Cement & Concrete Composites 32 (2010) 43–53

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Effect of temperature on the rheology of flowable mortars

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ARTICLE INFO

Article history:
Received 9 July 2009
Received in revised form 5 October 2009
Accepted 6 October 2009
Available online 13 October 2009

Keywords:
Temperature
Fresh concrete
High-range water reducer
Rheology
Supplementary cementitious materials

ABSTRACT

In addition to the characteristics of mixture constituents and mix design, the rheological behavior of concrete is influenced by material temperature and time after water–cement contact. The study presented herein evaluates the combined influence of time and temperature on the workability of micro mortars. The mixtures were proportioned with polymelamine (PMS), polynaphtalene (PNS), polycarboxylate (PCP) polymer, and made of different supplementary cementitious materials. Seven micro mortars proportioned with various binder compositions and water-to-binder ratio of 0.42 and 0.53 were prepared at 10–33 °C. Test results show that the yield stress and plastic viscosity vary linearly with the coupled effect of time and temperature for mixtures made with PNS or PMS superplasticizers. However, for mixtures made with PCP superplasticizer, both the material temperature and type of supplementary cementitious materials are shown to influence the evolution of rheology with time.

1. Introduction

High-range water-reducing admixtures (HRWRAs), such as polynaphtalene sulfonate (PNS) and polymelamine sulfonate (PMS), are incorporated in cement-based materials to enhance workability. Such water-soluble organic polymers can enhance flowability of cement paste by dispersing the cement particles into the interstitial solution, thus reducing the inter-particle friction among cement grains and decreasing the degree of water entrapment among flocculated particles. New classes of long-chained polymers, such as polycarboxylate polymers (PCPs), have recently been developed to further enhance water reduction and its retention with time using efficient steric dispersing mechanism. PCPs have high cement dispersion properties, especially in mixtures made with low water-to-binder ratios (W/Bs). PCP HRWRAs can exhibit lower water demand, better fluidity retention, and, in some cases, no delay in setting time compared to PNS or PMS HRWRAs [1].

Several parameters affect the efficiency of HRWRAs and their ability to reduce water demand and retain workability. For example, the grinding history of the cement, the mixture composition, batching and mixing procedures can influence the efficiency of PCP HRWRA in improving fluidity of cement-based materials. It has been demonstrated that a relatively high concentration of sulfate-ion in the interstitial solution can lead to some incompatibility between the binder and HRWRA. This can affect the adsorption of PCP onto cement particles, resulting in loss of workability [2–8]. The cement hydration process can reduce the dispersion efficiency of HRWRA due to some intercalation of the HRWRA into the cement hydration products [7–9]. Interaction between cement, viscosity-enhancing agents (VEAs), and HRWRA can also lead to loss in fluidity or delay in set time; this depends on the concentration and type of the admixtures [10–13].

Temperature also affects HRWRA efficiency and incompatibility with the cementitious materials and other admixtures [13–17]. Golaszewki and Szwabowski [14] showed that the rheological properties of mortars made with PNS and PCP HRWRAs are strongly influenced by mixture temperature. An increase in mixture temperature can lead to an increase in yield stress (τ_0) and a decrease in initial plastic viscosity ($\mu\,(t = 0)$). For mortars prepared at 0.40–0.50 W/B and 1–2.25% HRWRA, by mass of binder, the increase in temperature from 10 to 30°C was found to decrease plastic viscosity (μ) and its rate of increase with time; the effect of temperature was shown to depend on the type of binder. Similar results were found on micro mortars prepared with W/B of 0.42–0.53 and either PNS or PMS HRWRA incorporated at 0.28% and 0.8%, respectively, by mass of binder [15]. The increase in mixture temperature from 10 to 30 °C resulted in a linear increase in μ with time and decrease of the initial μ value. The decrease in temperature of the micro mortar resulted a reduction of cement hydration rate and HRWRA adsorption, thus lengthening the duration of the dormant period [15,16].

Changes in rheological properties with time of cement-based materials can also be due to the restructuring of the microstructure,

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doi:10.1016/j.cemconcomp.2009.10.003

cement hydration, variation in free water content with temperature, water evaporation, and interaction between binder and HRWRA. For micro mortars prepared with a W/B of 0.53, μ was reported to increase by 50% over the dormant period, from 0.25 to 0.35 Pa s for mixtures prepared with 0.28% PNS HRWRA and from 0.20 to 0.30 Pa s for mortars made with 0.27% PCP HRWRA [18]. Similar results were found for cement pastes prepared with PNS HRWRA at dosage rates ranging from 0.4% to 1%, by mass of binder, and W/B of 0.35. Fluidity measurements of these mixtures, defined as the inverse of viscosity ($1/\mu$), decreased by 40%–60% within 2 h, depending on the initial HRWRA concentration [19].

The fineness of the binder and mineral additions is another factor influencing the rheology. The addition of fly ash as partial replacement of the cement improves workability [20] and leads to a decrease in HRWRA demand at a given viscosity of cement paste [21]. The workability enhancement is explained by the spherical shape of the fly ash particles which decreases interparticle friction in the powder phase [22]. In addition, the spherical shape also reduces the surface-to-volume ratio of the particles, resulting in a higher packing density and lower water demand for a specific workability [23]. Fluidity is, however, strongly influenced by the average particle size with a optimum value [23]. Ferraris et al. [21] evaluated cement paste prepared at 0.35 W/C and 0.45% HRWRA, by active mass of cement, and reported that the lowest yield stress was achieved for a 12% replacement of cement mass with ultra fine fly ash of 3.1 μm mean particle diameter. This was attributed to increase in packing density enabling the reduction in μ and increases fluidity [21,23].

The addition of silica fume (SF) increases water demand to attain specific workability due to the increase in surface area of the SF. Limited results are available on the effect of SF on cement paste, while contradictory results can be found for concrete [24,25]. Zhang and Han [26] found that both μ and τ_0 decrease in cement paste with W/B of 0.25 when 10% of the cement is substituted by SF compared to OPC paste. Park et al. [27] found on the other hand, that use of SF increases μ and τ_0 steeply in paste with 0.35 W/B. It was shown, on cement paste made with 0.40 W/C and fast hardening CEM I 42.5 R cement, that the influence of SF replacement on flow resistance depended on the HRWRA type [28]. On paste made with 1.32% PNS HRWRA, the flow resistance can increase with increasing SF replacement, while the flow resistance decreases when 0.78% polyacrylate (PA) was used for the HRWRA [28].

It can be concluded from this literature survey that the selection of a couple mineral addition – HRWRA to increase workability of cement based materials, depending on the temperature of the mixture, is not a trivial problem.

As shown above, the rheology of cementitious materials is influenced by the type of HRWRA in use and other factors that have some impact on their efficiency, such as the grinding history of the cement, mixing procedure, temperature and the type of mineral additions used as partial replacement of the cement.

