Research paper

Effect of hydroxypropyl methyl cellulose on rheological properties of cement-limestone paste

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Abstract: The effects of hydroxypropyl methylcellulose (HPMC) on the rheology and viscoelasticity of cement-limestone paste were evaluated, as was the mechanism of HPMC from the viewpoint of zeta potential and adsorption amount. The results revealed that the greater the content of HPMC or the viscosity of its aqueous solution, the lower the fluidity of the composite paste and therefore the higher the rheological parameters. The relation between torque and rotational velocity of cement-limestone paste is linear; nevertheless, the shear thickening degree of paste increased following the addition of HPMC, demonstrating typical viscoelastic properties. The addition of HPMC prolonged the induction duration and delayed the emergence of the exothermic peak of hydration, decreased zeta potential and conductivity, and increased the propensity of suspension particles to agglomerate. The adsorption amount of polycarboxylate superplasticizer (PCE) decreased with increasing aqueous solution viscosity and HPMC concentration due to the winding effect of HPMC's high molecular chain structure and the competing adsorption of HPMC and PCE.

Keywords: hydroxypropyl methylcellulose (HPMC), cement-limestone paste, rheological properties, viscoelasticity

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1. Introduction

Although Portland cement (PC) has become the primary binder in building concrete since its advent, its high energy consumption (approximately 10–11 EJ of energy annually for manufacturing) and high concentration of CO_2 emissions will inevitably place a great deal of pressure on the environment if used in large quantities, which contradicts the concept of sustainability in the construction industry. As a consequence of the ongoing advancement of concrete technology, mineral admixtures have increasingly become vital components of high-performance concrete. The incorporation of mineral admixtures can save cement consumption and therefore reduce carbon emission in the process of cement production [1, 2]. Limestone powder (LP) is a common mineral admixture applied in concrete, and LP is usually used as an inorganic thickening component in self-compacting concrete (SCC) [3, 4]. Meanwhile, it can promote the early hydration degree and strength of concrete [5]. LP can be used as nucleation site to accelerate the adsorption of Ca_{2+} in cement paste, thus accelerating the hydration reaction of C_3S [6, 7]. From the perspective of optimizing the workability of SCC, cellulose ether is also applied as a common water-retaining agent and thickening agent besides LP [8, 9]. The addition of cellulose ether can improve the viscosity of cement mortar, increase the homogeneity and prevent the occurrence of segregation and bleeding [10].

Although many studies around the influence of cellulose ethers on properties of cement-based materials have been carried out, the mechanism of different types of cellulose ethers on cement particles still needs to be further explored. Pourchez et al. [11] found that cellulose ether could be completely adsorbed in the dilution medium within hours after cement hydration. Hurnaus et al. [12] noted that the residual amount of cellulose ether in cement was generally low, and silica as the model substrate did not maintain the monomer unit D-glucose of cellulose. Therefore, they thought that cellulose ether was not adsorbed on the surface of cement particles. In contrast, Bessaies-Bey et al. [13] considered that there was competitive adsorption between superplasticizer and cellulose ether. Through a new dynamic light scattering scheme, it was found that the results of competitive adsorption were not only related to the physical or chemical properties of the mixture, but also closely related to the surface coverage. In other studies, the elongation of setting time and the variation of rheological properties were similarly ascribed to the adsorption of cellulose ether on hydrated phases [14, 15]. Ridi et al. [16] believed that the incorporation of methyl hydroxy ethyl cellulose decreased the density of C-S-H gel but did not change the activation energy required for nucleation.

Fresh cement paste is a complex multiphase suspension system, and rheological property is the essential manifestation of the working performance of cement mix. The rheological properties of cement mixes can be separated into two categories: rheological parameters and rheological characteristics. Rheological parameters are important indexes to quantify the rheology of cementitious materials, which mainly include plastic viscosity and yield stress calculated by Bingham model [17–19]. Rheological characteristics relate to the phenomenon that the shear stress-shear rate relation of cement paste changes due to external shear force disturbance. When the relationship between shear stress and shear rate

is non-linear, the paste can be characterized by shear thickening or shear thinning [4,20,21]. Thixotropy is the reflection of flocculation structure in cement paste [22, 23]. Brownian motion and shear rate will affect the build-up and breakdown rate of flocs [24]. The density of floc structure and firmness of the connection between colloidal particles are two important factors affecting the thixotropy of cement paste [25]. In addition to fluid properties, cement paste exhibits specific elastic properties when exposed to external shear forces of varying amplitude or frequency, which is known as viscoelasticity [26]. When the viscosity is low, the cement paste shows the characteristics of plastic fluid; With the increase of viscosity, the paste will have elastic deformation under small shear stress, and the deformation can be basically recovered after the shear force is removed, during which the paste has the properties of elastomer [27]. Dynamic shear rheological test (DSRT) is an appropriate method to measure the viscoelasticity of cement paste [28]. It can reveal the evolution law of paste rheology without significantly destroy the internal net-work structure of cement.

Overall, the rheological parameters, rheological characteristics and viscoelasticity are all important indexes to evaluate the cement paste rheology. Since there is still few research on the early rheological properties, especially viscoelastic properties of cement-limestone powder pastes incorporating cellulose ether, this paper examines the effects of hydroxypropyl methylcellulose (HPMC) on the rheological properties and viscoelasticity of cement-limestone paste from the perspective of parameter characterization and mechanism discussion. The mechanisms were analyzed from the aspects of hydration exothermic rate, zeta potential and conductivity and adsorption amount.

