

Study on the rheological properties of Portland cement pastes with polycarboxylate superplasticizers

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Abstract The coupling effects of temperature and time on the fluidity of fresh cement mixtures were investigated. Mini-cone tests on cement mortars and rheological tests on cement pastes under different temperatures (0 to 60 °C) were conducted to characterize the development of the fluidity of fresh cement mixtures over time. In addition, total organic carbon tests were performed to quantify the adsorption amount of superplasticizers on the cement surface. The amount of free water in cement pastes was determined via centrifugation. Isothermal calorimetry was employed to characterize the hydration kinetics of cement under different temperatures. Results show that the spread diameter of mortars decreases in a roughly linear fashion over elapsed time. Higher temperature facilitates a sharper decrease in fluidity with time, although the initial fluidity of fresh mortars is not significantly affected by temperature. Higher temperature results in a greater amount of adsorbed polycarboxylate ester/ether on the cement surface and a lower amount of free water in fresh cement pastes, which is believed to result from the higher hydration rate of cement. The evolution of rheological properties over time can be attributed to the development of hydration degree. Relative hydration degree is introduced to indicate the development of rheological properties with time. Two models to describe the evolution of yield stress and plastic viscosity for fresh cement pastes were developed.

Keywords Cement paste · Rheology · Yield stress · Plastic viscosity · Hydration degree

Introduction

Modern concrete has undergone significant changes (Brouwers and Radix 2005; Chong and Francois 1996; Sari et al. 1999) in various aspects, including formulation, rheological properties, mixing and casting technologies, mechanical properties, etc. A wide range of mineral admixtures such as fly ash, slag, and other industrial wastes called supplementary cementitious materials (SCMs) are currently being blended into cement. A large number of chemical admixtures have become necessary concrete components to meet increasing performance requirements including high strength, high durability, and good workability. One of the key components of modern concrete is the superplasticizer, which gives the concrete excellent workability even at a very low water-to-binder (W/B) ratio. Moreover, the superplasticizer makes concrete, including self-consolidating concretes and pumping concretes, practically feasible even at high pumping distances for skyscraper construction, long transportation time, etc.

Fluidity and fluidity retention over a certain period of time are two of the most important elements of concrete workability (Zhao et al. 2006). Apart from the formulation of the concrete mixture including W/B ratio and binder-to-aggregate ratio, the fluidity of concrete is primarily determined by the rheological properties of the cement paste phase, which are affected by factors such as grinding history during cement manufacturing, particle shape and particle size distribution of the cement mixture, the use of SCMs and superplasticizers, mixing conditions, etc. (Ferraris et al. 2001; Rubio-Hernández et al. 2013; Sheinn

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et al. 2002). After mixing, the rheological properties of cement paste develop over time because of cement hydration, which results in the consumption of the free water, restructuring of the microstructure, etc. Cement hydration and interactions between cement particles and superplasticizers are key factors to be considered in the fluidity retention of a concrete mixture.

The use of superplasticizers substantially changes the rheological behaviors of cement-based materials through the disassembly of flocculated cement particles via electrostatic and/or steric repulsion, which are induced by the adsorbed superplasticizer molecules. The adsorption of superplasticizers onto cement particles improves the rheological properties of cement paste and at the same time often visibly affects the cement hydration process, mostly by retarding cement hydration (Heikal et al. 2005; Jolicoeur and Simard 1998; Kreppelt et al. 2002).

Several researchers have worked on the rheological properties of cement-based materials. Struble and Sun (1995) proposed a quantitative relationship between viscosity and concentration of Portland cement pastes by using the Krieger–Dougherty equation. Murata (1984) investigated methods characterizing rheological behaviors of fresh mortar and concrete, including the use of a double-cylinder rotation viscometer, slump test, and inclined pipe flow test. Flatt and Bowen (2006) deduced a Yodel model for concentrated particle suspensions, which could accurately predict the dependence of yield stress on the volume fraction of solids. Pioneering work on the rheological properties of cement pastes that are prepared with superplasticizers was conducted by Golaszewki and Szwabowski (2003), who found that polycarboxylate ester/ether (PCE)-type superplasticizers were more effective than sodium naphthalene sulfonate formaldehyde superplasticizers.

Higher temperature usually accelerates cement hydration and setting. In practice, it is often seen that the fluidity and fluidity retention of concrete mixture are dropping at elevated temperatures. Petit et al. (2005, 2006, 2007, 2009, 2010) and Nehdi and Martini (2009) conducted a large number of studies on the effect of temperature on the rheological properties of mortars that were prepared with various superplasticizers. It was found that yield stress as well as plastic viscosity of micromortars developed with elapsed time after cement–water contact in an efficient linear manner while an exponential growth of these rheological parameters is seen in self-consolidating concrete (Petit et al. 2007). General equations were proposed to predict the variation of yield stress and plastic viscosity with time by using the initial values on mortars. It has been reported that higher temperature results in faster growth of yield stress and plastic viscosity over elapsed time, whereas temperature seems not to affect the rheological parameters of mortars or

concrete at zero time point (Nehdi and Martini 2009; Petit et al. 2007). The introduction of normalized time (Petit et al. 2005, 2006, 2007, 2009, 2010), which is defined as the elapsed time after cement–water contact divided by the time corresponding to the end of the dormant period of cement hydration, enabled direct comparisons of the variations of yield stress and plastic viscosity of cement mortars that were prepared at various temperatures. It was shown that yield stress and plastic viscosity linearly varied with the normalized time, independent of temperature in micromortars (Petit et al. 2007).

As described above, the rheological properties of mortar and concrete continuously develop over time, which majorly originates from the continuous cement hydration after contact of cement with water. Changes in the composition and in the microstructure of the cement mixtures lead to the changes in rheological properties. Temperature only affects the kinetics of cement hydration (Petit et al. 2007). Therefore, the hydration degree should be considered as the fundamental factor that determines the variations in rheological parameters over time. However, the relationship between the variations in rheological parameters over time and cement hydration degree remains unclear.

Considerable effort has been made to establish correlations of the rheology of concrete with the rheology of mortar or with the rheology of cement paste (Hammer and Wallevik 2005; Rubio-Hernández et al. 2013; Sheinn et al. 2002). The rheology of cement paste, a highly concentrated suspension, is primarily governed by the colloidal force between cement particles, whereas the rheology of concrete is dominated by more complex processes like friction between the aggregates and the packing structure of the aggregates, in which the size, shape, and volume fraction of the aggregates are involved. The correlation between rheological behaviors of the concrete and the cement paste is poor (Hammer and Wallevik 2005; Rubio-Hernández et al. 2013), while the rheological properties of concrete could be somehow predicted by the use of the so-called concrete equivalent mortar (Rubio-Hernández et al. 2013; Schwartzentruber and Catherine 2000).

