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Research Article

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Superplasticizers and Rheological Properties of Highly Concentrated Cement Pastes

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Abstract

With the growing demand for higher mechanical properties and durability, the water-to-cement mass ratio (W/C) of modern cementitious materials is progressively decreasing, leading to poor workability. In this paper, we focus on the effects of polycarboxylate superplasticizers (PCE) on the rheological properties of highly concentrated cement pastes to optimize the mix design for high-performance concrete. Our adsorption measurements show that PCE adsorption at low W/C still follows the Langmuir-type isotherm. In line with the previous work, the rheological measurements suggest that the adsorbed PCE can indeed deflocculate the concentrated system, which is at the origin of the decreasing yield stress and residual viscosity. Moreover, the residual viscosity scales with the square root of yield stress for a given solid volume fraction. We, therefore, suggest that the role and the action mechanism of PCE should not be affected by the W/C ratio. All the consensuses drawn from previous studies can be applied to highly concentrated cementitious materials.

Keywords

Superplasticizer, Surface coverage, Adsorption, Rheology, Highly concentrated cement paste

Introduction

Concrete is the most widely used construction material in the world. Recent trends in mix design show the W/C of modern cementitious materials is progressively decreasing [1], especially after the advent of ultra-high-performance concrete, to meet the demand for higher mechanical properties and durability [2]. However, the decrease in W/C has serious consequences on the workability (i.e., rheological properties) of cementitious materials, bringing difficulties to the placement process [2, 3] and even weakening the hardened properties [4]. In the last decades, superplasticizers have been widely used in cementitious materials due to their extremely efficient dispersing ability. Within this frame, to improve the technique for designing concrete with optimal fresh and hardened properties, a deep understanding of the role of superplasticizers as well as their action mechanisms in highly concentrated cementitious materials, normally with a W/C ratio lower than 0.22, is highly required.

Extensive research [3, 5-11] has been conducted to identify the effects of superplasticizers on the rheological properties of cementitious materials, reaching the following consensuses: (1) Superplasticizers can adsorb on cement grains via electrostatic forces or the complexation bonding between the anionic groups and Ca^{2+} [5], complying a Langmuir-type adsorption isotherm [6]. (2) The conformation of adsorbed PCE can be simplified as a chain of hemispheres on a surface [7, 8]. Therefore, the conformation distance, the surface occupied by a molecule and the saturated adsorbed amount, can be computed by the structural parameters. More details on these calculations can be found elsewhere [7-9]. (3) The macroscopic viscosity of cementitious suspension is controlled by three independent interactions, i.e., colloid attractive interactions, hydrodynamic effects, and particle inertia [3, 10]. (4) Deflocculation is at the origin of the decrease in yield stress and residual viscosity, mainly the viscous dissipation. Yield stress scales with the inverse power two of the surface-to-surface separation distance [3, 10, 11] and residual viscosity scales with the inverse power of separation distance [3]. However, all the aforementioned conclusions are derived from cementitious materials with a W/C higher than 0.22. More recently, the focus shifted towards highly concentrated cementitious suspensions. Liu et al. [12] investigated the influence of PCE dosage on the viscosity of cement pastes with W/C ratios of 0.32, 0.24, 0.20, and 0.16. The results suggest that, at very low w/c (i.e., 0.20 and 0.16), PCE cannot further decrease apparent viscosity on account of the small space between cement grains and the high concentration of non-adsorbing PCE. For the relationship between viscosity and yield stress, Zhang et al. [13] mentioned that pastes with higher molar mass PCE exhibit lower residual viscosity when the yield stresses are almost the same. Contrary to molar mass, the phosphate group content was proved to have minor effects on the relationship between apparent viscosity and yield stress [14]. Even if some breakthrough results are obtained in this research, it is rarely systematically reported on the role of superplasticizers on the rheological properties of highly concentrated cementitious suspensions. Whether the above consensuses are valid or not in such dense systems still remains unclear.

