Research Article

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Shear thinning and thickening of cemented paste backfill

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Abstract: Cemented paste backfill (CPB) is considered to be a concentrated suspension in which tailings are bonded together by the hydraulic binder and water, and it has a high solid volume concentration (≥ 50 vol.%). Although the shear thinning and thickening of CPB has been extensively reported in literature, the shear history effects have been ignored in previous studies. In this paper, by using rheometer and Focused Beam Reflectance Measurement, the relationship between the rheological properties and microstructure of the paste under different shear histories was studied. The results have shown that at a low shear rate, CPB revealed shear thinning, low yield stress and low index parameters; while exhibited shear thickening, high yield stress and high consistency index when at high shear rates of shear history. This agreed with the general trends shown in the FBRM analysis. It was proposed that the action of shear is beneficial to particle dispersion, whereas a high shear rate history tends to promote the aggregation of particles. It was revealed that both shear thinning and thickening of paste are related to the situation of particles (flocculation, dispersion and aggregation), and shear history effects play an important role in rheological properties of CPB.

Keywords: shear thinning; shear thickening; microstructure; mixing; cemented paste backfill

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1 Introduction

Utilizing concentrated suspensions for tailings disposal and other complex multiphase mixtures requires studying interesting rheological phenomena, such as shear thinning and thickening [1, 2]. Shear thinning and thickening are typical rheological behaviors associated with concentrated particulate suspensions [3, 4]. They are two opposing phenomena that can often be observed with suspensions undergoing shear, and the two rheology phenomena of concentrated suspensions have been well studied for many years, and some progress has been made [5–7]. They have a common feature in that the material rheograms show a sharp change in flowcurves of concentrated suspensions under different shear histories, and were often referred to as nonlinear change in rheological behavior [8]. It is challenging to do the rheological characterization of shear thinning or/and thickening of concentrated suspensions due to the complexity and occasional discontinuity of the rheograms produced. Several explanations have been frequently proposed for the change in rheological parameter when deemed as a function of shear rate, including the development of doublets, network structures and a variety of other shear-induced structures [9, 10].

Although the above-mentioned explanations about shear thinning and shear thickening have yet to be perfected, they all believe that it is related to the microstructure of the suspension. As proposed by Larson [11], the rheometry has advantages when supplemented by other experimental approaches that characterize fluid structures and flow-induced structural changes. Mixing, a significant factor for the microstructure development, is commonly encountered in many engineering applications within the domain of process engineering, as well as in cement-based materials, for instance, in mixing plants. More than homogenizing the suspension constituents into the suspending medium, it plays an important role in characterizing the rheological properties of fresh suspensions [12, 13]. So when we study the rheological proper-

Table 1: Chemical characteristics of the tailings

Compound	SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	SO_3	rests
Content/%	50.63	25.54	9.39	5.39	2.72	1.92	4.40

ties of suspensions, we need to understand the following: Is the material flocculated? Is the material used downstream of some high shear event? Is the material used upstream of some high shear event? Are there any on-going chemical changes? [14, 15] From the microstructural point of view, some rheology phenomena, such as shear thinning and shear thickening, could be described as suspension deflocculation and breaking down of the interparticle forces under shearing, and flocculation and formation of interparticle forces over at rest. However, it is very difficult to directly measure the initial microstructure of fresh state suspensions, especially in concentrated suspensions systems, which have issues such as polydispersity, low-transparency, high solid volume fraction, and hydration [16]. Therefore, the internal structure of concentrated suspensions that is of special significance to the preparation processes of CPB (*i.e.* thickening, mixing, and pumping), is not fully understood [17]. Although most of the above studies were conducted in cement slurries, they contribute to our understanding of the rheology of CPB because both cement slurry and CPB are considered to be a suspension consisting of different kinds of particles suspended in a paste matrix [18].