The goal of this paper is to understand the scientific mechanism of the time evolution of the rheological parameters of fresh cement mixtures. In the first part of the paper, we show the testing result of the fluidity of micromortars developing over time under varied temperatures. As the temperature in real construction environments varies from 0 to 40 °C, the fact that the rheological properties of cement paste develop with temperature was given special emphasis in this study. Fluidity of mortars was tested over varied elapsed time up to 120 min under controlled temperatures ranging from 0 to 60 °C. Since the time evolution of rheological properties is basically a result of cement

hydration, it should be relevant to focus on the rheology of cement paste because the aggregates in mortar or concrete could be assumed as inert materials suspended in the paste matrix (Sheinn et al. 2002). In order to construct the correlation between the variation of rheological parameters over time and the cement hydration, cement paste, as the matrix of mortar, is then focused. Given that PCEs continue to be the most widely used superplasticizers, all mortars and cement pastes investigated in this paper were prepared with PCEs. Adsorption of PCE on cement surface was measured by total organic compound (TOC) test. Free water amount in cement paste was obtained by centrifugation separation. Calorimetry was employed to measure the cement hydration degree with increasing hydration time, especially before cement setting. Yield stress and plastic viscosity were measured on cement pastes by using a Brookfield rheometer. Finally, temperature and time were integrated into relative hydration degree as a significant factor to describe the relationship between the evolution of rheological properties of cement pastes and the environmental factors such as temperature and elapsed time.

Experiments

Materials and mixture proportioning

Ordinary Portland cement classified by P.O.42.5 and compliant with the Chinese National Standard GB8076–1997 was used to prepare the cement pastes and mortars. The chemical and mineral compositions of the cement are presented in Table 1. ISO 679 sand was used as fine aggregates to prepare cement mortars for fluidity tests. Self-synthesized PCE superplasticizer was employed (Kong et al. 2009), which has a solid content of 40 %. Figure 1 presents the chemical structure of the synthesized PCE.

The water-to-cement mass ratio in all cement pastes and mortars was fixed at 0.35. Moreover, 0.2 % of PCE superplasticizer by weight of cement was added into the cement pastes or mortars. Cement mortars with a fixed sand-to-cement ratio of 1.33 were prepared for fluidity tests. All other tests were conducted based on cement pastes. Table 2 presents the mixing proportions of the mortars and the cement pastes for all tests.

Test methods

In this paper, mini-cone tests on the cement mortars and measurements of yield stress and plastic viscosity on cement pastes were conducted to characterize the rheological behavior of fresh cement mixtures. The amount of adsorbed PCE on cement was measured by using TOC measurements. The amount of free water in the fresh cement pastes was approximately quantified via centrifugation. Isothermal calorimetry was employed to reveal the hydration kinetics of cement. To determine the effects of temperature on the rheological properties of cement mixtures, all preceding measurements were performed at selected temperatures ranging from 0 to 60 °C.

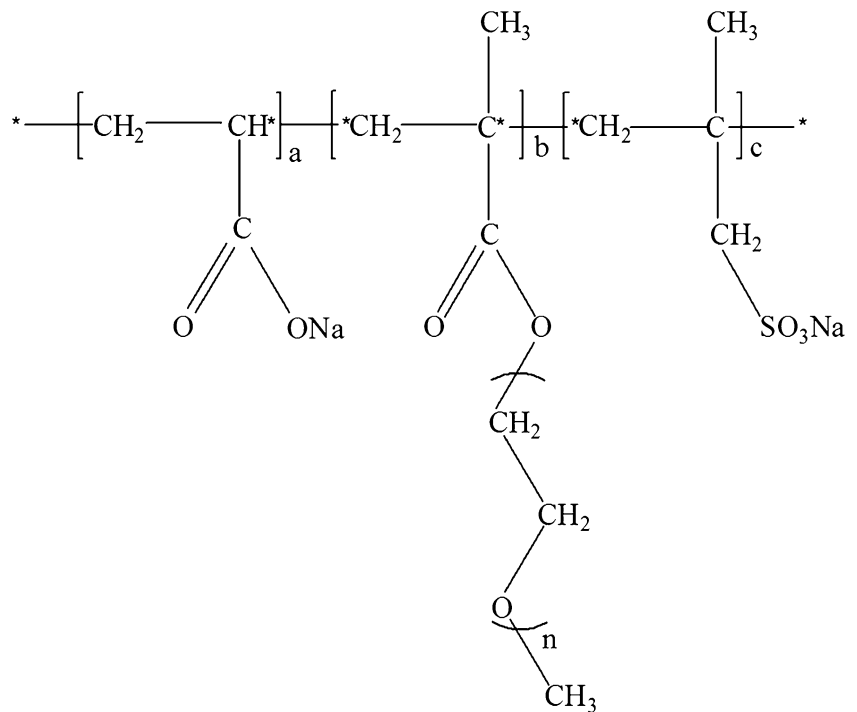
Mini-cone tests

The mini-cone tests were conducted according to the Chinese National Standard GB/T 2419-2005 (Standardization Administration of China and Chinese National Committee of the ISO and IEC 2005) to evaluate the fluidity of fresh mortars. To maintain the targeted temperature of the fresh mortars, all raw materials, the mixing bowl, and the rotor of the mixer were pre-stored at the targeted temperatures before mixing. The mixing procedure is as follows: water and PCE superplasticizer were firstly added into the mixer. Blended cement and sand was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10-s interval, mixing was resumed for another 2 min at 125 rpm. The whole mixing process took about 5 min in total. To avoid water evaporation, the mixing bowl is covered with a wet cloth immediately after the mixing of the fresh mortars and is then stored at constant environmental temperatures equal to the targeted test temperatures for 0, 25, 55, and 115 min. At a predetermined interval, a portion of the fresh mortar was extracted and then remixed at a speed of 125 rpm for 30 s to ensure homogeneity. After that, the fluidity of the fresh mortar was measured by mini-cone test which was represented by the spread flow. A cone with an upper diameter of 36 mm, lower diameter of 60 mm, and height of 60 mm was used in the test. The spread diameter was recorded as the average of two perpendicularly crossing diameters. Thus, counting from the time point of water-cement contact, each mortar was actually tested at 5, 30, 60, and 120 min after the contact of cement with water. The fluidity tested at 5 min was defined as the initial fluidity.

