behavior in simulated cement pore solution were characterized. The results indicate that, compared with TX100, PONPE9 can be absorbed by MK more easily. After functionalization at 1.0 and 6.0 CEC, MK exhibited surfactant mass fractions of 1.85% and 3.81% for TX100, and 1.95% and 5.39% for PONPE9, respectively. The intercalation of surfactants resulted in an up to 28.6% increase in the swell index of MK when absorbing water. A more robust aluminum and silicon dissolution behavior in the simulated cement pore solution was observed from the functionalized MK. Increases in reaction heat and lime consumption capacity were obtained in the MK-lime blends indicating the enhanced pozzolanic reactivity of MK after functionalization and paving a path to enhance the role of MK in future sustainable concrete design.

KEYWORDS: *Metakaolin, functionalization, non-ionic surfactants, swelling, pozzolanic reactivity*

1. Introduction

Metakaolin (MK) has been widely used as a supplementary cementitious material (SCM) in concrete to improve mechanical and durability properties due to its highly pozzolanic reactivity. However, it was reported by Wild and Khatib (1997) that the pozzolanic reaction of MK in the cement matrix becomes low after 14 days, due to the formation of an inhibiting layer of reaction products on the MK particles, resulting in less strength gain. Moreover, the optimal cement substitution with MK was found to be between 10% to 15%. A higher dosage is desired to achieve robust reductions in cement consumption and CO₂ intensity of concrete, while it might lead to compromised mechanical strength, which might be caused by its extremely high-water absorption capacity (Brykov et al. (2015)), poor dispersion in the ion-rich cement matrix (Paiva et al. (2012)) and low degree of reaction. Although the use of MK in concrete becomes increasingly common, the aforementioned challenges still remain and impede the high-volume incorporation of MK in the development of sustainable and high-performance cementitious composites. Organic functionalization has been validated as an effective approach to modify clay particles, e.g., montmorillonite (MT), as the surfactants can be intercalated into the interlayer space, thereby enhancing the pozzolanic reactivity, water uptake capacity, and dispersion of clay particles to improve the performance of concrete (Luo and Wei (2022a)). Different from the 2:1 layered structure of MT, MK possesses a unique 1:1 layer structure of tetrahedral silicate and octahedral aluminate. Our previous success in functionalizing MT paves a path for the modification of MK. In this study, the functionalization of MK with two non-ionic surfactants and its effect on the properties of MK in terms of dispersion, swelling, ion exchange, and pozzolanic reactivity are investigated.

2. Materials and methods

2.1 Materials and functionalization of MK

The MK used in this study has a mean particle size, specific surface area, and cationic exchange capacity (CEC) of 3.79 μm , 3.0 m^2/g , and 7.47 meq/100g respectively. Two non-ionic surfactants, polyoxyethylene (9) nonylphenylether (PONPE9) and t-octyl phenoxy poly ethoxyethanol (TX100) with an average molar mass of 660 and 647 g/mol, respectively, were used to functionalize MK by following the ionic exchange method (Taleb et al. (2018)). Firstly, the raw MK was oven-dried at 105°C for 24 h. Then, the MK particles were mixed with aqueous surfactant solutions with dosages of 1.0CEC and 6.0 CEC of MK at a clay concentration of 100g/L by stirring at 500 rpm for 30 min at room temperature. The organically functionalized MK (OMK) was collected by centrifuging the suspensions at 14000 rpm for 15 min followed by oven drying at 70°C for 24 h and grinding with a ball mill at 900 rpm for 2 h.