To fill this gap, in this paper, we aim at providing an understanding of the role of PCE, mainly surface coverage and molecular structure, in cement pastes with an extremely low W/C and verifying the applicability of the above consensuses to this type of system. For this, three PCE samples with different side chain lengths and densities were employed. The rheological properties of cement paste with W/C = 0.20 were carefully studied. Additionally, the adsorption isotherm of PCEs and the viscosities of cement pore solutions were also measured in this study to further discuss the effects of PCEs.

Materials and Experimental Protocols

Cement

A commercial ordinary Portland cement, P.I 42.5 according to the Chinese standard, was employed in this study, the chemical and mineral compositions of which are listed in table 1. Its specific density and Blaine specific surface are 3.14 g/cm^3 and 360 m^2/kg, respectively.

Table 1: Chemical and mineral composition of the studied commercial cement.

Chemical composition (wt.%)		**Mineral composition (wt.%)**	
SiO_2	23.28	C_3S	39.74
Al_2O_3	4.98	C_2S	31.49
CaO	60.60	C_4AF	10.78
Fe_2O_3	3.42	C_3A	2.01
MgO	2.08		
SO_3	2.02		
K_2O	0.41		
Na_2O	0.15		

Polymers

Three polymers were used in this study, which were specifically synthesized by Jiangsu Sobute New Materials Company through aqueous free radical polymerization. All of them are poly-carboxylates with similar molecular weights, consisting of the same acrylic acid backbone and methyl allyl polyethylene glycol side chains of different lengths. As defined [15], these PCEs are in the flexible backbone worm regime. Their structural parameters are given in table 2. Used materials are of nanoscale.

Mixing protocols

We here chose a mixing protocol, proven to eliminate almost all the consequences of early chemical processes (e.g., intercalation of PCEs) [3], to focus on the physical effects of PCEs on the rheological properties of concentrated cement pastes. Cement powder and 90% water were first mixed at 140 rpm for 1 min using a cement paste blender (NJ-160A, Wuxi Jianyi Instrument & Machinery), then rested for 19 min (i.e., most of the initial aluminates have already nucleated [3, 16]) before adding PCE and the remaining 10% water. Lastly, the mixture was mixed at 140 rpm for 2 min and 285 rpm for another 2 min.

All the prepared cement pastes are concentrated suspensions with a water-to-cement mass ratio of 0.20. Only PCE dosage and molecular structure vary from one sample to another. For the selection of studied samples, Cement pastes, bleeding or forming wall slip during the measurement procedures, are not considered in this paper to not misunderstand the PCE effects by the strong artifacts induced by these behaviors. The final studied PCE dosages are given in table 2. Note that the same pastes were used for adsorption and rheological measurements to observe the real adsorption behavior of PCE. In addition, all the experiments were carried out immediately after the mixing protocol and performed at 20 ± 2 °C and 55% relative humidity.

Table 2: Molecular structural parameters and studied dosages of the selected PCEs.

Sample No	PCE_{2400}	PCE_{3000}	PCE_{4000}
Side chain length (g/mol)	2400	3000	4000
Density of side chains AA: MPEG	4	5	6.67
Molar mass M_w (g/mol)	41016	41901	40891
Molar mass M_n (g/mol)	22934	23912	25222
PDI	1.788	1.752	1.621
Dosage (% of cement)	0.13, 0.14,0.15,0.16	0.131, 0.136, 0.14, 0.141, 0.143, 0.15	0.141, 0.144, 0.15, 0.16

Adsorption measurements

The adsorption of PCE was determined by a Total Organic Carbon analyzer (Multi N/C 3100, Analytik Jena AG). The liquid sample for Total Organic Carbon analyses was extracted by centrifugation at 10000 rpm for 10 min, which thereafter was acidized by 1 M HCl solution and diluted with ultrapure water. The PCE solutions and cement paste in the absence of PCE were also measured as references. The specific adsorption amounts of PCEs can therefore be calculated based on the comparison between the organic carbon amounts of tested samples and the reference values.