2. Materials and experimental programs

2.1. Materials and sample preparation

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly de-scribed and appropriately cited.

P·I 42.5 PC which conforms to standard GB175-2007 was used in this test, and its chemical and physical parameters were presented in Table 1. Limestone powder (LP) was produced in Baoding, Hebei Province, with a specific surface area of 494.3 m^2/kg. The particle size distribution of PC and LP is shown in Fig. 1. Polycarboxylate superplasticizer (PCE), produced by Shanxi Jiawei New Material Co., Ltd, is composed of macromolecular mixture with carboxylate, hydroxyl and polyoxyethylene side chain. The appearance of PCE is light yellow liquid, and its specific parameters are shown in Table 2. HPMC adopted in this study contains ether groups of $-OCH_3$ and $-O[CH_2CH(CH_3)O]_nH$, and its appearance

Table 1. Chemical composition and physical properties of PC

Raw material	Content/%							Loss on ignition	Density	Specific surface area
	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO^3	f-CaO	(%)	(g·cm^{-3})	(m^2/kg)
Cement	62.26	20.76	7.31	3.25	2.91	2.81	0.70	2.10	3.15	350
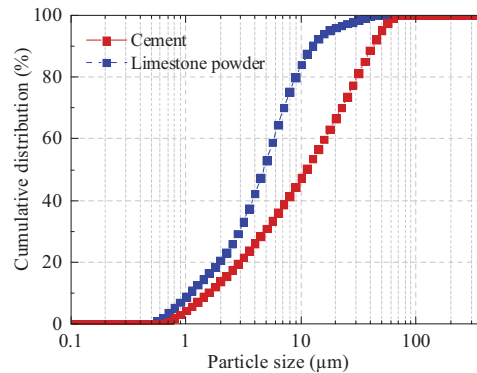
Fig. 1. Particle size distribution of cementitious materials

Table 2. Performance parameters of PCE

Index	Water-reducing rate	Gas content	Chloride ion content	Alkali content	Sodium sulfate content
Percentage	24.2	2.3	0.14	2.13	2.11

is white powder. According to the viscosity of their aqueous solution, HPMC can be divided into CQ-60, CQ-65 and CQ-70, and their properties are presented in Table 3.

The mixture proportions in this study are given in Table 4. Considering the viscosity of cellulose ether aqueous solution, 0.1% and 0.2% HPMC were used to substitute for the

Table 3. Physical and chemical properties of HPMC

Sample	Content (%)		pH	Pass rate of 100 mesh	Viscosity (mPa·s) (The concentration of aqueous solution is 1%)
	Methoxy	Hydroxypropoxy			
CQ-60	27.8	7.4	5.4	98.4	4860
CQ-65	28.5	6.5	5.1	100	8170
CQ-70	19.2	8.4	5.8	100	15100

Table 4. Mixture proportion of composite pastes

No.	Sample No.	PC (g)	LP (g)	HPMC (g)			Water (g)	PCE (g)
				CQ-60	CQ-65	CQ-70		
1	L0	500	0	0	0	0	175	1.5
2	L10	450	50	0	0	0	175	1.5
3	L10-0.1H1	449.5	50	0.5	0	0	175	1.5
4	L10-0.2H1	449	50	1	0	0	175	1.5
5	L10-0.1H2	449.5	50	0	0.5	0	175	1.5
6	L10-0.2H2	449	50	0	1	0	175	1.5
7	L10-0.1H3	449.5	50	0	0	0.5	175	1.5
8	L10-0.2H3	449	50	0	0	1	175	1.5

equal quality of cement. In order to control the fluidity of pure cement paste in a reasonable range, it was determined that the dosage of PCE is 0.3% and the water-to-binder ratio (w/b) is 0.35.

2.2. Testing methods

2.2.1. Flow spread

The test for cement paste fluidity is conducted in accordance with GB/T 8077-2012. To begin with, mixed PC and LP evenly by electric mixer, and then water, HPMC and PCE were added respectively. Due to the small content of HPMC, water and HPMC were mixed first to form a uniform solution before adding to the mixing pot. The whole mixing process includes slow-speed mixing for 90 s at 60 rpm, resting for 15 s, and then fast-speed mixing for 90 s at 120 rpm. The paste was poured into the mini-slump cone after a 3-minute rest, then the cone was raised vertically to allow the paste to flow freely. When the paste ceased to flow, the average values of two mutually perpendicular diameters were measured.

2.2.2. Rheological parameters

The rheometer used for the rheological experiments was an Anton Paar MCR 102. To reduce the influence of cement thixotropy on the accuracy of parameters, the test scheme of rotational velocity rose linearly and then descended in the form of steps was adopted. After obtaining the torque-speed relationship, yield stress and plastic viscosity were calculated by Reiner–Riwlin equation derived from Bingham model [29]:

(2.1)
$$\tau_0 = \frac{\left(\dfrac{1}{R_i^2} - \dfrac{1}{R_0^2}\right)}{4\pi h \ln\left(\dfrac{R_0}{R_i}\right)} G$$

$$(2.2) \qquad \mu = \frac{\left(\dfrac{1}{R_i^2} - \dfrac{1}{R_0^2} \right)}{8\pi^2 h} H$$

where τ_0 is the yield stress; R_i and R_0 are the inner diameter and outer diameter of the coaxial cylinder system respectively ($R_i = 1$ cm, $R_0 = 3$ cm); $h = 4$ cm is the rotor height; μ is the plastic viscosity; G and H are the intercept and slope of the rheometer torque-speed linear fitting function ($T = G + HN$).