2.3 Characterization methods

The intercalation of the surfactants in MK and the pozzolanic activity of the Mk samples in terms of lime consumption capacity were determined via thermogravimetric analysis (TGA) using a TGA 4000 from PerkinElmer. Approximately 30 mg of MK and OMK particles were tested from 30 °C to 800 °C at a heating rate of 15 °C/min in an inert environment of N₂ gas. UV-Vis spectroscopy was performed on suspensions of MK and OMK in both deionized (DI) water and a simulated cement pore solution (pH = 13.5) using a Cary 8454 spectrophotometer to evaluate the dispersion behavior of MK and OMK. ASTM D5890 was followed for the swelling behavior analysis. The heat flow and accumulative heat release from the reactions between MK/OMK and calcium hydroxide (CH) up to 50 h at 25 °C were performed with an I-Cal 2000 HPC high-precision isothermal calorimeter. For the lime consumption test, 39 g of MK/OMK-CH blends with an MK/OMK to CH ratio of 0.3 and a water/solid ratio of 2.0 was cast in a sealed bottle. The blends were collected at 1, 7, and 28 days to determine the CH consumption with the TGA procedures mentioned above. The Al and Si release behavior of MK and OMKs were determined by mixing 5 g of MK/OMKs with 200 mL of simulated pore solution stirred at 500 rpm and 40 °C. 2.5 mL of the solutions were withdrawn after 2, 5, 10, 20, and 30 min for inductively coupled plasma optical emission spectrometry (ICP-OES) after stabilizing with 2% nitric acid (a dilute factor of 250).

3. Results and discussion

3.1 Intercalation of surfactants into MK

As shown in Figs. 1a and 1b, TGA was used to determine the amounts of surfactants intercalated into MK based on the weight drop in the temperature range of 150°C to 375°C, which was observed from OMK only, but not appeared in raw MK. Another main mass loss between 375°C to 650°C was caused by the dehydroxylation of residual kaolinite in the MK. By quantifying the weight drop between the first peak, the amount of surfactant by mass of the clays can be extracted and shown in Fig. 1c. 1.9% and 2.0% of 1.0TX100-MK and 1.0PONPE9-MK were occupied by the surfactants, respectively, while they increased to 3.8% and 5.4% when 6.0 CEC surfactants were applied.

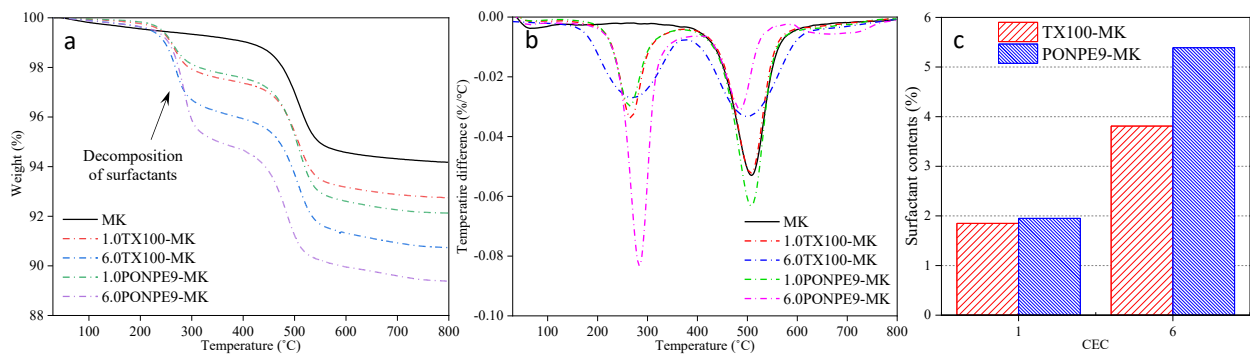


Fig. 1 (a) TGA, (b) DTG curves of MK/OMK, and (c) surfactant contents intercalated into MK.