Table 1 Chemical composition and mineral composition of the Portland cement (in weight percent)

Chemical composition								Mineral composition			
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	f-CaO	C ₃ S	C ₂ S	C ₄ AF	C ₃ A
22.84	4.28	2.86	66.43	1.8	0.48	0.67	1.03	58.44	21.41	8.71	6.49

Fig. 1 Schematic drawing of the chemical structure of the synthesized PCE superplasticizer ($a/b = 2$, n denotes the number of ethylene oxide units in side chain, $n = 45$)



Adsorption amount of PCE on cement particles

The dispersing function of PCE in cement pastes is facilitated by the adsorption of PCE on the surface of cement particles. The adsorption amount of PCE on cement particles was measured by using a TOC Analyzer (Shimadzu, TOC-VCPH, Japan). Cement pastes were prepared following the same procedure as the preparation of the cement mortar in the mini-cone tests. The freshly mixed cement pastes were centrifuged at 4,000 rpm for 5 min, and the clear supernatant solutions were collected through a membrane filter with a pore diameter of $0.45 \mu\text{m}$. TOC tests were conducted to determine the concentration of PCE in the aqueous solution. Thus, the adsorbed amount of PCE on cement particles was then calculated by deducting the amount of PCE that remained in the aqueous phase from the initially added PCE amount in the cement pastes.

Free water content

During cement hydration, the mixing water in cement pastes can be sorted as follows: chemically bonded water in the form of hydrates and hydroxides in hydration products;

adsorbed water, i.e., the physically bonded water on the cement surface; the entrapped water in the flocculated cement structure; and the free water, which contributes to the fluidity of cement pastes. Changes in free water content were monitored for fresh cement paste at four different temperatures (0, 20, 40, and 60°C). After mixing, a certain amount of fresh cement paste m_1 was centrifuged at 4,000 rpm for 15 min. The supernatant liquid m_2 was then collected. Thus, the free water fraction (FW%) can be calculated by using the equation below:

$$\text{FW}\% = \frac{m_2}{\left(m_1 \times \frac{m_w}{m_w + m_c}\right)} \quad (1)$$

where m_w corresponds to the mass of the total water added to the cement paste and m_c is the mass of the cement in the cement paste.

Isothermal calorimetry tests

Isothermal calorimetry tests were conducted on the cement pastes at 20, 40, and 60°C by using a TAM Air calorimeter (Thermometric AB, Sweden). Prior to the calorimetry tests, the calorimeter was regulated at selected temperatures and then equilibrated for 24 h. Thereafter, 6 g cement was placed in a 20-mL ampoule bottle and then introduced into the channel of the microcalorimeter. After the channel was sealed and the baseline reached the equilibrium, 2.13 g PCE aqueous solution with a mass concentration of 1.4 wt% was

Table 2 Mix proportions of mortars and cement pastes

Sample	Water/cement	Sand/cement	PCE/cement
Mortars	0.35	1.33	0.2 %
Cement pastes	0.35	–	0.2 %

injected into the ampoule bottle and then stirred for 10 min. The heat evolution was evaluated for 3 days.

Rheological tests

Yield stress and plastic viscosity of the prepared fresh cement pastes were tested by using a rheometer (Brookfield RV-III, USA). Four-bladed vane spindle V-72 (diameter = 21.7 mm, length = 43.3 mm) was applied for the measurement of yield stress, which effectively eliminates slippage phenomenon, because yield stress is measured along a cylindrical surface defined by the outer tips of the vane blades. Before testing, the fresh paste was well mixed with a rotator mixer at a rotation speed of 125 rpm for 30 s to break the particle agglomerates in the suspension. After a pause of 10 s, stress–strain curve of the fresh cement paste under shear stress was recorded at a rotation speed of 2 rpm by the rheometer. Yield stress was finally obtained when the fresh paste started to yield. Regarding the measurement of plastic viscosity, a standard disc spindle RV3 (diameter = 34.5 mm, thickness = 1.5 mm) was applied for the fresh cement pastes at 0, 20, and 40 °C while RV4 (diameter = 27.2 mm, thickness = 1.5 mm) was used for the measurements at 60 °C because the viscosity of fresh cement paste was significantly increased at elevated temperature. The same procedure of pre-shearing was carried out in the fresh cement paste before tests. Plastic viscosity of the fresh cement paste was measured at different rotation speeds, which ramped up stepwise from 5 to 150 rpm (5, 10, 15, 20, 40, 60, . . . , 150 rpm). At each rotation speed, viscosity was recorded after the equilibrium was reached. An example of torque–rotation speed curve is given in Fig. 2. It is seen that the

cement paste fairly behaves like a Bingham fluid, whose viscosity keeps almost constant after yield with change of shear rate. Therefore, in this paper, we choose the viscosity at a rotation speed of 60 rpm as the representative plastic viscosity. The temperature of the cement pastes was kept constant during rheological tests by using a water bath that is regulated at targeted temperatures. Similarly, the values of yield stress and plastic viscosity at 5 min after the contact of cement with water were defined as the initial values.

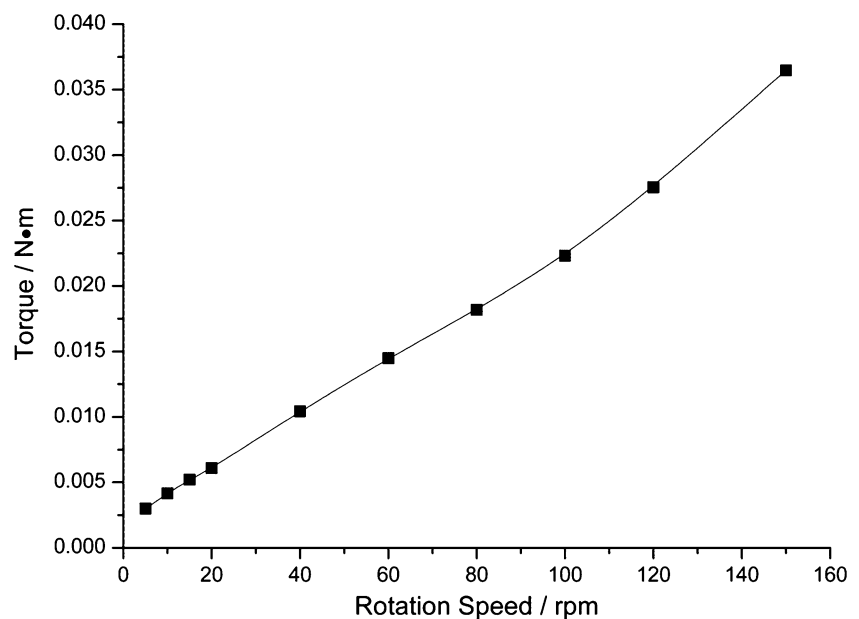
Results and discussion

Effects of temperature and time on fluidity of fresh mortar

Fluidity of mortars

Figure 3 shows the spread diameters of the cement mortars with the same mixture proportion at four different temperatures of 0, 20, 40, and 60 °C. The spread diameters of all tested mortars at various temperatures decreased roughly in a linear fashion over time. Higher temperature tends to slightly depress the initial fluidity, but results in a sharper fluidity drop with time. The mini-cone test results correlate in certain cases with the yield stress measurement (Kada-Benameur et al. 2000). Similar results were found by Petit et al. (2007). By fitting the measured result, Petit et al. reported that yield stress as well as plastic viscosity of micromortars developed with elapsed time after cement–water contact in an efficient linear manner. They also showed that higher temperature results in faster growth of