Rheological measurements

The shear rheology measurements were performed on a rheometer (MCR302, Anton Paar) with a coaxial cylinder bob and cup geometry (CC27), which consists of three steps: (1) the cement pastes were pre-sheared at 100 s^{-1} for 30 s and then the shear rate linearly decreased to 0 s^{-1} within 10 s; (2) the shear rate kept at 0 s^{-1} for 60 s and followed by an increase to 100 s^{-1} within 10 s; (3) the shear rate decreased from 100 s^{-1} to 1 s^{-1} in a manner of logarithmic for 120 s, based on which the apparent viscosity of the cement paste can be obtained.

Polymer solution viscosity measurements

The viscosity of the interstitial solution was measured by the same rheometer with a coaxial cylinder bob and cup geometry (CC39). A mixture of PCE and salty alkaline solution (1.72 g/L $CaSO_4.2H_2O$, 4.757 g/L K_2SO_4, 6.959 g/L Na_2SO_4 and 7.12 g/L KOH) [17] was prepared to simulate the reality, and the concentration of PCE was determined by the results of adsorption measurements. The apparent viscosity of the interstitial solution was recorded by shearing the simulated solution with a constant shear rate of 10 s^{-1} for 2 min.

Results and Discussion

Adsorption isotherms

We plot in figure 1a the measured adsorption isotherms for PCE_{2400}, PCE_{3000}, and PCE_{4000} in contact with cement at W/C of 0.20. We note that all the adsorption curves have similar shapes, i.e., an increase of the adsorbed amount with polymer concentration remaining in the pore solution followed by a saturated plateau at high concentrations. Our data are in agreement with previous results measured at comparatively high W/C [3, 6, 18, 19], indicating PCE adsorption still follows a Langmuir-type isotherm in concentrated cement pastes. Therefore, surface coverage (see figure 1b), defined as the ratio between adsorbed amount and the average value at the adsorption plateau, can be introduced to reflect the working efficiency of PCE at a certain dosage.

It can also be seen from figure 1a that the average plateau values are almost equivalent for all the studied PCEs considering the relative uncertainties of measurements. It suggests that the saturated adsorbed amount does not vary significantly with the polymer structure. Flatt et al. [9] also reported the weak dependency of this parameter on the molecular structure of absorbed polymers, which is in accordance with our study.

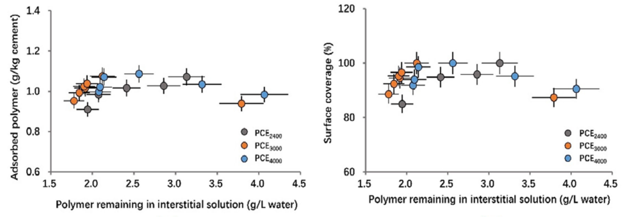
Apparent viscosity measurements

For clarity, three dosages of PCE_{3000} are chosen as the representations of all the tested samples and their apparent viscosity as a function of shear rate is plotted in figure 2a. We note a shear thinning behavior at low shear rates along with a shear thickening behavior at intermediate and high shear rates in all the curves, similar to literature [3]. Moreover, as PCE dosage increases, shear thinning becomes less pronounced whereas shear thickening shows an opposite trend. This can be attributed to the decrease in yield stress, which can push the critical shear rate corresponding to the transition between these two regimes to a lower value [20].

Given the macroscopic behavior of tested cement pastes, as shown in figure 2a, a pseudo-Newtonian plateau [3], i.e., a regime where hydrodynamic effects dominate other interactions in the pastes, may be masked by the pronounced shear thinning and shear thickening behavior. It means that there is a high risk of misunderstanding the effects of PCE on the hydrodynamic contributions to the macroscopic viscosity of cement pastes. Hence, we assumed the pastes can be described as modified Bingham fluids and their apparent viscosity is given by:

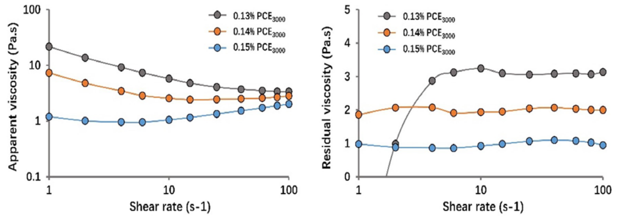
$$\eta_{app} = \tau_0 / \dot{\gamma} + \eta_{res} + k\dot{\gamma} \qquad (1)$$