3.2 Dispersion and swell behavior

As shown in Fig. 2a, no absorbance peak can be observed from the UV-Vis spectra of the raw MK-DI water suspension, while two peaks at 224 nm and 274 nm appeared from the suspensions with the functionalized MK, which increased with the dosage of surfactants. PONPE9 showed a higher efficiency than TX100 in improving the dispersion behavior of MK. Lower absorbances were yielded from the MK/OMK-simulated cement pore solution suspensions (see Fig. 2b), unveiling the lower dispersion of clay particles in the ion-rich cement matrix than that in DI water. A peak at 216 nm was observed from the suspension with the raw MK, while the higher dispersion of OMKs was indicated by two peaks at 224 nm and 274 nm. As shown in Fig. 2c, the raw MK exhibited a swell index of 3.5 mL/2g, which was increased to 4 mL/2g and 4.5 mL/2g, respectively, when 1.0CEC and 6.0CEC surfactants were applied for functionalization. The increased swelling behavior of MK might be favorable for using OMK as an internal curing agent to partially replace cement in concrete, as the improved swelling of MK can provide additional precipitation space for the gradual formation of cement hydration products, i.e., C-S-H and C-A-S-H. It is interesting to see the comparable role of PONPE9 and TX100 in this test.

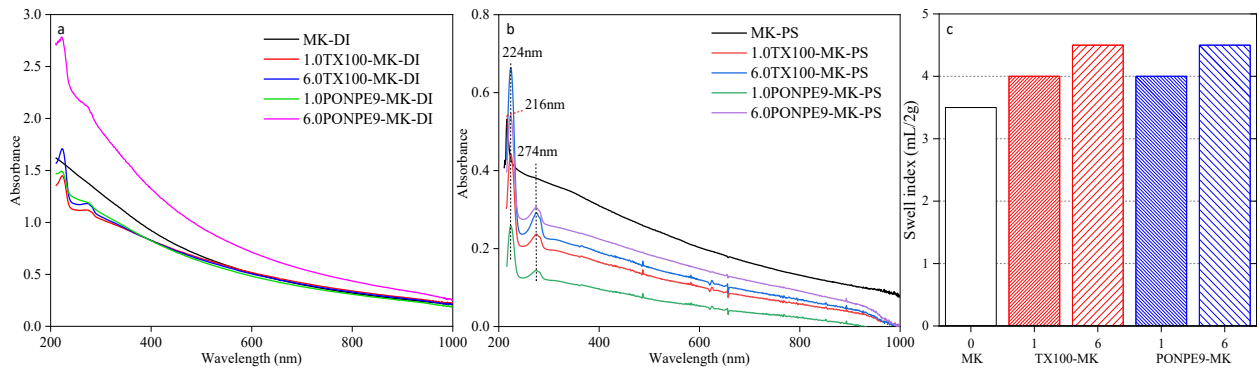


Fig. 2 UV-Vis spectrum of MK and OMKs in (a) DI water and (b) simulated pore solution, and (c) swell index

3.3 Pozzolanic reactivity

The heat flow and cumulative heat release generated from the reactions between MK/OMKs and CH are shown in Figs. 3a and 3b, respectively. A higher heat flow peak at 0.04 h and more cumulative heat release than that of MK were yielded by 6.0PONPE9-MK indicating the improved pozzolanic reactivity after functionalization. However, the heat flow peaks observed from other OMKs are lower than MK, indicating the decreased pozzolanic reactivity, at least during the early-age reactions. Although 1.0PONPE9-MK yielded a lower heat flow peak, its cumulative heat release exceeded that of MK after 9 h, indicating the retarded reaction, but a higher overall pozzolanic reactivity.

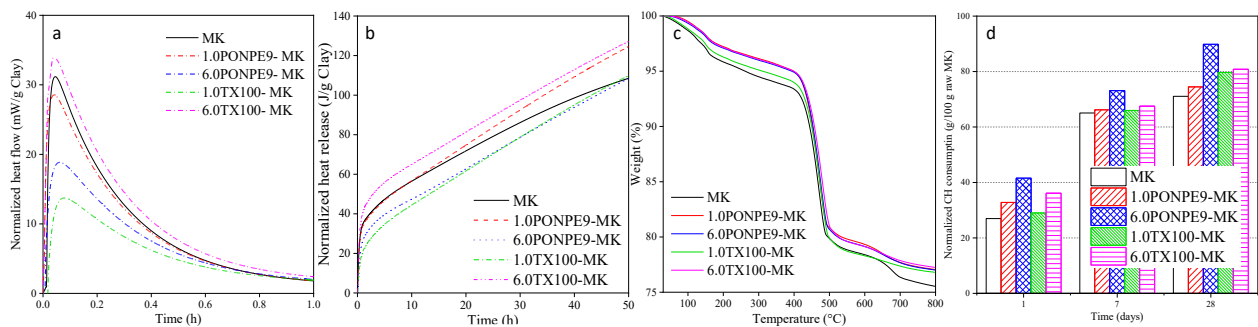


Fig. 3 (a, b) Calorimetry results, (c) representative TGA curves, and (d) normalized CH consumption.