Fig. 2 Plot of torque versus rotation speed for the cement paste at 20 °C (30 min)



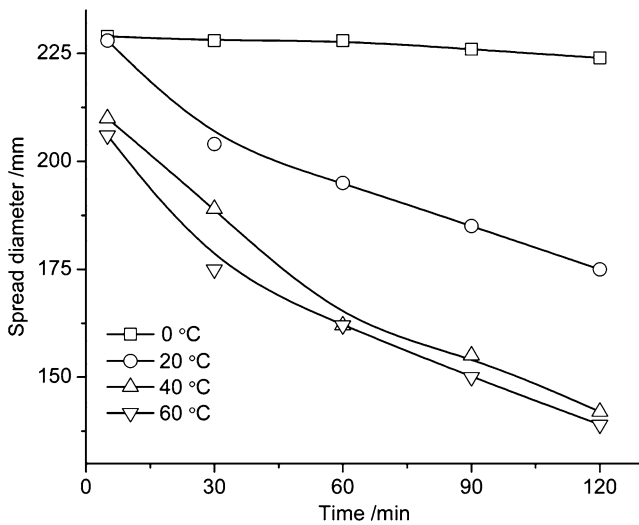


Fig. 3 Spread diameters of mortars at different temperatures

yield stress and plastic viscosity over elapsed time, whereas the temperature does not affect the rheological parameters of mortars or concrete at zero time point (Petit et al. 2007), which is fully in agreement with what is found in Fig. 3. By introduction of the so-called normalized time, they found that temperature only changes the hydration kinetics and thus the dormant period. Therefore, the sharper change in the fluidity over elapsed time is believed to be related to the accelerated hydration of cement and larger consumption of mixing water at elevated temperatures.

In the fluidity measurement of cement pastes, the microstructure of cement pastes and the adsorption behavior of superplasticizers on the cement surface must be considered. When cement comes into contact with water, the fast dissolution and early hydration of cement build surface charges on cement particles. Silicate phases were found to possess a negatively charged surface, whereas aluminate hydrates possess a positively charged surface. The heterogeneous charge distribution leads to the formation of flocculated cement particles that entrap large quantities of mixing water as illustrated in Fig. 4a. Therefore, the microstructure is a decisive factor for the initial rheological behavior of cement pastes. As temperature increases, more flocculated structures are formed because of faster dissolution and early hydration and more free water is consumed due to the entrapment of water by the flocculates. Consequently, higher temperature leads to a decrease in the initial fluidity of mortar.

The function of superplasticizers in improving the initial fluidity of cement pastes is achieved through adsorption on the cement surface (as seen in Fig. 4b). The adsorbed superplasticizer molecules on a hydrating cement surface neutralize the heterogeneous charge distribution and provide electrostatic/steric repulsion among cement particles.

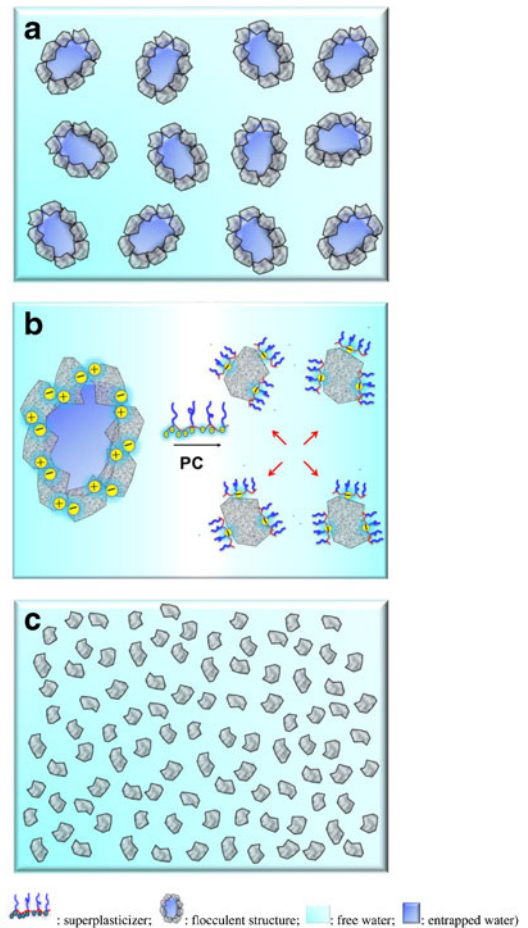


Fig. 4 Schematic illustration of the effects of superplasticizer on the fluidity of fresh cement paste: **a** flocculated cement particles in the cement paste without superplasticizer, **b** disassembly of the flocculates by adsorption of superplasticizers on cement particles, and **c** well-dispersed cement particles in cement paste with superplasticizer

The deflocculation allows better dispersion of cement particles and releases the entrapped water to turn into free water (Fig. 4c). As a result, the fluidity of cement mixtures is extremely enlarged. This way, the changes in the initial fluidity of cement mixtures under different temperatures may also result from the changes in the adsorption behavior of superplasticizers on the cement surface.

Adsorption amount of PCE on cement surface at different temperatures

The adsorption amount of PCE on cement surface (0.2 % PCE dosage relative to cement mass) at different temperatures was measured via TOC, as shown in Fig. 5. Higher temperature results in a higher initial adsorption amount of PCE on cement particles, which is considered to be attributed to the faster dissolution and early hydration of cement. Generally speaking, more adsorption amount of

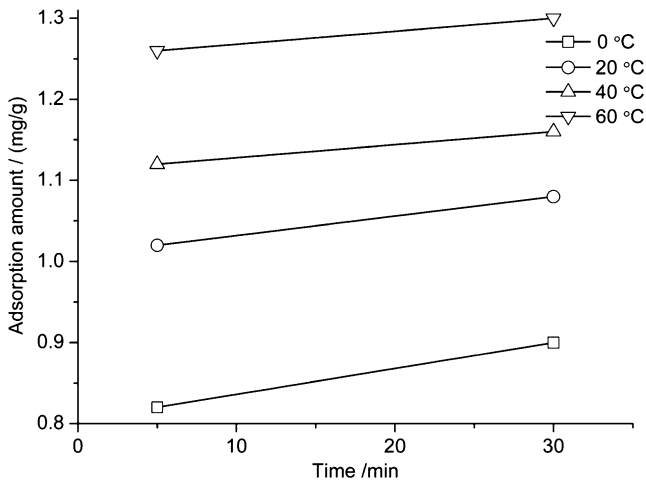


Fig. 5 Adsorption amount of PCE on cement particles

PCE should result in higher fluidity of cement mixtures. However, cement mortars subjected to an increase in temperature do not achieve higher fluidity, as seen in Fig. 3. This implies that the effect of temperature on cement hydration must be the decisive factor in the initial fluidity of cement pastes.