A large amount of tailings waste accumulated at the surface during mining operations. This may cause heavy metal pollution in soils and water. To solve these problems, one of the most important technological innovations in the last two decades [19], is the technology of CPB. CPB is a mixture of fine particles, mainly superfine tailings, and cement dispersed in water, and is considered a concentrated suspension with a high solid volume concentration ($\geq$ 50 vol.%) [20]. In some reports, CPB appears to have shear thinning or/ and shear thickening, with complex rheological behavior that varies with time, temperature and shear rates, and these reports present different understandings of shear thinning and shear thickening [21, 22]. Previous studies of the rheology of CPB have inconsistently demonstrated shear thinning or shear thickening. The reason can be that they did not consider the shear history of the suspensions, such as the mixing process. The mixing of CPB is yet to be completely comprehended, as many parameters affect the properties of the resulting fresh and hardened CPB. In particular, with the application of some new mixing equipment in CPB technology, such as high shear mixers (the mixing speed exceeds 1000 rpm), the problem of mixing process becomes more complicated since an economical and efficient shear rate is difficult to determine, and it has not received enough attention [23]. When under shearing, the intrinsic network structure of CPB responds to the shear-induced stresses with the interference of interparticle forces, leading to changes in the rheological behavior [24]. Optimization of the mixing process requires detailed knowledge of the rheological properties of the paste and flow hydrodynamics. Thus, understanding the influence mechanism of mixing (shearing) on the properties of CPB is a priority for improving the mixing technique.

The main objective of this paper is to evaluate the relationship between the rheological properties and the microstructure of fresh CPB under different shear histories. This study will contribute to our better understanding of the shear history effects, which play an important role in rheological properties of CPB. The microstructure of CPB under different preparation conditions was measured by using the FBRM technique, in terms of the size distribution of particles/agglomerates, and rheological properties tested by a rheometer. The influence of polycarboxylate superplasticizer and cement content of CPB on the shear thinning and thickening behavior was presented and finally, the relationship between shear thinning, shear thickening and thixotropy of CPB was discussed.

2 Materials and methods

2.1 Materials

2.1.1 Tailings

The tailings sampled for the CPB preparation is unclassified tailings obtained from an iron mine, and the specific gravity is 2.69. It was grounded into powder below 80 μm and analyzed by X-ray Fluorescence (XRF). Chemical characteristics of the tailings are listed in Table 1. The tailings mainly consist of silicon dioxide, iron sesquioxide, calcium oxide, magnesium oxide, aluminum oxide and sulphides.

The particle size distribution is shown in Figure 1 which was tested with a Topsizer 2000 Laser Particle Characterization System made by the OMEC, Ltd., PRC. The range of measurement covers particles of 0.02 to 2000 μm,

Table 2: Characteristics of the cement.

Compound	MgO	SiO_2	Na_2O	K_2O	Al_2O_3	SO_3	Fe_2O_3	CaO
Content/%	1.40	20.70	0.18	0.48	4.50	2.60	3.30	65.10

Table 3: Mixture proportions of CPB. w/c refers to the water-to-cement ratio, whereas c/p refers to solid content volume and is the volume of cement and tailings per volume CPB.

Code	w/c	c/p	Quantity for 1 L paste			
	(by mass)	(by volume)	SP(g)	Cement (g)	Water (g)	Tailings (g)
CPB-A	3.00	0.56	0	140.00	420.00	1440.26
CPB-B	3.00	0.54	0	146.67	440.00	1380.75
CPB-C	3.00	0.52	0	153.33	460.00	1321.24
CPB-D	3.00	0.52	1.53	153.33	460.00	1321.24

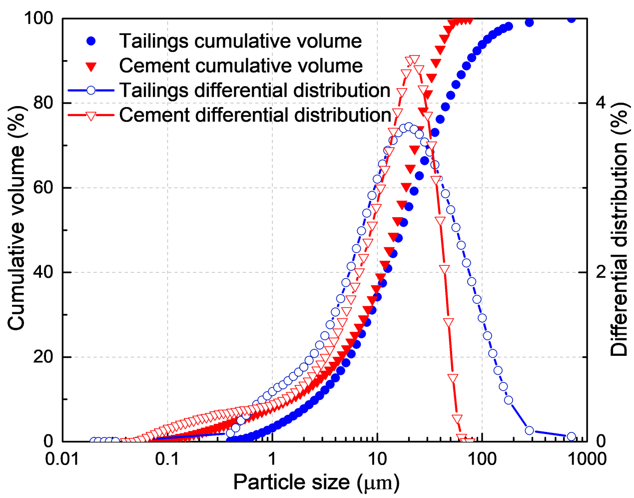


Figure 1: Particle size distribution of the unclassified tailings and cement.

with a ±1% precision. As shown in Figure 1, the tailings contain about 54 wt.% of fine particles smaller than 20 μm, 69 wt.% below 37 μm, and 87 wt.% below 74 μm, and can be classified as fine tailings [25]. Furthermore, the tailings were tested for various index properties, that is liquid limits and plastic limits, according to the American Society for Testing and Materials (ASTM) international standards [26]. From the test report, the tailings were considered as clay of high plasticity, and can be classified as CH by the Unified Soil Classification System. Categorization as CH is typical for tailings from soft rock mines as also determined by Vick [27].