From the TGA curves in Fig 3c, the remaining CH from the reactant system can be quantified, which enables the quantification of the consumed CH (Fig. 3d). The raw MK yielded a lime consumption capacity of 27.0, 65.1, and 71.1 g/100g MK after 1, 7, and 28 days, respectively. Enhanced pozzolanic reactivity was obtained from the functionalized MK. 6.0PONPE9-MK exhibited the most enhanced lime consumption, which are 54.1%, 12.3%, and 26.3% higher than that of MK for the three testing ages.

3.4 Ion release behavior

The dissolution of MK in terms of Al and Si releases in the cement system governs its pozzolanic reactivity and the formation of additional C-S-H or C-A-S-H. As shown in Fig. 4, the raw MK released 6.6 mmol/100g Al and 2.7 mmol/100g Si after 30 min. Slight increases in Al dissolution were observed from 1.0PONPE9-MK and 1.0TX100-MK. However, significant enhancements of Al release were observed from 6.0PONPE9-MK and 6.0TX100-MK at an early age and they gradually increased to 10.9 mmol/100g MK and 9.5 mmol/100g MK, respectively, after 30 min. Different from the release of Al, the functionalization did not result in a remarkable increase in early-age Si dissolution, until 20 min. After 30 min, 4.5 mmol/100g MK and 4.3 mmol/100g MK of Si were released from 6.0PONPE9-MK and 6.0TX100-MK, respectively, which are 1.7 and 1.6 times that of MK.

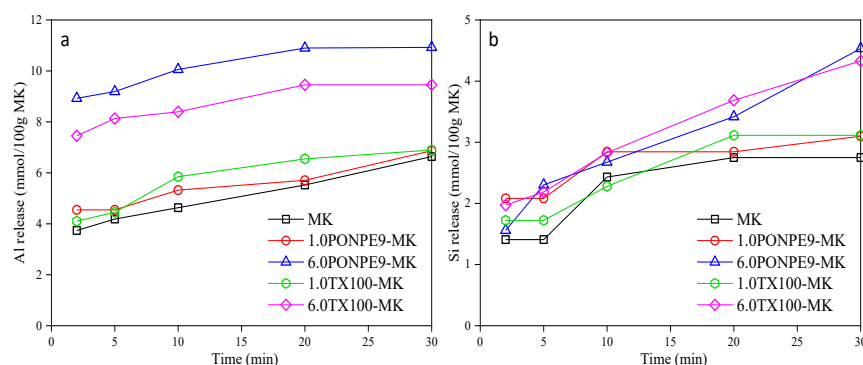


Fig. 4 (a) Al and (b) Si release behavior of MK and OMKs in a simulated cement pore solution.

4. Conclusions

The functionalization of MK by two non-ionic surfactants and its effects on modifying the properties of MK were investigated in this study. Through a simple functionalization procedure, intercalations of 5.4% PONPE9 and 2.0% TX100 (by weight of MK) into MK were reached at a dosage of 6.0 CEC. An increased hygroscopic swelling index of MK by up to 28.6% was obtained after the functionalization. The dispersion of MK in both DI water and simulated cement pore solution was also improved. Moreover, improvement in the pozzolanic reactivity of MK after functionalization was demonstrated by the increased reaction heat and the raised lime consumption capacity, which can be further explained by the enhanced dissolution of OMK in terms of Al and Si releases in the simulated pore solution.

Acknowledgements

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