The influence of temperature on hydration kinetics and setting of cement is well documented [4,15,18,19]. However, limited data are available on the combined effect of HRWRA type, temperature, and the type of supplementary cementitious materials (SCM) used as partial replacement of cement on the variation of fluidity of cement-based materials over the dormant period. The study reported herein evaluates the combined effect of temperature, time, mineral addition, and HRWRA type on the initial values of τ_0 and μ and the variations of yield stress and plastic viscosity of micro mortars based on self compacting concrete mixtures (SCC). Such data are necessary to highlight some of the mechanisms affecting workability retention of SCC over transport time, which affect concrete processing.

2. Materials and mixture proportioning

As summarized in Table 1, rheological parameters and heat flux were determined to monitor the variations of yield stress, plastic viscosity, and hydration kinetic during the dormant period of cement hydration. The testing program was carried out on micro mortars made with three types of HRWRA (PNS, PMS, and PCP), five binder compositions, and two W/B of 0.42 and 0.53. The mortars temperatures ranged from 12–33 °C. Table 2 summarizes the mixture proportioning for the tested micro mortars.

The micro mortars are based on SCC mixtures whereby aggregate particles coarser than 315 μm are excluded from the mixture by sieving. The cut-off of sand fraction at 315 μm was chosen to enable the assessment of rheological properties without the risk of blockage or slippage inside the bowl of a co-axial rheometer [29]. The rheometer has a gap between the inner and cylinder of 1.17 mm. A natural siliceous sand of fineness modulus of 2.35 was employed for the mortars.

M1 to M5 mixtures were prepared with the same materials and mixture proportioning, except for the binder type. The M1 mixture was prepared with blended fly ash cement containing Type GU ordinary Portland cement (OPC) complying with Canadian Standards CSA-CAN A5 (similar to ASTM C150 Type I cement) and 22% Class F fly ash substitution, by mass of binder. The M2 mixture was prepared with a binary binder containing 6% silica fume substitution. The M3 mixture was proportioned with a ternary binder containing 6% SF and 22% FA, by mass of binder. A PNS HRWRA was incorporated for the M1 to M3 mixtures. The M4 and M5 mortars were prepared as variants of the M3 mixture. PMS HRWRA was incorporated instead of the PNS HRWRA for the M4 mortar, and PCP HRWRA was used for the M5 mixture.

The M6 and M7 mixtures were prepared with CEM II /B-M (S-L) 32.5 R cement, complying with the European EN 197-1 Standard. This cement contains approximately 73% of clinker, 21% of granulated blast furnace slag and 6% of limestone filler.

The M6 micro mortar was based on a cast-in-place SCC used in Northern France. This non-air entrained SCC was proportioned in compliance with European EN 206-1 Standard, with a relatively high water-to-binder ratio (W/B) of 0.53. The M6 mixture was proportioned using crushed limestone sand with a fineness modulus of 2.60, limestone filler, and PCP-HRWRA incorporated at 0.27%, by mass of cement.

In the case of the M7 mixture, 12.5% of the cement volume, or 50 kg by mass, was replaced by the same volume of Class F fly ash, without altering the W/B, and hence the paste fraction. This choice was made to keep the paste-to-aggregate volume ratio constant, thus enabling comparison between the two mixtures in terms of rheology. Otherwise, the M7 mixture had the same mixture proportioning and materials as that of the M6 micro mortar.

The dosage rates of the HRWRA for M1 and M4 to M6 mixtures were determined using a modified Marsh cone to obtain the same flow time [30]. The targeted flow time through 8 mm opening of a sample of 1200 mL was 78 ± 1 seconds for a flow of 1000 mL. The

Table 1
Summary of experimental program.

Micro mortar	M1	M2	M3	M4	M5	M6	M7
10 or 12 °C	–	–	X	–	X	X	X
14, 15 or 18 °C	X	X	X	X	X	X	X
20 or 23 °C	X	X	X	X	X	X	X
25 or 27 °C	–	–	–	–	–	X	–
30° or 33 °C	X	X	X	X	X	X	X
Calorimetry	X	X	X	X	X	X	X
Rheology with co-axial rheometer	X	X	X	X	X	X	X

X refers to tested combinations.

Table 2
Micro mortar mixture proportioning.

Materials	Micro mortar mixtures						
	M1	M2	M3	M4	M5	M6	M7
Type GU cement, kg/m^3	737	905	705			–	–
CEM II/B-M (S-L) 32.5 R cement, kg/m^3	–	–	–			837	732
Silica fume, kg/m^3	–	57	57			–	–
Fly ash, kg/m^3	215	–	215			–	76
Sieved sand ($\leqslant$315 μm), kg/m^3	686					728	
PCP-HRWRA, % of binder mass	–	–	–	–	0.39	0.27	0.27
PNS-HRWRA, % of binder mass	0.50	0.50	0.50	–	–	–	–
PMS-HRWRA % of binder mass	–	–	–	0.88	–	–	–
W/B	0.42					0.53	

All HRWRA contents are expressed in solid content.

M2 and M3 mortars were prepared with the same PNS HRWRA dosage as that of the M1 mixture. The M6 and M7 mixtures were prepared with the same PCP HRWRA dosage. The HRWRA dosage was adjusted for the micro mortar mixtures to exhibit fixed flow time. The corresponding SCC had approximately the same slump flow of 600–650 mm. Table 2 summarizes mix designs and the chemical composition and physical characteristics of the cements are summarized in Table 3.

3. Test methods

As mortar rheology can be affected by the mixing procedure and equipment, and in order to have comparable results, the same mixer and the same mixing sequence were used for each set of mortars. The SCM were incorporated to the cement prior to mixing. The mortars were prepared in batches of 6 L using a helicoidal mixer rotating at successive speeds ranging between 140 and 285 rpm. The mixing procedure was in compliance with ASTM C 305 [30]. The raw materials were conditioned to secure to the targeted test temperature of the mixed mortars. In order to avoid heat loss or gain during mixing, all apparatuses used for mixing and testing were maintained at the targeted temperature. At the end of mixing, samples were taken to monitor heat generation during the dormant period of cement hydration.

A semi-adiabatic calorimeter was employed to evaluate heat flux for the tested micro mortars [31]. In this method, the sample is introduced into an isolated cell, knowing its heat loss coefficient (α). The increase in temperature of the mixture due to cement hydration is then measured. The heat Q, expressed in Joule per gram of binder (J/g), is obtained by adding the heat produced by the binder. The heat lost is obtained by integrating the lost heat flux with time, knowing the mixture design and thermal capacity of the various materials.