2.2.3. Thixotropy

The thixotropy of cement paste is measured by three interval thixotropy test (3ITT). By this method, it can be observed how long it takes for the sample to recover to the static stage after high-speed shear force. 3ITT includes three stages: (1) Static stage: applying a constant and small rate shear force (0.1 s^{-1} for 60 s); (2) Shear stage: applying a constant and large shear force (100 s^{-1} for 60 s); (3) Structural recovery stage: applying the same shear force as the first stage (0.1 s^{-1} for 60 s). In this study, 3ITT was performed by rotation test method.

2.2.4. Viscoelasticity

The DSRT was chosen to characterize the viscoelasticity of composite pastes. The control frequency of amplitude sweep process was 10 rad/s, and the amplitude increased from 0.001% to 100% logarithmically. Five test points were selected for each order of magnitude. The amplitude of frequency sweep was kept constant at 10^{-2}%, and the amplitude increases from 0.1 rad/s logarithm to 100 rad/s.

2.2.5. Hydration heat evolution

A TAM Air 8-channel calorimeter was used to determine the hydration heat release rate and cumulative heat release of cementitious materials. Maintain a temperature of 20±0.1°C during the test. The delay between consecutive test points is 10 min.

2.2.6. Hydration heat evolution

A TAM Air 8-channel calorimeter was used to determine the hydration heat release rate and cumulative heat release of cementitious materials. Maintain a temperature of 20±0.1°C during the test. The delay between consecutive test points is 10 min.

2.2.7. Zeta potential and conductivity

Zeta potential and conductivity were measured using the Zeta Probe automated interface potential analyzer from American Colloidal Dynamics Company. The instrument comprised a mixing unit and employed electroacoustic measuring technology. To prevent interference from neighboring cement particles, the cement particles had to be sufficiently dispersed, requiring a suitably sparse cement paste. Therefore, the w/b ratio of the test was determined to be 10:1. The total number of test points was 21, and the period between each point was 20 s.

2.2.8. Adsorption amount

The adsorption capacity was measured by total organic carbon (TOC) method. First, the evenly mixed 50 g paste was poured into the centrifugal tube, mixed by magnetic stir-ring for 3 min, and then centrifuged at the speed of 6000 r/min for 5 min. 10 mL of super-natant was taken and filtered through 0.22 μm pore size filtration membrane. After adding appropriate amount of deionized water to dilute 100 times, the organic matter content was measured by TOC instrument. Finally, the adsorption amount of HPMC and PCE can be calculated by the concentration difference between HPMC and PCE before and after mixing with cementitious materials.

3. Results

3.1. Flow spread

Figure 2 presents the flow spread of PC-LP paste incorporating different content and type of HPMC. It can be seen from Fig. 2 that the spread diameter of pure cement paste was the largest (240 mm) among 8 groups, while the diameter decreases to 210 mm after mixing 10% LP. For different types of HPMC, the fluidity of paste all decreased with in-creasing HPMC content. Higher viscosity of HPMC aqueous solution corresponds to smaller flow spread diameter. When the HPMC with viscosity of 15100 m·Pa·s was incorporated into PC-LP system, there is a dramatic decline in the fluidity of composite paste and the fluidity of paste with 0.2% CQ-70 drop to 156 mm. The HPMC aqueous solution is a significant consideration. 0.1% CQ-70 can reduce the fluidity remarkably, while fluidity still has no remarkable change after adding 0.2% CQ-60.
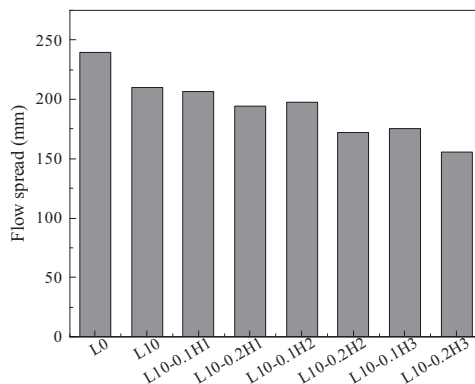
Fig. 2. Effects of HPMC on flow spread of PC-LP pastes