2.1.2 Water, binder and additive

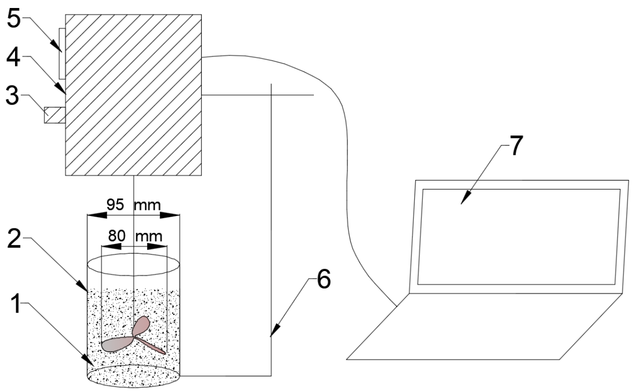
The Ordinary Portland Cement (OPC) was used as the binder, and the particle size distribution is shown in Figure 1. The oxide composition of the cement is shown in Table 2. According to the factory report, the Blaine fineness of the cement is 402 m^2/kg, the specific gravity 3.14 and the initial setting time 120 min. The utilized Type F polycarboxylate superplasticizer (SP) powder is widely used in engineering cases which is available in the market and complying with ASTM C494 [28]. Deionized water was used to mix the cement and tailings.

2.2 Mixture proportions

The CPB-A, B, C and D, was prepared at three levels of solid content, as shown in Table 3, with a constant water-to-cement (w/c) ratio of 3.0. The additive SP was added for the preparation of CPB-D at a proportion of 1 wt.% of the cement used as was advised by the production company in a range of 0.5 wt.% to 1.5 wt.%. In Table 3, the mixture proportions are shown in 1 L CPB.

2.3 Preparation of samples

In the experiment, the authors used a cement mortar mixer for initial mixing, and a high-shearing-type mixer, as showed in Figure 2, for second mixing. The velocity of latter was under control of the pre-set computer programs at an environment temperature of 20°C. As shown in Figure 2, the mixing equipment employed a beaker, a mixer, and a controled computer.



1- Fresh CPB sample; 2- Beaker; 3- Manual controller; 4- Mixer;5- Speed display; 6- Holder; 7- Control computer.

Figure 2: High-shearing-type mixer.

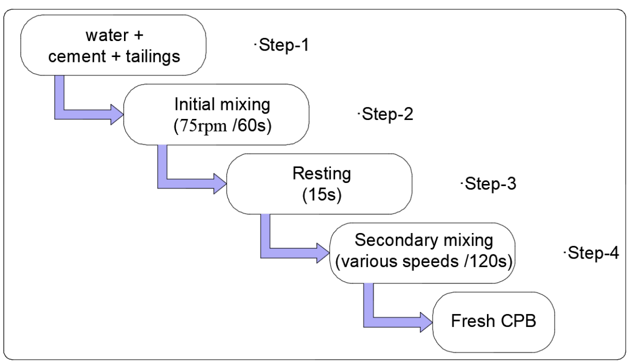


Figure 3: Mixing protocol to prepare CPB; Shear rates for Step-4 were 120, 240, 360, 480, 600, 720 s^{-1}.

Four steps of mixing were performed for the homogenization of CPB which was a simulation of the industrial mixing, as illustrated in Figure 3. In Step-2, a relatively low speed (75 rpm) was set for initial mixing, using a cement mortar mixer. In Step-4, a high-shearing-type mixer was used to produce six degrees of shear rate, 120 s^{-1}, 240 s^{-1}, 360 s^{-1}, 480 s^{-1}, 600 s^{-1}, 720 s^{-1}, which was a rotary vane approximate value [29]. The setting was to highlight the differences in the rheological behavior of CPB under different shear histories. The first three steps should be capable of fully homogenizing the paste, and Step-4 was applied to assess the effect of shear rate on the CPB.