It has been often reported that, when PCE is added into cement mixtures, the C_3A phase in clinker and the ettringite phase in hydration products are the two phases that have the most capability to adsorb PCE due to their positive charge, while C_3S and $C-S-H$ are reported to be negatively charged (Plank and Hirsch 2007). Thus, the higher adsorption of PCE at higher temperature suggests faster formation of ettringite during early hydration. The more ettringite formed in the cement mixtures leads to lower fluidity.

Free water content of cement paste

As seen from Fig. 4, among the four types of water existing in hydrating cement pastes (chemically bonded water, adsorbed water, entrapped water by the flocculates, and the free water), only the free water contributes to the fluidity of fresh cement pastes. As shown in Fig. 6, the free water content of cement pastes is measured via centrifugation. When the free water amounts at different temperatures are compared, the amount of free water is found to decrease with increasing ambient temperature at the same hydration time. This observation verifies that higher temperature accelerates the consumption of free water because of accelerated hydration. The initial free water content of cement paste prepared at 60 °C is very low, which must result from the fact that high temperature facilitates the formation of more flocculated cement particles and more mixing water is entrapped.

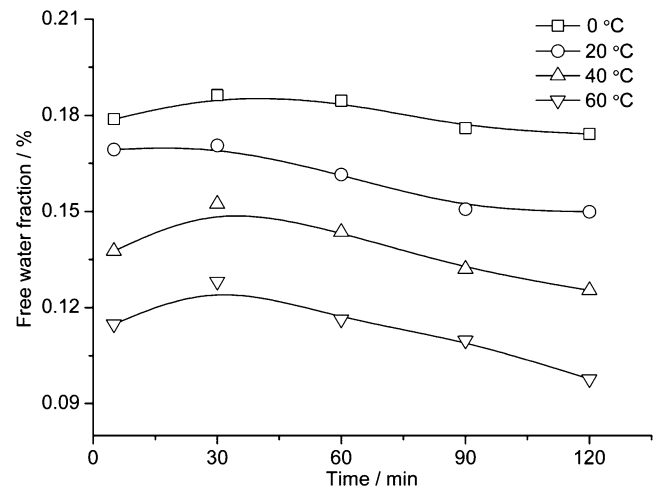


Fig. 6 Free water content of cement pastes at various temperatures

As a result, temperature and time primarily affect the fluidity of cement pastes in two aspects: higher temperature accelerates the microscopic structure development of cement paste and higher temperature and longer hydrating time increase the consumption of free water. Both aspects are determined by the hydration degree of cement. That is to say, the changes in the rheological behavior of cement pastes with temperature and time must be closely related to the hydration degree of cement.

Cement hydration

Calorimetry has been one of the mature methods used to investigate the kinetics of cement hydration. Figure 7 shows the heat flow curves and accumulative heat generation curves of cement pastes that were prepared with and without PCE at different temperatures. The characteristic parameters are listed in Table 3. Figure 7 and Table 3 show that elevated temperature shortens the dormant period and increases the hydration rate during the acceleration period, which implies accelerated hydration. During the dormant period, cement hydration is slow and often remains at a relatively constant rate. Previous studies proved that the end of the dormant period in the heat flow curve corresponds to the initial setting of cement pastes (Petit et al. 2006, 2009). As shown in Fig. 7 and Table 3, higher temperature evidently increases hydration rate during the dormant period, as well as the hydration degree at the time point of initial setting. This is in accordance with the higher adsorption of PCE at higher temperature (Fig. 5). That is to say, at higher temperature, the lower fluidity and the higher adsorption of PCE must be related to the higher hydration rate during the dormant period and the formation of more ettringite. At a certain temperature, the addition of PCE in cement pastes prolongs the dormant period because of the so-called

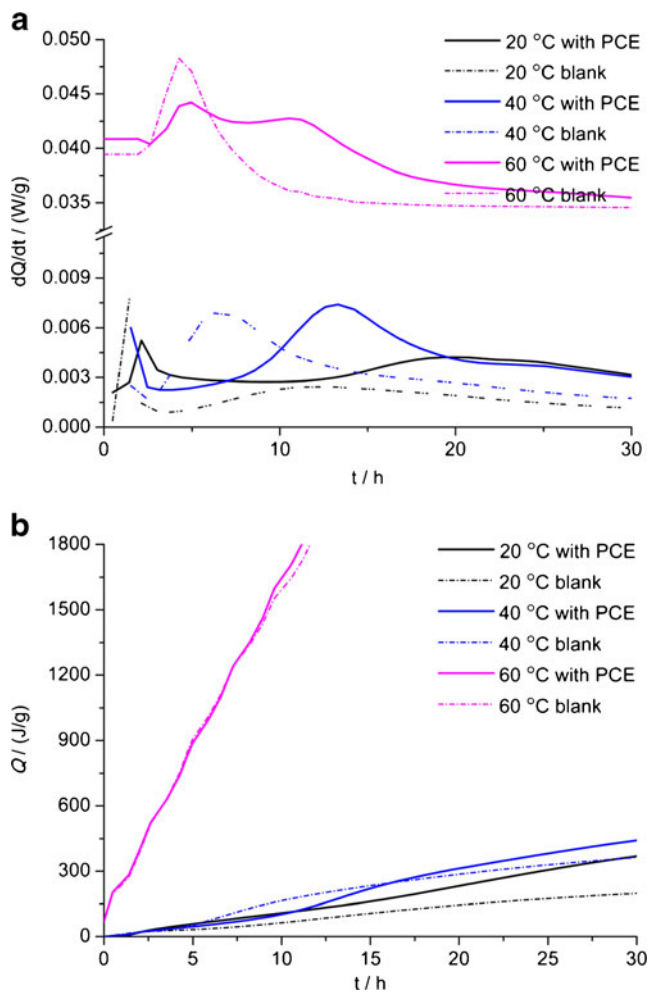


Fig. 7 Isothermal calorimetry curves of cement pastes with and without superplasticizer at varied temperatures: **a** differential curves and **b** integral curves

retardation effect. However, it is interesting to note that during the dormant period, the cement pastes with PCE maintain a higher hydration rate than the cement pastes without PCE at the same temperature, which is believed to result from the fact that the better dispersion of cement particles in the aqueous phase provide a larger contact surface

area of cement particles with water when PCE is added in cement pastes.