3.2. Rheological parameters

The variations in rheological parameters (yield stress and plastic viscosity) of pastes with eight mix proportions were evaluated at different HPMC content and types (see Fig. 3). It can be seen that the change of rheological parameters is similar to that of fluidity. Both
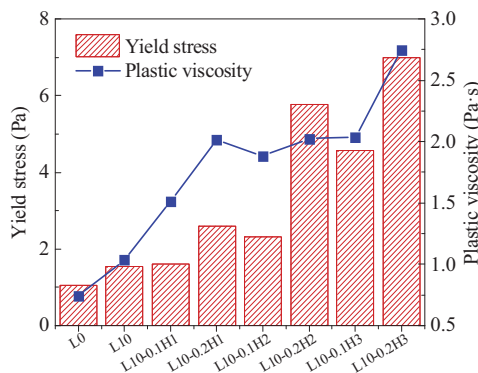
Fig. 3. Rheological parameters of composite pastes

yield stress and plastic viscosity increase with the addition of HPMC. Compared with fluidity, the rheological parameters are more sensitive to the change of HPMC con-tent. The yield stress of paste incorporating 0.1% CQ-60 HPMC has no prominent change, but when the content of CQ –60 HPMC increases to 0.2%, the yield stress and plastic viscosity rise from 1.602 Pa and 1.51 Pa·s to 2.794 Pa and 2.06 Pa·s, respectively. Previous research [30] have shown that the viscosity of cement paste incorporating HPMC is not a simple addition of the viscosity of cement paste and HPMC aqueous solution, but a "composite superposition effect". The viscosity of HPMC aqueous solution mainly comes from the hydrophilicity of hydroxyl group and ether bond and the stereoscopic network structure formed by HPMC molecule, while the viscosity of pure cement mainly comes from the network flocculation structure generated from colloidal particles [9, 24, 31]. At the same time, due to the large specific surface area of LP, the water demand on the surface of solid particles in composite paste increases, which reduces the volume of free water for lubrication in cement suspension, thus decreasing the fluidity [32]. The yield stress and plastic viscosity of composite paste increase with the combined action of HPMC and LP, and higher viscosity of HPMC corresponds to more significant increasing degree.

3.3. Rheological characteristics

Figure 4 shows the torque speed test points and fitting curves of pastes under different HPMC types, and the rheological indexes of all fitting functions for the investigated pastes are compared in Fig. 5. The goodness of fit R2 based on exponential function is more than 0.99 under each mix proportion, indicating that the exponential fitting can well character-ize the torque-speed relationship of composite pastes. At the same time, according to the variation of rheological index shown in Fig. 5, It can be discovered that the rheological index of cement paste and paste with 10% LP is slightly less than 1, showing the char-acteristics of shear thinning. After incorporating HPMC, the rheological index is greater than 1, indicating that the rheological characteristics change from shear thinning into shear thickening, and the higher HPMC content is, the larger extent shear thickening is.
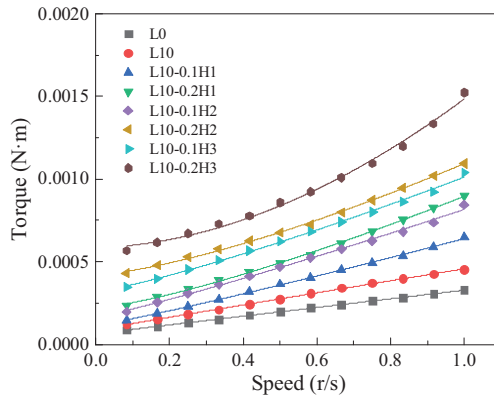
Fig. 4. Rheological curves and fitting exponential function of composite pastes
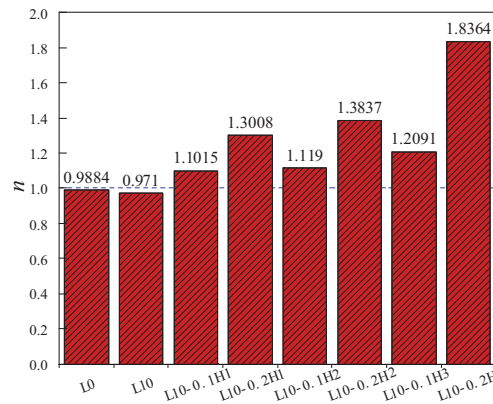

Fig. 5. Rheological index of composite pastes

According to the particle cluster theory [2, 33], when the flow velocity of cement particles in suspension increases to a certain extent, the water pressure of particles is larger than the repulsion force between them, and then the particle clusters are formed temporarily, which makes the cement paste need to exert greater shear force at the same shear rate, thus showing the rheological behavior of shear thickening. HPMC is a kind of non-ionic cellulose ether and it belongs to the polymer long chain structure with large number of structural units [34]. The incorporation of HPMC can make the cluster effect more obvious through the winding effect of its own molecular chain, making the PC-LP paste change from Newtonian fluid to shear thickening fluid.

3.4. Thixotropy

In the field of rheology, thixotropy is defined as a time-dependent property. The structural strength of thixotropic fluid will decrease under the action of constant shear force. However, in the subsequent resting process, the structure will finally recover to the reference

state at different rates [35]. The process of structural damage and recovery is a completely reversible cycle. In fresh cement paste, cement particles spontaneously coagulate into flocculation structure under the action of electrostatic force, thermal motion and Van der Waals force. Thixotropy is the reflection of flocculation structure in cement paste, so the density of flocculation structure and the firmness of the connection between particles may have a significant impact on thixotropy [25]. Fig. 6 displays apparent viscosity evolution of composite pastes under eight mix proportions. As is shown in Fig. 6, in the first stage, the apparent viscosity of each group increased slowly with time at low shear rate.
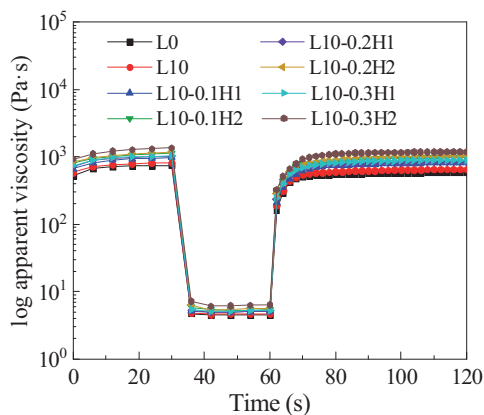
Fig. 6. Apparent viscosity evolution with time measured by 3ITT method