Monitoring of rheological parameters was done during the plastic state and terminated when an increase of heat flux (φ) was obtained from the calorimetric testing. The end of the dormant period was identified from the heat flux (Φ) curve with the t_f parameter, corresponding to the first loss of linearity of the Φ *vs* time chart [15,17,18]. This reflects the beginning of the accelerating period where an evolutive flux due to acceleration of the rate of cement hydration takes place, resulting in an increase of heat flux [31,32].

Rheological measurements were determined at set intervals using a micro mortar remixed at low speed of 140 rpm during 60 s. The mortar was kept in the mixing bowl with proper cover at the targeted temperature. A 350-mL sample was used for the rheological measurement using a coaxial cylinder viscometer. The shear stress (τ) was determined at each shear rate ($\mathring{\gamma}$) after a stabilization period of 20 s at constant shear. In total, five rotation speeds varying between 3 and 300 rpm, corresponding to shear rates of 5.1–510 s^{-1}, were applied. The yield stress (τ_0) and plastic viscosity (μ) were derived from the shear stress-shear rate data assuming a polynomial response (modified Bingham model) [33]. The second order value in this model is very low and was suppressed. Two replicates were made and tested at 15 and 20 °C for each mixture. Repeatability experiments showed little dispersion of the results since the maximal relative deviation was of 6% for the τ_0 and μ parameters. Nevertheless, for each test and given the (τ, $\mathring{\gamma}$) matrix, the data were computed omitting successively data obtained at the highest shear rates to obtain, by linear regression analysis, the maximum and minimum values of τ_0 and μ. Then, for each of these two parameters, a maximum deviation

Table 3
Characteristics of cements.

Chemical composition (Bogue) (%)			Physical characteristics		
	CEM II/B-M (S-L) 32.5 R cement	Type GU cement		CEM II /B-M (S-L) 32.5 R cement	Type GU cement
SiO_2	22.4	20.8	Blaine fineness, m^2/kg: setting time (Vicat), min:	320	340
Al_2O_3	6.2	4.1			
Fe_2O_3	2.7	3.1			
CaO	58.8	63.4	• Initial	180	145
			• Final		
MgO	2.2	2.5			261
NaO_2 Eq	0.73	0.77	Compressive strength, MPa		
Clinker	73	100			
Limestone			2 d	21	22.9
filler	6		7 d	–	30
Blast furnace			28 d	48	35.9
slag	21				

was calculated using Eq.(1), giving an idea on the maximal possible dispersion for each test:

$$\text{Maximum deviation} = \frac{1}{n}\sum_{i=1}^{n}|x_{i,\max} - x_{i,\min}| \qquad (1)$$

After each rheological test, the sample which has been already sheared was discarded to ensure the same shear history between replicate test samples.

4. Results and discussion

4.1. Combined effect of supplementary cementitious materials, temperature, and time on changes in rheological parameters of micro mortar

The non-dimensional normalized time parameter t' enables direct comparisons of the variations of τ_0 and μ with time for mixtures prepared at various temperatures using a common relative time scale. The normalized t' value ($t' = t/t_f$) is defined as the elapsed time after water–cement contact divided by the time corresponding to the end of the dormant period [15,17,18]. The use of the t' parameter can enable the elimination of the effect of temperature on hydration kinetics affecting the duration of the dormant period.

As shown in Figs. 1 and 2, the variations in τ_0 and μ values with time of the M1 micro mortar prepared with PNS HRWRA at 18, 23, and 30 °C show good linear correlation (R^2 greater than 0.90). The results obtained at 18 °C are shown to be lower than those plotted for the M1 mortar tested at 23 °C while the contrary was expected as an increase in temperature results in an increase in HRWRA adsorption, resulting in a decrease in the initial value of τ_0. This may be due to the dispersion of the results and the precision of the measurements (Table 4).

The initial τ_0 and the increase in yield stress over time ($\Delta\tau_0$), which corresponds to the slope of the τ_0 vs. elapsed time linear

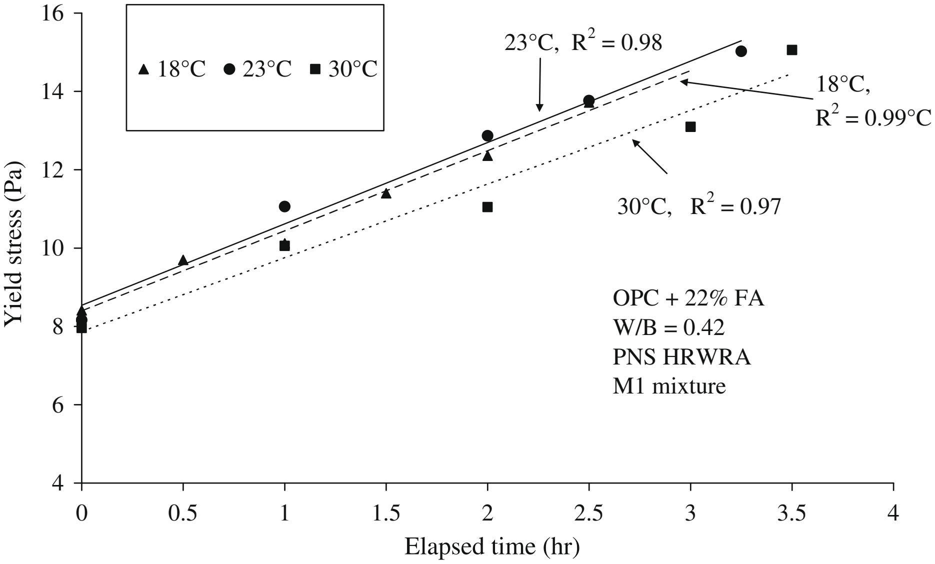

Fig. 1. Variation of yield stress with elapsed time for the M1 mixture tested at 18–30 °C.

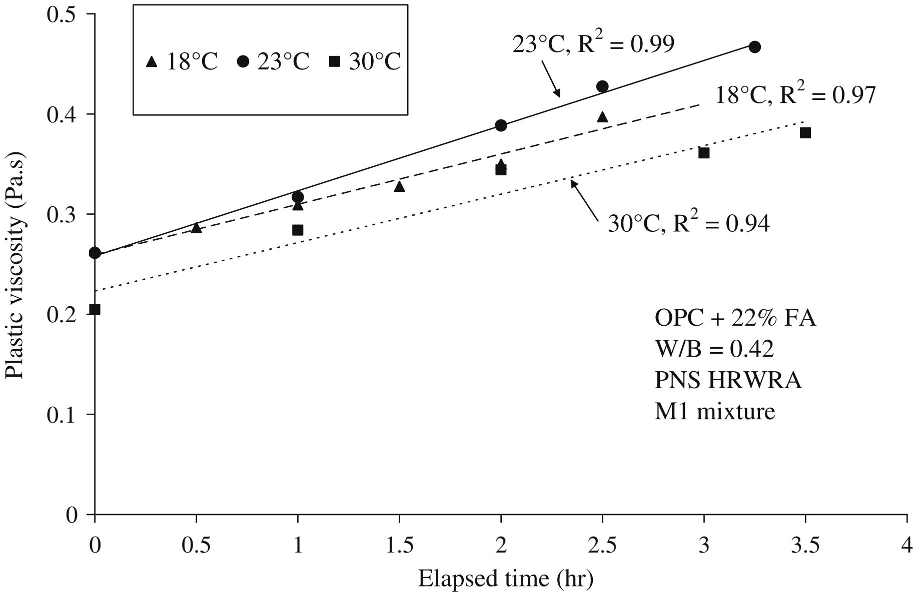

Fig. 2. Variation of plastic viscosity with elapsed time for the M1 mixture tested at 18–30 °C.