As a solid–liquid dispersion system, the rheological behavior of a fresh cementitious mixture is mainly dependent on the volume fraction of the solid phase as well as on the microstructure of the dispersion system. During cement hydration, the volumes of the solid phases in fresh cement pastes keep continuously increasing, whereas the volume of the aqueous phase changes in an opposite manner. As a result, the fluidity of fresh cement pastes changes over elapsed time. The effect of temperature on the fluidity over elapsed time can be attributed mainly to the temperature effect on cement hydration. When PCE is added into the cement and water mixtures, it changes the volume fractions of solid and liquid phases because of the dispersing effect. Moreover, PCE alters the hydration kinetics due mainly to the retardation effect. In summary, the effects of time and temperature on the fluidity of fresh cement pastes can be integrated into the effect of cement hydration degree.

Rheological models with influences of temperature and time

Yield stress model

Many models have been developed to describe the rheological behaviors of cement pastes such as Bingham, Herschel–Bulkley, Casso, and Sisko models (Banfill 2006). Among those models, Bingham model is the most commonly used model for rheological investigations on cement paste (Aiad 2003; Axelsson and Gustafson 2006; Banfill 2006; Banfill et al. 2006; Roussel et al. 2005), in which two intrinsic rheological parameters, yield stress τ_0 and plastic viscosity μ , are involved to roughly describe the rheological properties of cement paste in certain cases. In this paper, yield stress and plastic viscosity are employed to characterize the rheological behaviors of cement paste.

As shown in Fig. 8 the τ_0 values of the cement pastes that were prepared with PCE at certain temperatures rise in a relatively linear fashion over time which is in good agreement

Table 3 Characteristic parameters of the heat evolution curves of cement pastes

Temperature	t_{is}/h	$(dQ/dt)_{is}/(W/g)$	Q_{is}/J	t_{peak}/h	$(dQ/dt)_{peak}/(W/g)$
20 °C blank	4.089	0.00098	22.533	12.786	0.00147
40 °C blank	2.369	0.00169	17.654	6.569	0.00693
60 °C blank	2.112	0.0392	103.163	4.387	0.0483
20 °C with PCE	11.145	0.00277	123.090	19.369	0.00253
40 °C with PCE	5.083	0.00238	49.643	13.178	0.0074
60 °C with PCE	2.595	0.0402	177.763	4.726	0.0443

t_{is} and t_{peak} refer to the time point of the ending in the dormant period and the hydration rate peaking in the acceleration period, respectively

with the results on cement mortars reported by Petit et al. (2007). The rising slope of yield stress increases with temperature, which could be ascribed to the accelerated cement hydration at elevated temperatures. The variations of yield stress correlate well with the results of the spread diameters shown in Fig. 3.

A general expression for yield stress of solid–liquid dispersion has been developed by Flatt and Bowen (2006, 2007) as follows:

$$\tau_0 = m_1 \frac{\phi(\phi - \phi_0)^2}{\phi_M(\phi_M - \phi)} \tag{2}$$

where τ_0 is the yield stress of the solid–liquid dispersion, ϕ is the volume fraction of the solid phase, ϕ_M denotes the geometrical maximum packing when the solid particles are well dispersed, ϕ_0 represents a percolation threshold, and m_1 is a pre-factor that accounts for interparticle forces, particle size, and particle size distribution. It should be noted that ϕ_M is affected not by particle size but rather by the particle-size distribution. The maximum volume fraction typically falls between 0.6 and 0.7 for mono-sized spherical particles. When $\phi > 0.25$ (Petit et al. 2005), Eq. 2 can be simplified as:

$$\tau_0 \cong m_1 \frac{\phi^3}{\phi_M(\phi_M - \phi)} \tag{3}$$

In a freshly mixed cement paste system, the volumes of the solid phases and of the aqueous phase continuously change over time because of cement hydration. For a fresh cement paste, if we denote the volume fraction of the solid phase at any elapsed time t and ambient temperature T as $\phi(t, T)$, the initial volume fraction of solid phase as $\phi(0, T)$, and the ultimate volume fraction of the solid phase at the 100 %

hydration degree as $\phi(\infty, T)$, then the cement hydration degree at time t , $\alpha(t, T)$, can be defined as:

$$\alpha(t, T) = \frac{\phi(t, T) - \phi(0, T)}{\phi(\infty, T) - \phi(0, T)} \tag{4}$$

At the time point of initial setting of the cement paste, the fresh cement paste totally loses fluidity. Therefore, one can suppose that the maximum solid volume fraction ϕ_M is achieved at the time point of initial setting because of the dense particle packing caused by cement hydration. Namely, $\phi(t_{is}, T) = \phi_M$. Then, the equation below can be derived:

$$\alpha(t_{is}, T) = \frac{\phi(t_{is}, T) - \phi(0, T)}{\phi(\infty, T) - \phi(0, T)} \cong \frac{\phi_M - \phi(0, T)}{\phi(\infty, T) - \phi(0, T)} \tag{5}$$

where $\alpha(t_{is}, T)$ and $\phi(t_{is}, T)$ are the hydration degree and volume fraction of solids at the time point of initial setting t_{is} , respectively. Before initial setting, the hydration degree at time t to the hydration degree at initial setting must be considered as the factor that determines the fluidity development of the fluid cement mixtures.

Correspondingly, at any elapsed time t and ambient temperature T , Eq. 3 could be written as follows:

$$\tau_0(t, T) \cong m_1 \frac{\phi(t, T)^3}{\phi_M[\phi_M - \phi(t, T)]} \tag{6}$$

Based on Eq. 6, at the time point $t = 0$ min, yield stress $\tau_0(t, T)$ can be written as follows:

$$\tau_0(0, T) \cong m_1 \frac{\phi(0, T)^3}{\phi_M[\phi_M - \phi(0, T)]} \tag{7}$$