When shear rate increases to 100 s^{-1}, the apparent viscosity decreases significantly and the internal microstructure of cement paste is disturbed, and the interaction force be-tween particles changes. In the last stage, the apparent viscosity increased gradually to the original value, reflecting the process in which the flocculation structure begins to recover. For each time point indicated, the higher HPMC content or viscosity of HPMC aqueous solution is, the larger apparent viscosity of paste is. By comparing the three stages simultaneously, it can be found that larger apparent viscosity of paste in the first two stages corresponds to faster structure recovery rate in the third stage.

3.5. Viscoelasticity

3.5.1. Amplitude sweep

For further investigating the rheological properties of PC-LP pastes mixed with HPMC, the viscoelasticity of composite pastes was characterized by amplitude sweep under different mix proportions. Figure 7 presents the variation of storage modulus G'/loss modulus G'' with rotor amplitude for composite pastes incorporating different types of HPMC. As shown in Fig. 7, for HPMC-PC-LP system, the two moduli of all paste keep constant under low strain and are independent of frequency and amplitude (the relationship between G'

and G'' is $G' > G''$). This reversible range of linear elastic deformation is called the linear viscoelastic range (LVR) [26]. With the increase of the amplitude applied to the paste, G' and G'' began to decrease, indicating that the microstructure of systems began to be destroyed. When the strain increases to a certain extent, the G' curve and G'' curve intersect at a certain value. Then the paste begins to flow and behaves as a viscoplastic liquid, and the corresponding intersection point is the flow point. Whether for pure cement paste or HPMC-PC-LP paste, the results of amplitude sweep show that paste has viscoelastic properties when HPMC content is in a certain range.
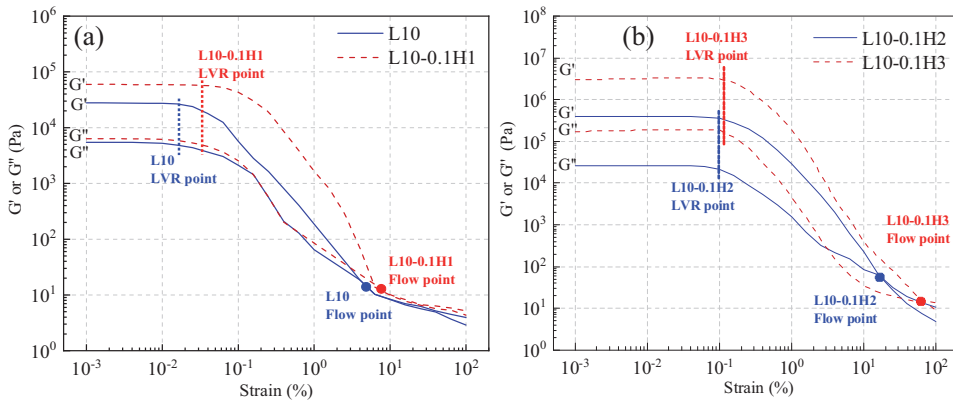
Fig. 7. Amplitude sweep curves of composite paste: (a) L10 and L10-0.1H1; (b) L10-0.1H2 and L10-0.1H3

Figure 8 depicts the strain values corresponding to the LVR points and flow points of pastes under different mix proportions. Compared with PC-LP paste, the LVR strain and flow point strain increase after incorporating HPMC, and the amplitude rise signif-
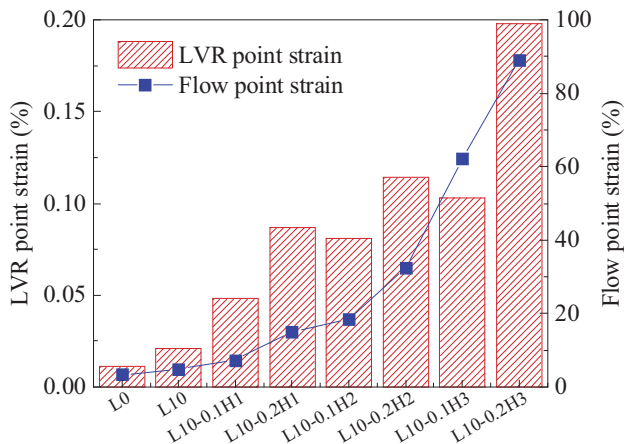
Fig. 8. LVR point strain and flow point strain of composite paste

icantly with increasing viscosity of HPMC aqueous solution. In LVR, G' and G'' are both constant, indicating that although composite pastes still belong to a concentrated colloidal suspension, they show more elastic properties. The winding effect of cellulose ether polymer chain makes the structure of colloidal particles more compact. In the period of initial reaction, cement hydration occurred but the hydration degree was generally low, mainly due to the slow dissolution rate of C_3S [36]. In all mineral phase compositions, C_3A plays a significant role in the rheological properties of fresh cement paste [37]. C_3A dissolves very quickly and forms hexagonal lamellar hydration product structure rapidly, which makes the LVR of paste increase in the initial stage. By comparing the two strain values, it can be found that the LVR strain is more sensitive to the HPMC content. When the HPMC content increases from 0.1% to 0.2%, LVR strain increases significantly. However, the type of HPMC has a great influence on flow point strain. The flow point strain of paste incorporating 0.1% CQ-70 is even larger than that of paste with 0.2% CQ-65.