Table 4
Maximum deviation for the variation of rheological parameters with time, at various temperatures, for the tested micro mortars.

Mixture	Binder	W/B	HRWRA	10 or 12 °C	15 or 18 °C	20 or 23 °C	27 °C	30 or 33 °C
Maximum deviation for yield stress (Pa)								
M1	OPC + FA	0.42	PNS	–	2.2	2.2	–	–
M2	OPC + SF	0.42	PNS	–	2.2	3.0	–	–
M3	OPC + SF + FA	0.42	PNS	2.3	2.4	2.9	–	2.3
M4	OPC + SF + FA	0.42	PMS	–	1.7	1.7	–	–
M5	OPC + SF + FA	0.42	PCP	1.8	2.3	2.0	–	1.8
M6	CEM II B	0.53	PCP	2.2	1.9	2.9	2.2	2.2
M7	CEM II B + FA	0.53	PCP	1.8	1.9	0.8	–	1.8
Maximum deviation for plastic viscosity (Pa s)								
M1	OPC + FA	0.42	PNS	–	0.06	0.07	–	0.03
M2	OPC + SF	0.42	PNS	–	0.06	0.06	–	0.07
M3	OPC + SF + FA	0.42	PNS	0.05	0.14	0.08	–	0.11
M4	OPC + SF + FA	0.42	PMS	–	0.03	0.03	–	0.04
M5	OPC + SF + FA	0.42	PCP	0.06	0.07	0.08	–	0.07
M6	CEM II B	0.53	PCP	0.02	0.02	0.02	0.04	0.03
M7	CEM II B + FA	0.53	PCP	0.028	0.04	0.02	–	0.02

–: Test not realized.

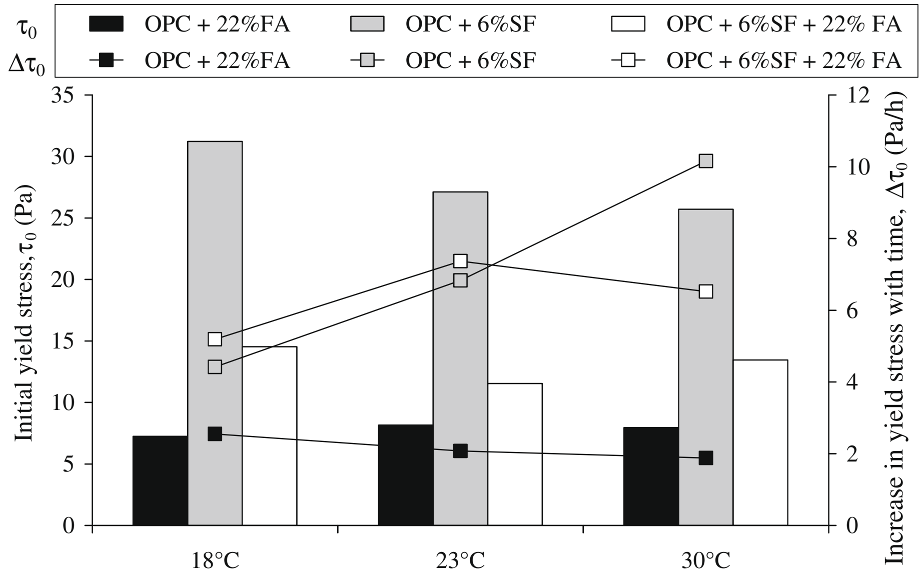

Fig. 3. Variation of initial yield stress (τ_0) and increase in yield stress with elapsed time ($\Delta\tau_0$) for the M1 to M3 mixtures tested at 18–30 °C.

regression, are plotted in Fig. 3 for the M1 to M3 mixtures. On one hand, it is observed that, while the initial τ_0 is quite constant for the micro mortars containing FA, the M2 mixture made with SF show a continuous decrease in τ_0 with the increase in temperature. On the other hand, the $\Delta\tau_0$ value remains constant for the M1 mixture (OPC + FA) and increases for the M2 and M3 mortars containing SF, except for the latter mixture between 23 and 30 °C where a slow decrease of $\Delta\tau_0$ is noted.

As for plastic viscosity and the increase in plastic viscosity with time ($\Delta\mu$), the results presented in Fig. 4 show a decrease in μ and $\Delta\mu$ values, except for μ of the M1 mixture at different temperatures which remains constant.

As shown in Figs. 5 and 6, the variation of τ_0 and μ with the normalized time t' for the M1 to M3 micro mortars prepared with PNS HRWRA at 12–30 °C is independent of temperature. The only effect of temperature is to accelerate or slow down the hydration of cement. Thus, comparing the evolution of rheological parameters using the same scale of relative time shows a unique variation for each mixture composition, independently of material temperature. Regardless of the temperature and initial adsorption of the PNS HRWRA for the M1 to M3 micro mortars, the rate of formation of hydrates, which is related to the slope of the variation of τ_0 and μ with t' ($\Delta\tau_{eq}$ and $\Delta\mu_{eq}$), can be considered to be constant (Figs. 5 and 6) (Table 5). It is to notice that the tested mixtures were designed with a constant 0.50% PNS HRWRA dosage but different binders, with no HRWRA adjustment to temperature. Hence, single $\Delta\tau_{eq}$ and $\Delta\mu_{eq}$ for each mixture, independent of the test temperature, was expected as the variation of rheological parameters is only dependant on the increase of residual PNS in the solution due to the decrease of adsorbed HRWRA with the hydration progress [15–17]. As the use of the normalized time suppress the kinetic effect of temperature, the relative rate of formation of hydrate is only related to the mix design, thus $\Delta\tau_{eq}$ and $\Delta\mu_{eq}$ values are only depending on the mixture composition.