Where, $\tau_0 / \dot{\gamma}$, η_{res}, and $k\dot{\gamma}$ represent the colloidal [3], viscous and particle inertia [10] contribution to the apparent viscosity of cement pastes, respectively. We then compute the residual viscosity η_{res} from the apparent viscosity η_{app}, yield stress τ_0 extrapolated at low shear rates and shear thickening intensity k fitted at high shear rates. Note that the residual viscosity studied here is completely distinct from the one in [3], containing both viscous and particle inertia contributions to apparent viscosity.



(a) (b)

Figure 1: (a) Adsorbed amount and **(b)** surface coverage as a function of PCE concentration remaining in the interstitial solution for PCE_{2400} (gray), PCE_{3000} (orange), and PCE_{4000} (blue).



(a) (b)

Figure 2: (a) Apparent viscosity and **(b)** residual viscosity as a function of shear rate for cement pastes with PCE_{3000} at three different dosages.

The residual viscosity as a function of shear rate for the same samples is shown in figure 2b. Except for some data points at extremely low shear rates, a plateau is observed in the full tested range of shear rate. It proves that the proposed analysis technique can indeed reflect the respective contributions of colloidal, viscous, and inertial forces to the macroscopic viscosity of the pastes. We therefore suggest that, in a concentrated cement paste, the energy dissipation is still a combined consequence of the three aforementioned interactions. From figure 2b, we moreover note a decrease in the plateau level with increasing polymer dosages. It indicates that PCE can strongly affect the viscous dissipation, which will be discussed in more details in the Residual viscosity section.

Yield stress

The measured yield stress as a function of surface coverage for PCE_{2400}, PCE_{3000}, and PCE_{4000} is shown in figure 3. As expected, yield stress declines with the increase of surface coverage, while it reaches a plateau as the surface coverage tends towards 100% [8]. In the increasing regime, an increase in surface coverage by 10% would at least decrease the yield stress by 80% for all the studied PCEs, implying a high dispersing ability of PCEs studied here. Furthermore, we note an almost negligible difference in the dispersing ability of the PCEs, which could only result from the uncertainties in surface coverage. It has been well-proven that yield stress shall scale with the inverse power two of the separation distance [3, 10, 11]. When the surface coverage is identical, this distance only depends on the theoretic conformation distance of the adsorbed polymers [19], of which the value is strongly controlled by the polymer structure, especially the side chain length (at the power 7/10) [7]. We, therefore, suggest that the structural difference between the studied PCEs is comparatively small and this may be at the origin of their similar dispersing ability.

Residual viscosity

We plot in figure 4a the calculated residual viscosity as a function of surface coverage for the polymers tested here. We first note a decrease in residual viscosity, i.e., viscous dissipation, with increasing surface coverage. It was shown in [3] that, shear shall concentrate in fluid layers between cement grains, leading the "residual viscosity" to scale with the ratio of the viscosity of pore solution and the separation distance. Despite the different definitions, this scaling law should be applicable to our residual viscosity in theory, because the one in [3] is level at the plateau where the particle inertia contributions to apparent viscosity are negligible.