Combining Eqs. 6 and 7 yields the following expression:

$$\frac{\tau_0(t, T)}{\tau_0(0, T)} = \frac{[1 + \alpha(t, T) \left(\frac{\phi(\infty, T)}{\phi(0, T)} - 1\right)]^3}{1 - \alpha'} \tag{8}$$

where a normalized parameter $\alpha' = \frac{\phi(t, T) - \phi(0, T)}{\phi_M - \phi(0, T)}$, called relative hydration degree, is employed. α' is defined as the hydration degree at any elapsed time after the contact of cement with water divided by the hydration degree corresponding to the initial setting time, which can be written as follows:

$$\alpha' = \frac{\alpha(t, T)}{\alpha(t_{is}, T)} \tag{9}$$

The values of the hydration degree $\alpha(t, T)$ and the relative hydration degree α' can be obtained from the calorimetry results shown in Fig. 7a and can be expressed as:

$$\alpha(t, T) = \frac{Q(t, T)}{Q_{total}} \tag{10}$$

$$\alpha' = \frac{Q(t, T)}{Q(t_{is}, T)} \tag{11}$$

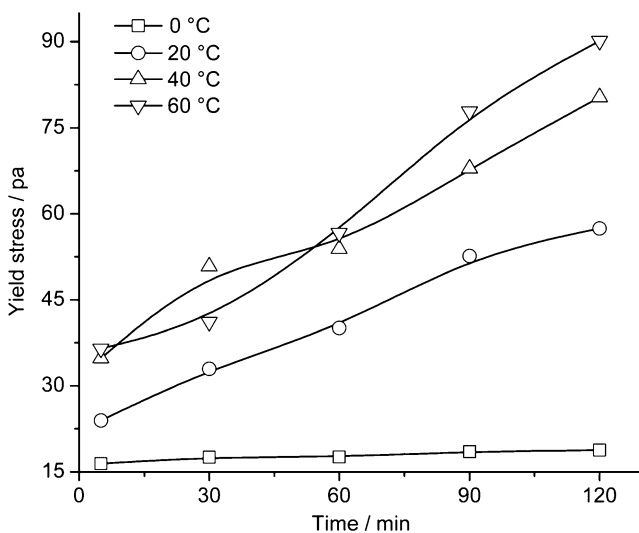


Fig. 8 Development of yield stress of cement pastes at various temperatures

where $Q(t, T)$, $Q(t_{is}, T)$ and Q_{total} represent the hydration heat at time t , t_{is} and at 100 % hydration degree, respectively.

As shown in Fig. 7, the cement hydration degree within the first 2 h is very low, usually less than 5 % (Lin and Meyer 2009). Thus, the numerator in Eq. 8 can be approximately regarded as constant 1, in which the item $\alpha(t, T) \left(\frac{\phi(\infty, T)}{\phi(0, T)} - 1 \right)$ is neglected. Equation 8 can be simplified as Eq. 12, which numerically describes the development of yield stress of fresh cement pastes as a function of the hydration degree before initial setting. The effects of time, temperature, and superplasticizer are integrated by the relative hydration degree:

$$\frac{\tau_0(t, T)}{\tau_0(0, T)} = \frac{\left[1 + \alpha(t, T) \left(\frac{\phi(\infty, T)}{\phi(0, T)} - 1 \right) \right]^3}{1 - \alpha'} \cong \frac{1}{1 - \alpha'} \quad (12)$$

Since it is hardly possible to obtain rheological parameters at zero time, the rheological parameters tested at 5 min are used to approximate the rheological parameters at zero time point. When $\tau_0(t, T)/\tau_0(0, T)$ is plotted in function with $1/(1 - \alpha')$, as presented in Fig. 9, it is seen that yield stress develops in a roughly linear fashion with $1/(1 - \alpha')$ under different temperatures, and the slopes are quite close to 1, which firmly validates Eq. 12. As a conclusion, the effects of time and temperature on the evolution of yield stress of fresh cement pastes can be unified into the relative hydration degree.

Plastic viscosity model

Plastic viscosity μ is another key parameter for the rheological properties of cement and water mixtures (Struble and Sun 1995). Plastic viscosity reflects the properties of mixing, flowing, pouring, pumping, and compacting of fresh concrete. Similar to yield stress τ_0 , plastic viscosity of fresh cement pastes also varies with time and temperature, as shown in Fig. 10. The μ values of fresh cement pastes that were prepared with PCE at different temperatures (0 to 60 °C) vary in a roughly linear fashion with time. The increase of μ with time is enhanced at elevated temperatures because of accelerated cement hydration.

The Krieger–Dougherty equation was proved to be applicable in describing the relationship between the viscosity and the concentration of fresh cement paste, which is expressed in the equation below:

$$\frac{\mu}{\mu_c} = \left(1 - \frac{\phi}{\phi_M} \right)^{-[\mu]\phi_M} \quad (13)$$

Where μ is the viscosity of a suspension, μ_c is the viscosity of the liquid phase, ϕ is the solid volume fraction, $[\mu]$ is the intrinsic viscosity of the suspension, and ϕ_M is the

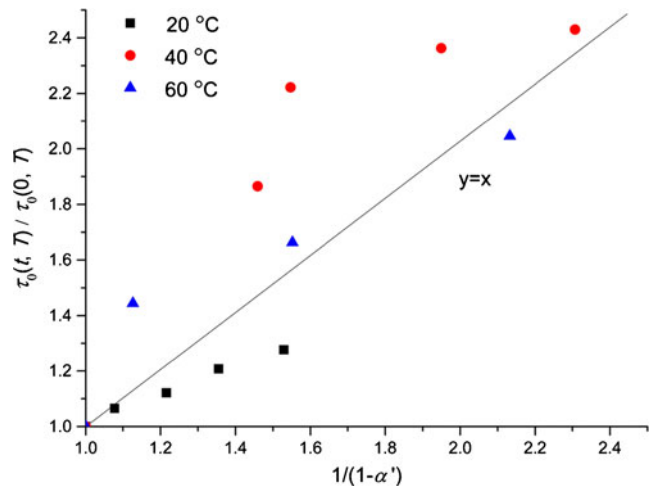


Fig. 9 Variations of yield stress with the relative hydration degree of fresh cement pastes at various temperatures

maximum solid volume fraction. The intrinsic viscosity $[\mu]$ is a measurement of the effect of individual particles on plastic viscosity and is also dependent on particle shape (Zingg et al. 2009). The intrinsic viscosity is expressed as:

$$[\mu] = \lim_{\phi \rightarrow 0} \frac{\frac{\mu}{\mu_c} - 1}{\phi} \quad (14)$$

For a given cement and water mixture, plastic viscosity varies with time because of cement hydration. If we assume that both the initial viscosity $\mu(0, T)$ and the viscosity at time t , $\mu(t, T)$, satisfy Eq. 13, then we have:

$$\frac{\mu(0, T)}{\mu_c(0, T)} = \left(1 - \frac{\phi(0, T)}{\phi_M} \right)^{-[\mu]\phi_M} \quad (15)$$

$$\frac{\mu(t, T)}{\mu_c(t, T)} = \left(1 - \frac{\phi(t, T)}{\phi_M} \right)^{-[\mu]\phi_M} \quad (16)$$