Nevertheless, this rate is greater for the ternary mixtures made with 72% OPC, 6% SF, and 22% FA (M3 mortar) than those with binary binder (M1and M2 mortars) either for the yield stress or for plastic viscosity, as observed on Figs. 5 and 6. It is also noted that this rate is greater for the M2 mortar containing 94% OPC and 6% SF than for M1 mixture made with 78% OPC and 22% FA. The greater $\Delta\tau_{eq}$ and $\Delta\mu_{eq}$ for mixtures made with binders containing SF (M2 and M3) than OPC and FA mixtures (Figs. 5 and 6) may be explained by the increase in water demand to attain specific workability given the higher surface area caused by SF. This

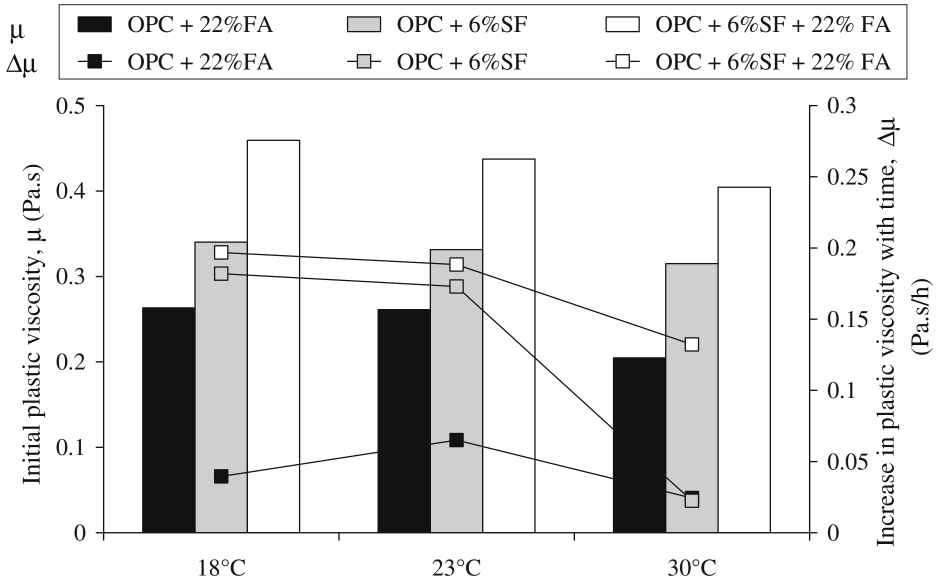

Fig. 4. Variation of plastic viscosity (μ) and increase in plastic viscosity with elapsed time ($\Delta\mu$) for the M1 to M3 mixtures tested at 18–30 °C.

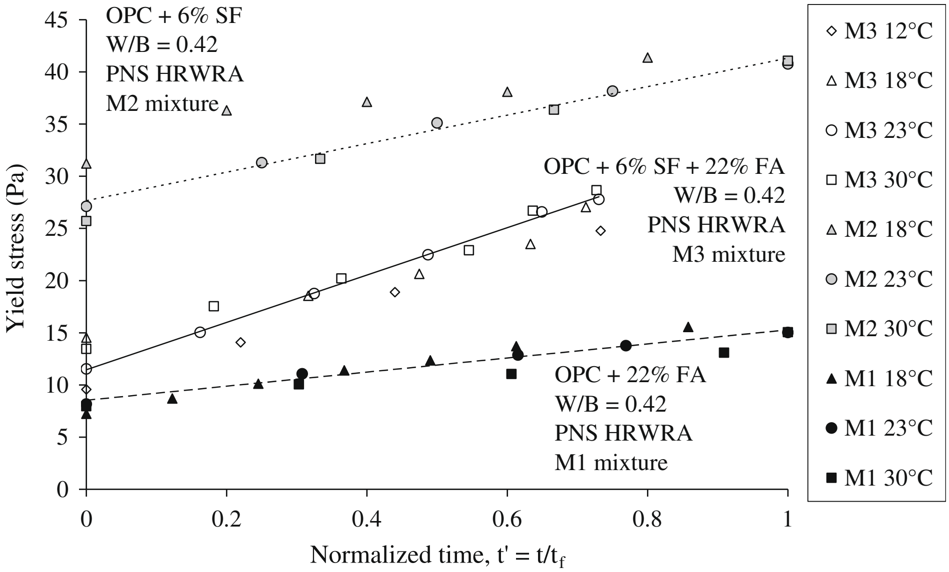

Fig. 5. Variation of yield stress with normalized time for the M1 to M3 mixtures tested at 12–30 °C (linear regressions for 23 °C only are shown).

phenomenon leads to a decrease in free water, resulting in a stiffening of the mixture and, hence, higher $\Delta\tau_{eq}$ and $\Delta\mu_{eq}$ values for SF mixtures compared to M1 mortars.

The initial difference in yield stress and plastic viscosity of mortars tested at 12–33 °C is due to the effect of temperature on the initial adsorption of HRWRA [16]. Table 5 summarizes the experimental data (τ_0, μ, $\Delta\tau_{eq}$, and $\Delta\mu_{eq}$) and Table 6 the correlation coefficients using linear regression on the evolution of τ_0 and μ with time, at various temperatures, obtained in this investigation. R^2 values greater than 0.95, except for M3 mortars tested below 23 °C show that the linear regression was the appropriate choice to describe the variation of τ_0 with time and temperature. As for the variation of μ with time, all R^2 values calculated are above 0.96, fitting with linear model. Table 4 summarizes the maximum deviation for all the tested mixtures.

4.2. Coupled effect of temperature, time and type of HRWRA on changes in rheological parameters of micro mortar made with ternary binder

The evolution of the initial yield stress and $\Delta\tau_{eq}$ as well as plastic viscosity and $\Delta\mu$eq for the M3 and M4 micro mortars time are presented in Figs. 7 and 8, respectively. Lower initial yield stress values is obtained for the M4 mixture than M3 mortars made with PNS HRWRA. Lower $\Delta\tau_{eq}$ value was also noted for the M3 mortar than the M4 mixture (Fig. 7). On the contrary, higher initial plastic viscosity values are obtained for the M4 mixture than for the mortar made with PNS HRWRA (Fig. 8), and a superior rate of variation of μ was observed on M4 mortar compared to the M3 mixture. Differences between the initial plastic viscosity values are larger on M4 mortar made with constant 0.88% PMS HRWRA and tested