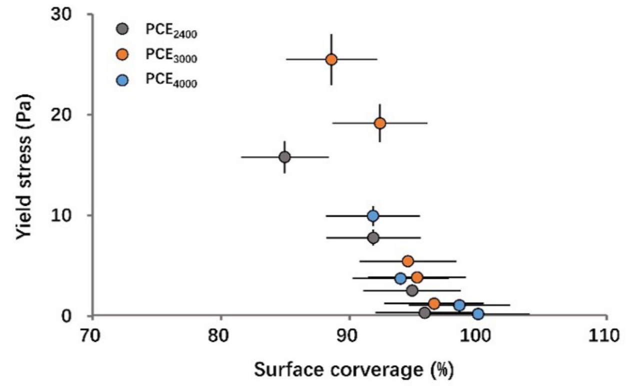
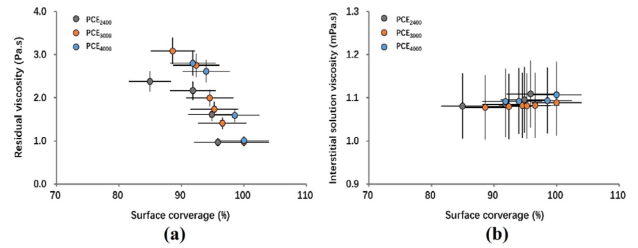


Figure 3: Yield stress as a function of surface coverage for PCE_{2400} (gray), PCE_{3000} (orange), and PCE_{4000} (blue).

In order to isolate the effect of interstitial solution viscosity from that of separation distance, we measured the viscosities of pore solutions for the studied cement pastes and plot them in figure 4b as a function of surface coverage. Within the permissible range of error, all the cement pore solutions display a similar viscosity. It suggests that the contribution of polymers remaining in the pore solution to residual viscosity is negligible and the increasing separation distance could be at the origin of the decrease in residual viscosity. Furthermore, the subtle difference among the residual viscosities of the pastes containing PCE_{2400}, PCE_{3000}, and PCE_{4000} further confirms the little structural difference of the studied PCEs.

To study the scaling relations, the residual viscosity as a function of the square root of yield stress is depicted in figure 5. It is demonstrated from this figure that all the data points form a unique linear curve. It suggests that the residual viscosity scales with the square root of yield stress at a constant solid volume fraction [3]. Hence, we conclude that, in a highly concentrated cement paste, both yield stress and viscous dissipation display the same scaling laws with the separation distance as that in the pastes with higher W/C.



(a) **(b)**

Figure 4: **(a)** Residual viscosity and **(b)** interstitial solution viscosity as a function of surface coverage for PCE_{2400} (gray), PCE_{3000} (orange), and PCE_{4000} (blue).

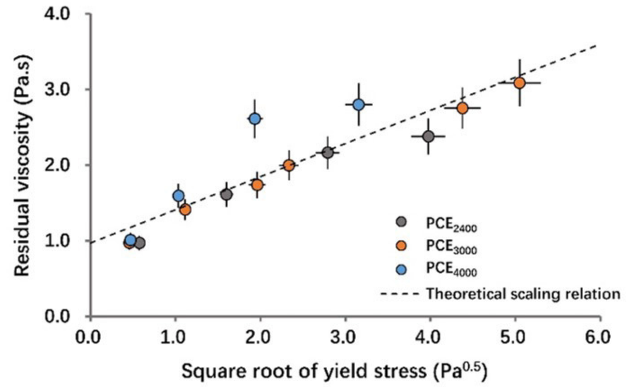


Figure 5: Residual viscosity as a function of the square root of yield stress.

Conclusions

In this paper, we studied the role of PCE, mainly the surface coverage and the molecular structure, in highly concentrated cement pastes and investigated the scaling laws for the rheological properties of the pastes. Based on the results, the following conclusions can be drawn:

- At low W/C, the adsorption behavior of PCE follows a Langmuir-type isotherm.
- The respective contributions of colloidal, viscous, and inertial forces to the macroscopic viscosity of the pastes can be well captured by $\tau_0/\dot{\gamma}$, η_{res}, and $k\dot{\gamma}$, respectively.
- In a highly concentrated system, both yield stress and residual viscosity display the same scaling laws with the separation distance as that in the pastes with higher W/C.
- The role as well as the action mechanism of PCE are not affected by the water-to-cement mass ratio. All the consensuses drawn from previous studies can be extended to highly concentrated cementitious materials.
- The selected PCE samples display a similar adsorption behavior and deflocculating action due to the slight difference in the molecular structure. Further studies are needed to thoroughly understand the influence of polymer structure.

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Conflict of Interest

The authors state that there is no conflict of interest.

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