3.5.2. Frequency sweep

Figure 9 presents the response of the composite pastes to the frequency sweep, and the strain remains constant at 10^{-2}%. When the frequency increases from 0.1 rad/s to 100 rad/s, the G' of paste decline in the range of LVR, while G'' and phase angle increase first and then decrease. The addition of HPMC increases the maximum phase angle in the frequency range from 0.1 rad/s to 100 rad/s. According to the definition, the tangent value of phase angle is the ratio of G'' and G'. The decline of phase angle means that paste shows more elastic properties during frequency test. The higher thickening degree of HPMC is, the denser network microstructure of paste is, thus increasing the elasticity. This trend is the same as that of amplitude sweep test.
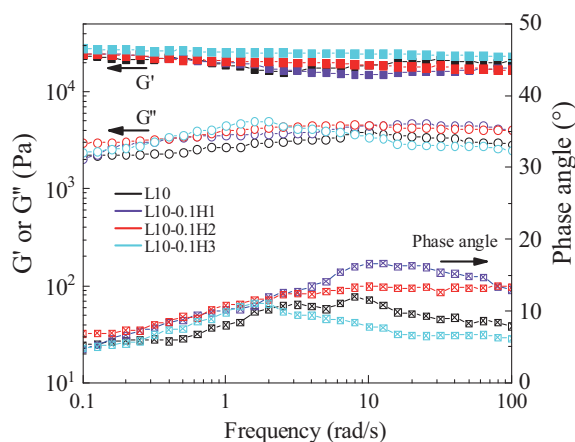

Fig. 9. Oscillatory frequency sweep of composite pastes

4. Discussion

4.1. Microscopic mechanism

4.1.1. Hydration

Due to the hydration reaction of cement resulting in the change of constituents and microstructure, there will be a fluidity loss of cement paste with the setting and hardening process [38, 39]. In order to reveal the relationship between the rheological properties and the early hydration heat release, the rate of hydration heat flow and cumulative heat release in 1 h and 48 h (Fig. 10) were tested to figure out the interaction and internal mechanism between HPMC and PC-LP paste. It is shown in Fig. 10 that HPMC can reduce the hydration exothermic rate of composite paste in the early stage, mainly by pro-longing the induction period and delaying the emergence of the hydration exothermic peak. In the first hour of hydration, the exothermic rate and cumulative heat release of paste incorporating HPMC were low. It is generally considered that the adsorption of cellulose ether with cement hydration products is the reason why cellulose ether delays cement hydration [11, 15, 40]. C_3A is the single mineral with the largest hydration rate in cement clinker, and the addition of HPMC can delay the hydration of C_3A and change the morphology of hydration products [41]. Ca, Si and Al are metallic elements with high concentration in PC-LP paste, and their corresponding main hydration products are $Ca(OH)_2$, C-S-H gel and ettringite respectively. Cellulose ethers have delay effect on the formation of hydration products with different degree, resulting in the formation of early gel structure and thus changed the rheological properties and viscoelasticity [42].
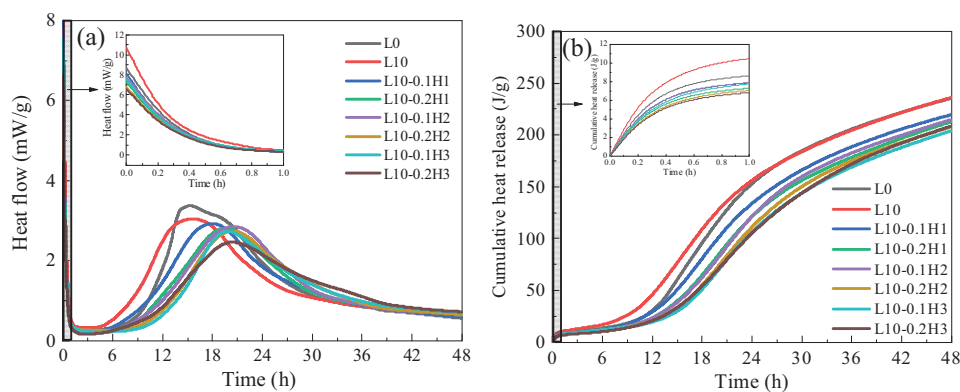

Fig. 10. Isothermal calorimetry test from the initial 1 h and 48 h of hydration: (a) Heat flow; (b) Cumulative heat release