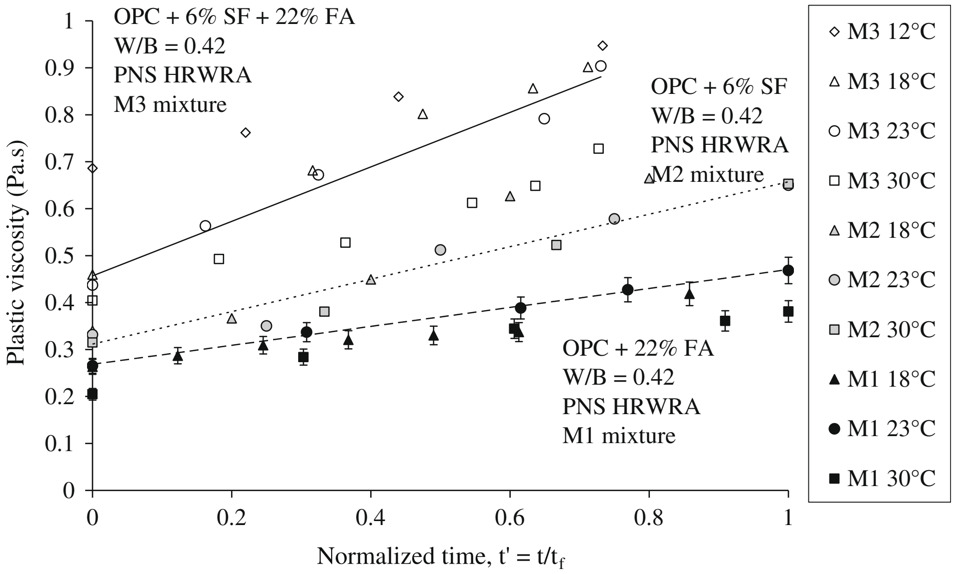

Fig. 6. Variation of plastic viscosity with normalized time for the M1 to M3 mixtures tested at 12–30 °C (linear regressions for 23 °C only are shown).

Table 5
Rheological parameters of micro mortars.

Mixture	Binder	HRWRA1	τ_0 (Pa)[b]	$\Delta\tau_{eq}$ (Pa)	μ (Pa s)[b]	$\Delta\mu_{eq}$ (Pa s)
Experimental data						
M1	OPC + FA	PNS	8	6	0.22	0.17
M2	OPC + SF	PNS	26	15	0.30	0.35
M3	OPC + SF + FA	PNS	13	22	0.42	0.16
M4	OPC + SF + FA	PMS	11	11	0.40	0.20
M5	OPC + SF + FA	PCP	2	[a]	0.40	0.42
M6	CEM II B	PCP	4	[a]	0.23	0.19
M7	CEM II B + FA	PCP	10	[a]	0.25	0.21

[a] Deviation from linear model with PCP HRWRA.
[b] Mean value.

Table 6
Correlation coefficients (R^2) for the variation of rheological parameters with time, at various temperatures, using linear regression for the tested micro mortars.

Mixture	Binder	W/B	HRWRA	10 or 12 °C	15 or 18 °C	20 or 23 °C	27 °C	30 or 33 °C
R^2 for yield stress								
M1	OPC + FA	0.42	PNS	–	0.99	0.98	–	0.97
M2	OPC + SF	0.42	PNS	–	0.95	0.99	–	1.00
M3	OPC + SF + FA	0.42	PNS	0.75	0.75	0.77	–	0.96
M4	OPC + SF + FA	0.42	PMS	–	0.99	1.00	–	0.99
M5	OPC + SF + FA	0.42	PCP	[a]	[a]	[a]	–	[a]
M6	CEM II B	0.53	PCP	[a]	[a]	0.96	0.94	1.00
M7	CEM II B + FA	0.53	PCP	[a]	[a]	[a]	–	[a]
R^2 for plastic viscosity								
M1	OPC + FA	0.42	PNS	–	0.97	0.99	–	0.94
M2	OPC + SF	0.42	PNS	–	0.97	0.98	–	0.99
M3	OPC + SF + FA	0.42	PNS	0.98	0.98	0.95	–	0.94
M4	OPC + SF + FA	0.42	PMS	–	0.98	0.97	–	0.83
M5	OPC + SF + FA	0.42	PCP	0.96	0.98	0.95	–	0.94
M6	CEM II B	0.53	PCP	0.71	0.63	0.96	0.94	0.97
M7	CEM II B + FA	0.53	PCP	0.83	0.95	0.92	–	0.89

–: Test not realized.
[a] Deviation from linear model with PCP HRWRA.

from 18 °C to 30 °C than on M3 mixture proportioned with constant 0.50% PNS HRWRA and tested from 12 °C to 30 °C.

Switching from PNS (M3 mixture) to PMS HRWRA (M4 mortar) induces a lowering of the rate of formation of hydrates, which is related to the slope of the variation of τ_0 and μ with t'. As the initial yield stress values are lower and plastic viscosity values are higher for mortars made with PMS HRWRA, it can be assumed that the observed phenomena are only due to the greater efficiency of the PNS HRWRAs to adsorb onto the surface of the cement grains [19,34]. The increase in temperature affects the degree of adsorption of HRWRA onto cement grains, thus resulting in variations in rheological properties. A lower degree of

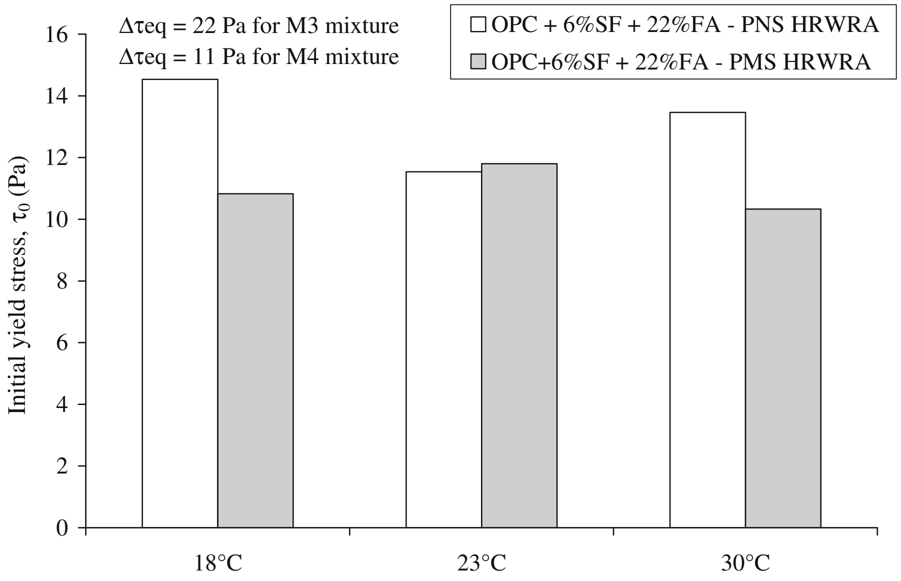

Fig. 7. Initial yield stress (τ_0) and increase in yield stress with normalized time ($\Delta\tau_{eq}$) for the M3 and M4 mixtures tested at 18–30 °C.