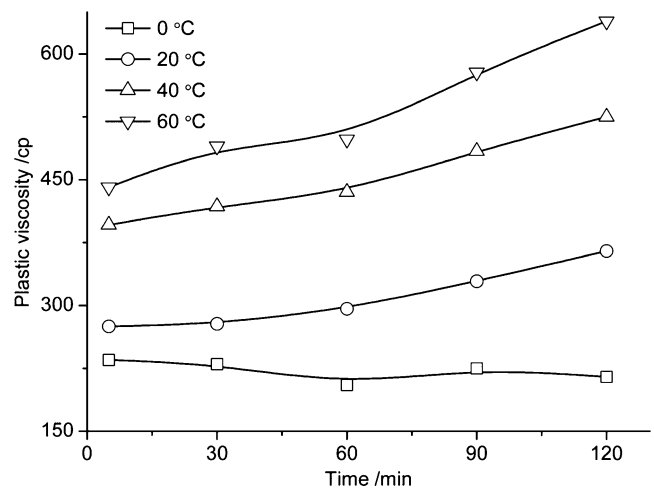


Fig. 10 Development of plastic viscosity of cement pastes at various temperatures

When Eqs. 15 and 16 are combined, assuming that the viscosity of the liquid phase μ_c does not change with time, the following equation can be derived:

$$\ln \frac{\mu(t, T)}{\mu(0, T)} = -[\mu]\phi_M \ln \left(\frac{\phi_M - \phi(t, T)}{\phi_M - \phi(0, T)} \right) \quad (17)$$

Further,

$$\ln \frac{\mu(t, T)}{\mu(0, T)} = -[\mu]\phi_M \ln \left(1 - \frac{\phi(t, T) - \phi(0, T)}{\phi_M - \phi(0, T)} \right) \quad (18)$$

According to the previous definition, $\alpha' = \frac{\phi(t, T) - \phi(0, T)}{\phi_M - \phi(0, T)}$, finally Eq. 19 is obtained:

$$\ln \frac{\mu(t, T)}{\mu(0, T)} = -[\mu]\phi_M \ln (1 - \alpha') \quad (19)$$

Thus, Eq. 19 expresses the link between plastic viscosity and relative hydration degree of fresh cement pastes. Equation 19 should be independent of time and temperature. Thus, when $\ln \frac{\mu(t, T)}{\mu(0, T)}$ versus $\ln (1 - \alpha')$ is plotted as shown in Fig. 11, relatively good linear correlations are found, especially for temperatures of 20 and 60 °C, which validates Eq. 19 to some extent. However, the slopes of the fitted curves at varied temperatures, which should have remained equal as described in Eq. 19, differ. This finding implies that there exist some other factors affecting the evolution of plastic viscosity of fresh cement pastes. It has been known that the interactions between particles in solid-liquid dispersion have more significant effects on plastic viscosity than on yield stress (Struble and Sun 1995). The variation in particle interactions at different temperatures may explain why the slopes of the $\ln \frac{\mu(t, T)}{\mu(0, T)}$ versus $\ln (1 - \alpha')$ curves are not equal for different temperatures. Apart from

the volume fraction of the solid phases, the microstructure of the solid-liquid dispersion, the changes in the shape of cement particles, and the interactions among particles are also essential for rheological behavior. However, Eqs. 12 and 19 do not consider these factors, which may result in deflection when calculating the yield stress and the viscosity of cement water mixtures.

Conclusions and perspectives

The coupled effects of temperature and time on the variations in the rheological properties of cement mixtures made with a PCE superplasticizer were investigated. The goal of this paper is to scientifically disclose the mechanism of the time evolution of rheological behaviors of fresh cement mixtures. Based on the results presented in this paper, the following conclusions can be drawn:

1. Temperature and time affect the fluidity of fresh cement mortars. The spread diameter of mortars at different temperatures (0 to 60 °C) decreases in a roughly linear fashion over time. Higher temperature results in a sharper decrease of the fluidity with time, although the initial fluidity of fresh mortars is not significantly affected by temperature.
2. Higher temperature facilitates greater adsorption of PCE on the cement surface and a lower amount of free water in fresh cement pastes, which is believed to result from the higher hydration rate of cement.
3. The evolution of fluidity over time can be attributed to the development of hydration degree. Relative hydration degree α' is introduced to indicate the development of fluidity over time.
4. A model to describe the evolution of yield stress was developed. The effects of time and temperature on yield stress can be integrated into the relative hydration degree. The relationship between yield stress and relative hydration degree is summarized: $\frac{\tau_0(t, T)}{\tau_0(0, T)} = \frac{1}{1 - \alpha'}$. Experimental results show that yield stress increases in a roughly linear fashion with $1/(1 - \alpha')$ at different temperatures and the slopes are quite close to 1, which validates the model firmly.
5. Similarly, a model to describe the evolution of the viscosity was also deduced by using the relative hydration degree based on the Krieger–Dougherty equation: $\ln \frac{\mu(t, T)}{\mu(0, T)} = -A \ln(1 - \alpha')$, therein $A = [\mu]\phi_M$. Although the fitted curves of viscosity present linear correlation at each temperature, the slopes differ from varied temperatures. It is supposed that the changes in microstructure and the interactions between particles in solid-liquid dispersion may contribute to the deflection of slopes.

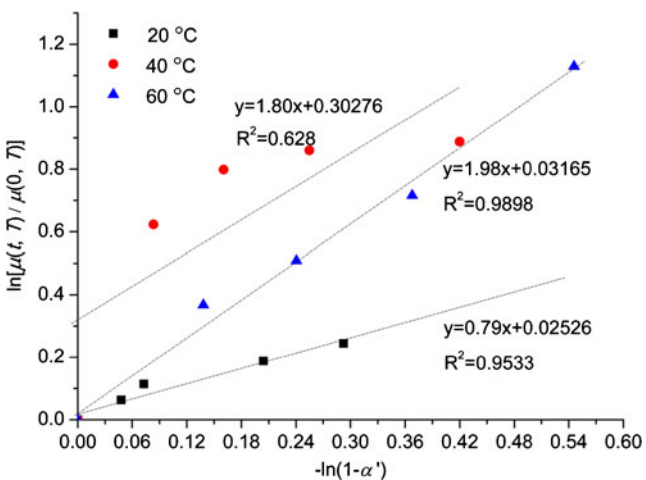


Fig. 11 Variations of plastic viscosity with the relative hydration degree of cement pastes at various temperatures

As discussed before, the correlations between the rheological behaviors of cement paste and the rheological behavior of mortar and concrete are usually poor, because the factors of aggregates including shape, size, volume fraction, and friction of the aggregates play an essential role in the rheology of mortar and concrete. However, when the time evolution of rheological parameters is concerned, we believe that the mechanism proposed in this paper should be relevant to mortar or concrete, although they are deduced from cement paste. This is because the aggregates could be regarded as chemically inert and cement paste, the reactive matrix, should be responsible for the time-dependent behaviors. The experimental validation of the models on mortar and concrete is underway.

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