4.1.2. Zeta potential and conductivity

Theoretically, cement particles in a fresh paste will be exposed to several effects, including Van der Waals force, electrostatic repulsion force, and steric hindrance, and will exhibit a high level of reactivity [24]. Ions in suspension liquid phase are attracted to charged sur-

faces by electrostatic interaction, resulting in the formation of an electric double layer that neutralizes particle surface charge [43, 44]. Initial zeta potential of CSH phase is negative, but it may turn positive when Ca_{2+} concentration in cement pore solution increases [45]. As seen by the zeta potential and conductivity of suspensions depicted in Figs. 11 and 12, all diluted pastes are positively charged.
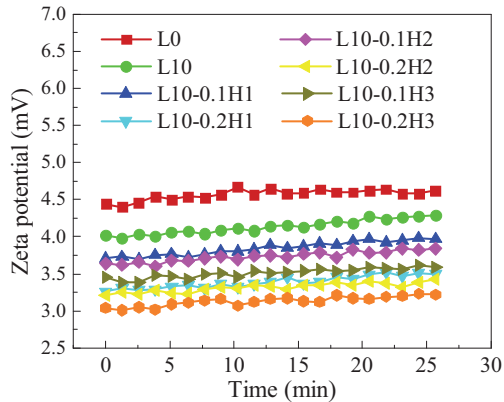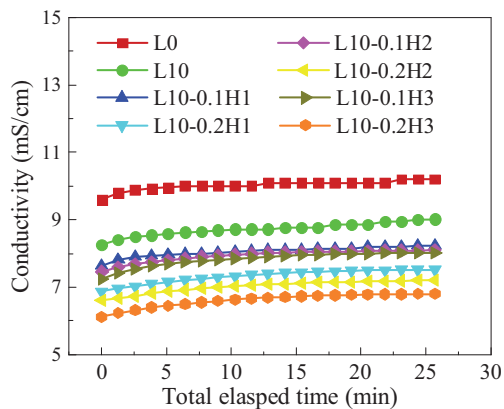

Fig. 11. Development of zeta potential with time

Fig. 12. Development of conductivity with time

With the addition of LP and HPMC, the zeta potential and conductivity of the paste reduced, and a greater viscosity of the HPMC aqueous solution corresponds to a lower zeta potential value. Zeta potential is a quantitative measure of repulsive or attractive force between particles [46]. The lower zeta potential is, the more suspension tends to coagulate or agglomerate, which means that the composite paste needs more shear force to maintain flow. Therefore, the decrease of zeta potential is responsible for the increase of rheological parameters. With the elevation of viscosity of HPMC aqueous solution and HPMC content, both the zeta potential and conductivity decrease.

4.1.3. Adsorption amount

The adsorption between non-ionic polysaccharide and mineral phase mainly includes hydrogen bonding and chemical complexation [47–49], and these two actions take place between the hydroxyl groups of polysaccharides and metal hydroxides on the sur-face of minerals [50]. Polycarboxylate superplasticizer greatly improves the fluidity of fresh paste by its adsorption on the surface of cement particles or hydration products [51, 52]. At the same time, cellulose ether absorbs water and expands in fresh cement paste to form colloidal membrane structure, and some colloidal films and their "CE micelles" can also be adsorbed on the surface of cement particles [53]. The adsorption capacity of polycarboxylate superplasticizer may change after incorporating HPMC. Accordingly, adsorption behavior of PC-LP pastes mixed with HPMC and PCE were investigated (Fig. 13). The results show that the total adsorption capacity of paste increases with the addition of LP and HPMC, and higher HPMC content or viscosity of aqueous solution correspond to greater adsorption capacity. Although the total adsorption capacity of paste increases, the adsorption capacity of PCE may decrease due to the competitive adsorption between HPMC and PCE on the surface of cement particles and hydration products. However, only the adsorption of PCE on the surface of cement particles can reduce the volume of flocculation structure and improve the fluidity of paste, so the incorporation of HPMC intensifies its competitive adsorption with PCE. At the same time, the network structure formed by HPMC polymer chain makes part of PCE further wrapped in the structure, which makes the adsorption capacity of PCE decrease.
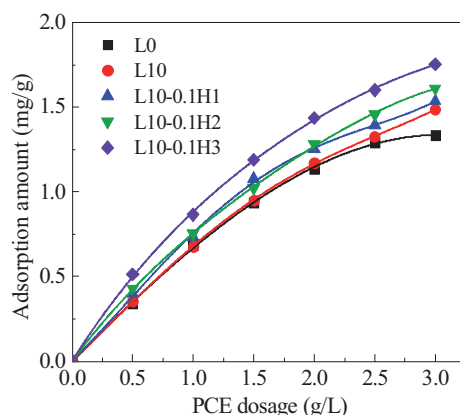