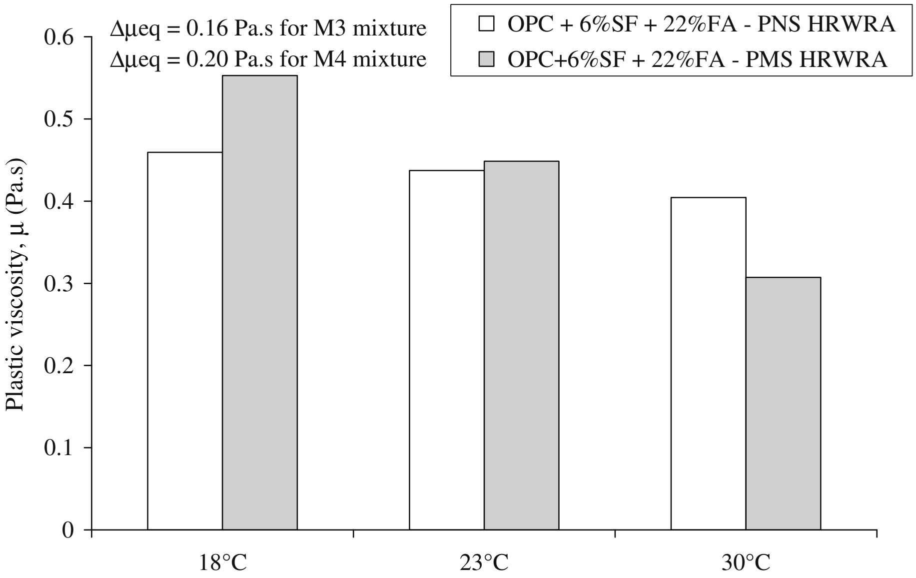

Fig. 8. Plastic viscosity (μ) and increase in plastic viscosity with normalized time ($\Delta\mu_{eq}$) for the M3 and M4 mixtures tested at 18–30 °C.

adsorption of the PNS HRWRA results in a greater residual concentration of free HRWRA in the pore fluid, which can ensure greater cement dispersion and better retention of fluidity over time for a given dosage of PNS HRWRA [12,16]. Table 5 summarizes the experimental data and Table 6 the correlation coefficients obtained in this investigation.

Variations in yield stress with the normalized time value (t') of the M5 mixture prepared at different temperatures is compared in Fig. 9. Although the plastic viscosity varies in a linear fashion with the normalized time, at first, the yield stress is shown to slowly increase or remain constant before undergoing decrease with time. After reaching a minimum value for t' of about 0.35, an increase in yield stress takes place up to the end of the dormant period. Such phenomenon has already been observed [6,15,18,35], despite the lack of threshold temperature for the M5 mixture given the relatively low 0.42 W/B and the higher water demand for SF mixtures [6,18,35].

The initial τ_0 values are reported to be lower for the M5 mixture made with PCP HRWRA (Fig. 9) than for the M3 mortar made with PNS HRWRA (Fig. 4). This may be due to the superior dispersing efficiency of the long-chained and high molecular weighted polycarboxylate polymer, drastically reducing the initial yield stress from 13 Pa for mixtures made with PNS HRWRA to 2 Pa for mortars designed with PCP HRWRA (Table 5). The initial μ values are close for the M3 to M5 mixtures, independently of the HRWRA in use, due to the mix design method that consisted in adjusting HRWRA to get the same Marsh cone time. Consequently, all initial plastic viscosity values were close to 0.40 Pa s (Table 5).

4.3. Effect of fly ash on the robustness to temperature variations of micro mortar mix designs made with PCP-HRWRA

The data plotted in Fig. 10 clearly indicate the presence of a critical temperature between 15 and 20 °C for the M6 mixture de-

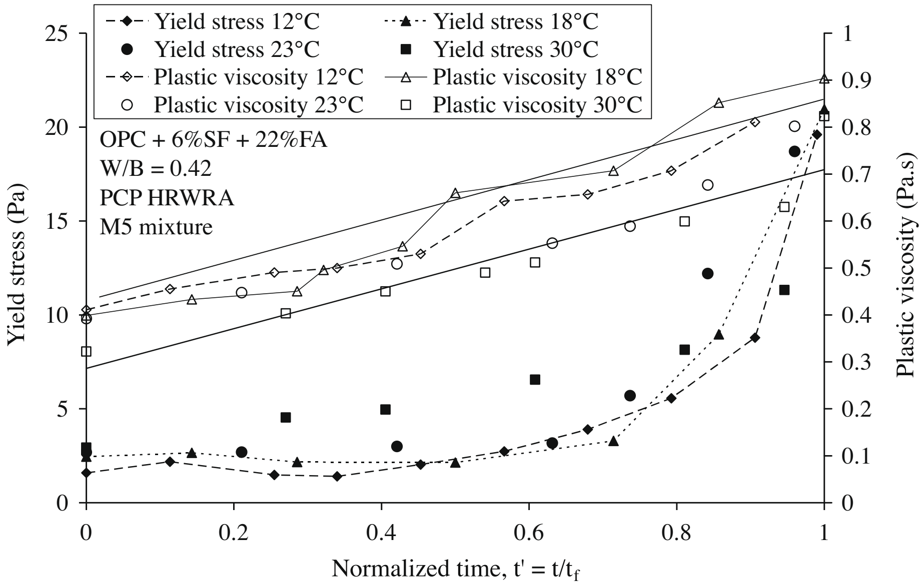

Fig. 9. Variation of yield stress and plastic viscosity with normalized time for the M5 mixture tested at 12–30 °C.

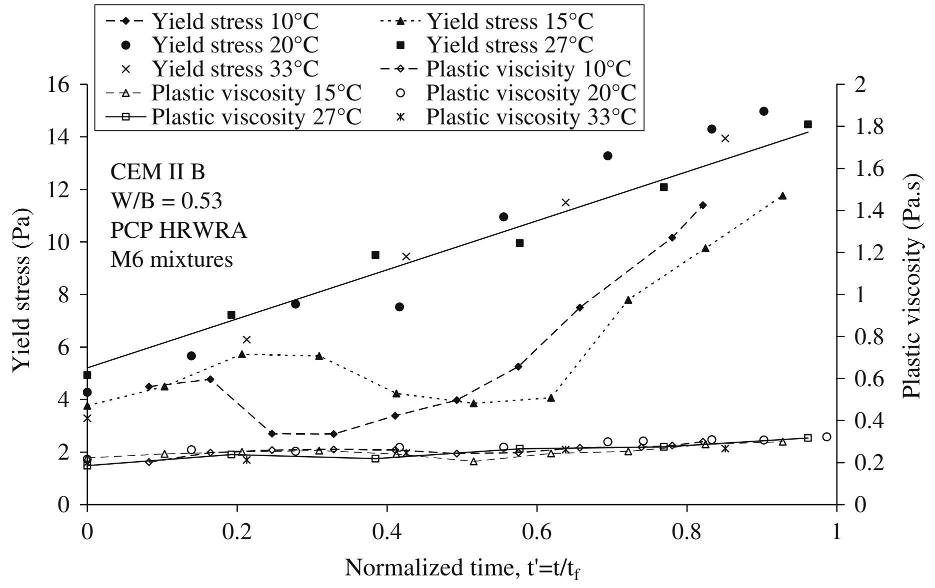

Fig. 10. Variation of yield stress and plastic viscosity with normalized time for the M6 mixtures tested at 10–33 °C.

signed with a high W/B of 0.53 where variations of τ_0 with time change from linear increase to initial reduction with time followed by sharp increase in τ_0. When the mixture temperature exceeds this threshold value, τ_0 is shown to vary linearly with the normalized time (Fig. 10) for the M6 mixtures prepared with PCP-HRWRA. For mixtures prepared below the critical temperature, the variation of the yield stress can be separated into three stages. As observed in Fig. 10, at first, the yield stress is shown to slowly increase or remains constant over 30% of the dormant period before undergoing a decrease with time. After reaching a minimum value, an increase in the yield stress will then take place up to the end of the dormant period. The threshold temperature for the M5 mixtures tested at 12–33 °C is not attained, and all mixtures undergo an initial decrease in yield stress before undergoing subsequent gain in τ_0 (Fig. 9).

The efficiency of PCP-HRWRA on dispersing cement particles is related the mixture temperature. Such temperature can have marked effect on the rate of adsorption of PCP-HRWRA onto cement grains, the rate of cement hydration, the concentration of ions in the aqueous solution, hydration layers growing from the surface of the cement grain and the steric size of the polymer [4,6,7,20,35,36].

A 9.5% volumetric replacement of cement by Class F fly ash resulted in higher initial yield stress values and no threshold temperature was observed. No noticeable effects were observed on plastic viscosity (Fig. 11). While it is commonly admitted that the addition of fly ash as partial replacement of the cement enhances workability [20,22,23], uncombusted carbons in the FA worsen workability of cementitious materials due to a higher rate of adsorption of HRWRA [37]. Such phenomenon can explain the

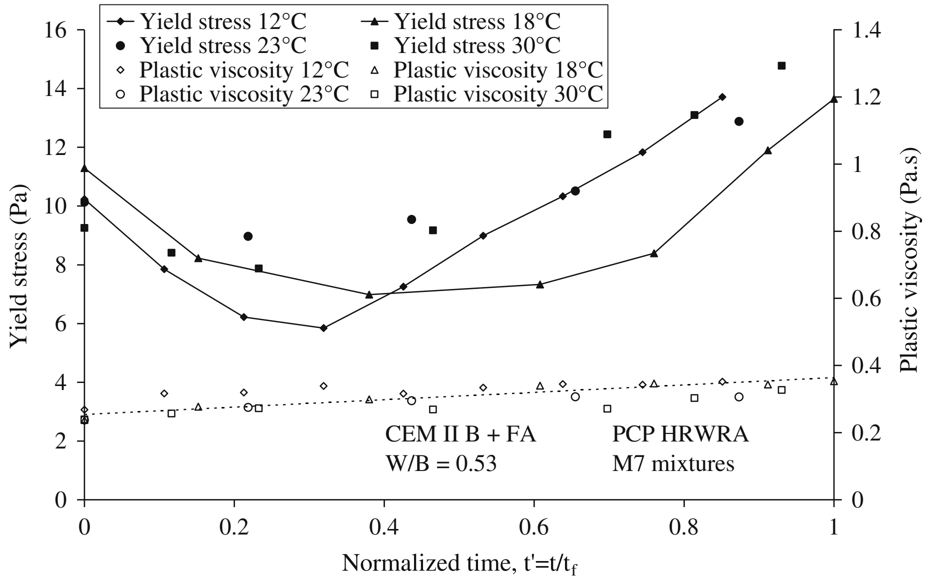

Fig. 11. Variation of yield stress and plastic viscosity with normalized time for the M7 mixtures tested at 10–33 °C.

variation of yield stress with *t'* on M7 mortars: a higher rate of adsorption of the PCP-HRWRA can slow down the growth of hydration layers from the surface of the cement grain. These hydration layers could incorporate the side chain of the polymer [7], resulting in an decrease of the dependency of the superplasticizer to temperature, but higher initial yield stress values. No noticeable effect is seen on initial plastic viscosity or $\Delta\mu$eq (Table 5). Table 6 summarizes the correlation coefficients obtained in this investigation, and Table 4 the maximum deviation for yield stress and plastic viscosity.

5. Conclusions

The influence of the coupled effect of temperature and time on the variations of rheological parameters was investigated for micro mortars derived from SCC mixtures made with various binder and HRWRA types. Based on the results presented in this paper, the following conclusions appear to be warranted:

1. Temperature has lower effect on the initial yield stress and on its increase in time in PNS mixtures containing 22% Class F fly ash than on mixtures with 6% silica fume. Sharper changes on initial plastic viscosity and its increase with time are observed on PNS micro mortars prepared with 6% silica fume than on mixtures containing 22% fly ash and no silica fume. The greater changes in rheology with time and temperature for mixtures made with silica fumes, compared to FA mixtures, may be explained by the increase in water demand to attain specific workability given the higher surface area caused by SF. The robustness to temperature variations of PNS mixes made with fly ash is greater than the one of mixes containing silica fume. Mortars are more affected by temperature variations when a ternary binder (OPC + 22% FA + 6% SF) is used.
2. For mortars made with PNS or PMS HRWRA, yield stress and plastic viscosity increase in a linear fashion with time up to the end of the dormant period (t_f), regardless of the material temperature (12–30 °C) and binder type. The variation of rheological parameters is only dependant on the increase of residual PNS in the solution due to the decrease of adsorbed HRWRA with the hydration progress. Depending on the HRWRA in use, temperature can have sharper effect on the variation of rheology with time, due to the greater efficiency of the PNS HRWRA to adsorb onto the surface of the cement grains.
3. In the case of the mortars prepared with 0.53 W/B and PCP-HRWRA, changes in yield value with time are shown to vary in different ways depending on mixture temperature and mixture proportioning. Above a given threshold temperature, the mortar made with PCP-HRWRA behaves in a similar manner as the mixtures made with PNS-HRWRA. Below a given threshold temperature, the mortar exhibits a considerable degree of retention, or even reduction, in yield value over 30% of the dormant period. A sharp increase in yield value is observed beyond 30% of the dormant period.
4. When FA is used as 12.5% volumetric replacement of OPC on mortars made with 0.53 W/B and PCP-HRWRA, no more threshold temperature is seen below 30 °C. A higher rate of adsorption of the PCP-HRWRA can slow down the growth of hydration layers from the surface of the cement grain that could incorporate the side chain of the polymer, resulting in a decrease of the dependency of the superplasticizer to temperature and higher initial yield stress values. No noticeable changes are observed on plastic viscosity or the variation of plastic viscosity with time and temperature when FA is used as partial replacement of cement. Fly ash seems to enhance the robustness of PCP mix designs to temperature variations.

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