Fig. 13. Adsorption capacity of PCE/HPMC in composite pastes

4.2. Origin of variation in rheology of the PC-LP-HPMC paste

The relationship between the hydration heat release, zeta potential, saturated adsorption amount and rheological parameters are shown in Fig. 14. For fresh cement paste, yield stress and plastic viscosity are usually used to characterize its fluidity, while thixotropy is often applied to evaluate colloidal particle interaction. As is shown in Fig. 14, there is no significant functional relationship between yield stress and heat release of composite
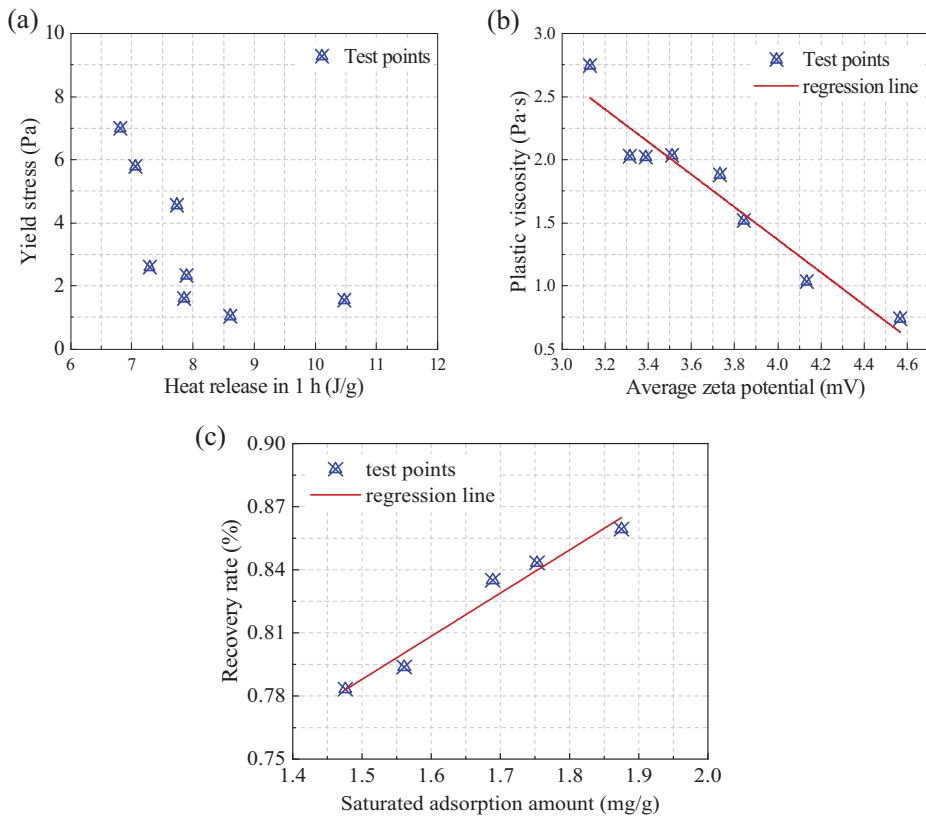
Fig. 14. Relationship between structural build-up and rheology of composite paste: (a) Yield stress vs. heat release; (b) Plastic viscosity vs. zeta potential; (c) Recovery rate vs. saturated ad-sorption amount

paste in early stage (within 1 h), but there is an inverse linear relationship be-tween the average zeta potential and the plastic viscosity and a positive linear relation-ship between the saturated adsorption amount and the recovery rate. It can be found that the delay effect of HPMC on the hydration of C_3S and C_3A is mainly reflected in the exo-thermic peak of $12 \div 24$ h, but not significant within 1 h. However, the zeta potential and adsorption amount showed great changes within 30 min after incorporating HPMC. Zeta potential and adsorption amounts of pastes at the initial hydration stage are important indexes to evaluate the interaction between paste particles. Yield stress and plastic viscosity are both affected by the cohesion and dynamic friction between paste particles [54]. Therefore, unlike total amount of hydration heat release in the early stage, zeta potential and adsorption capacity have notable correlation with rheological parameters. The effect of HPMC on the rheological properties of PC-LP paste is mainly due to its adsorption on the surface of cement particles in fresh stage, which not only changes the charge state on the surface of cement particles, but also reduces the adsorption amount of PCE. These two effects improve the yield stress and plastic viscosity of HPMC-PC-LP paste.

5. Conclusions

1. With the addition of HPMC, the fluidity of composite paste is on the decline, while the yield stress and plastic viscosity rise significantly. The torque-speed relationship of PC-LP paste is approximately linear but paste turn to shear thickening behavior after incorporating HPMC. Higher content of HPMC or viscosity of HPMC aqueous solution make the above changing trend more significant.

2. The PC-LP paste mixed with HPMC has typical viscoelastic properties. When the amplitude is low, G' and G'' of paste keep constant in a certain range; when the amplitude exceeds the flow point, the composite pastes experience the transition from elasticity to viscosity. Higher HPMC content or viscosity of HPMC aqueous solution correspond to the larger strain of LVR point and flow point. The strain at LVR point is more sensitive to HPMC content, while the strain of flow point is more sensitive to the type of HPMC.

3. HPMC can reduce the early hydration exothermic rate of PC-LP paste, mainly by prolonging the induction period and delaying the appearance of hydration exothermic peak. With the addition of LP and HPMC, the zeta potential and conductivity of paste de-creased, making the particles in suspension tended to agglomerate. The adsorption of HPMC on the surface of cement particles and hydration products makes the total adsorption amount change. With the increase of HPMC content and viscosity of HPMC aqueous solution, the total adsorption capacity increases, which intensifies the competitive ad-sorption between PCE and HPMC. Compared with the total amount of hydration heat re-lease in fresh stage, zeta potential and adsorption capacity have significant linear correlation with rheological parameters. The incorporation of HPMC not only changes the sur-face charge state of particles, but also increases the competitive adsorption between HPMC and PCE, thus increasing the yield stress and plastic viscosity.

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