After the sample was prepared, within a 45s resting time, the half of each sample was transferred to the rheological test and the remainder to the FBRM analysis which started 4 min after the addition of water. The rheological test was 5 minutes later than the FBRM analysis, and that is 9 min after the addition of water.

2.4 Experimental methods

2.4.1 Rheology

In order to observe rheological characteristics of the CPB samples, such as viscosity and yield stress, an R/S four-paddle rotational rheometer (Brookfield RST) was used. During the experiment, the four-paddle rotor was immersed into the slurry, spinning at various speeds to generate a range of shear rates. This process was under real-time monitoring and a shearing stress to rate curve was generated, and the flowcurves were exported by software for further analysis. The temperature of the water bath remained steady at 20°C.

The paste was poured into a beaker, 95 mm in diameter and 115 mm in height, to a level of 90 mm and thereafter the mixing rotor (VT-40-20) of the Brookfield RST was immersed into the paste and the beaker fastened. The paste was under a controlled shearing rate mode, and the shear rate increased continuously from 0 to 120 s^{-1} over 2 min via a step-up approach. A total of 120 points was obtained in the period of 120 s.

From a general view, the flow behavior of the non-Newtonian paste of unclassified tailings is generally represented by a simple relation between the shear stress τ and shear rate $\dot{\gamma}$, which includes a critical shear stress for the onset of flow [30, 31]. Hence, the rheological properties of the CPB samples have constitutive relationships that are generally described by the following Herschel–Bulkley flow model [32], shown in Equations 1, and it was used for data fitting.

$$\tau = \tau_0 + K\dot{\gamma} \qquad (1)$$

Eq. (1) represents the Herschel–Bulkley model: τ represents the shear stress, Pa; $\dot{\gamma}$ represents the shear strain rate, s^{-1}; τ_0 represents the HB yield stress, Pa; K represents the consistency index and n represents flow index.

To verify the repeatability of the test, each experiment was repeated once for each type of mixtures and the average value was adopted. For example, 12 samples were prepared for CPB-A to be mixed at six different shear rates in Step-4, with two samples for each speed and a half of each sample for rheological test and the other half for the FBRM analysis. A representative set of flow curves was reported to indicate the rheology of the paste.

2.4.2 Microstructure measurement

The real-time and field particle conditions of CPB were evaluated and the microstructure of CPB in fresh state was

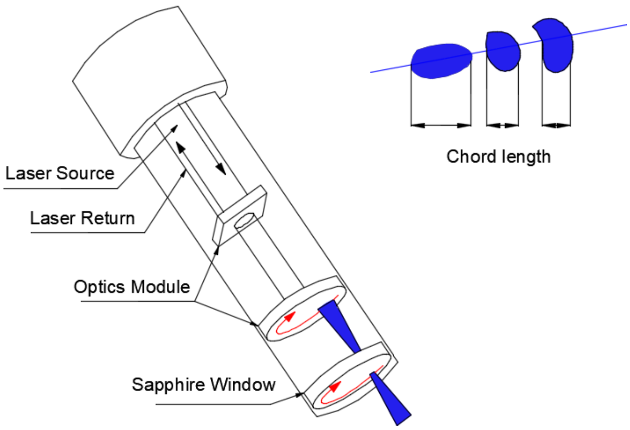


Figure 4: FBRM probe operation principle.

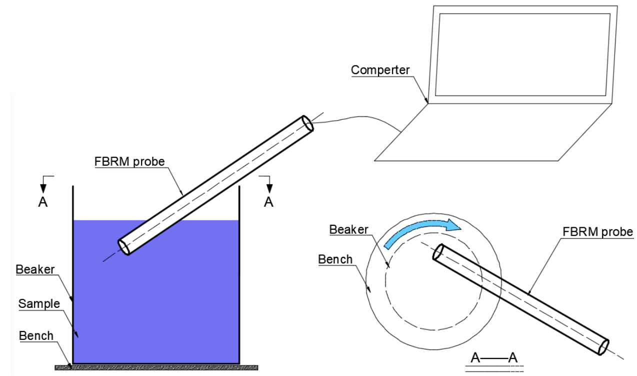


Figure 5: FBRM experiment equipment.

measured by using a focused beam reflectivity measurement (FBRM) system [33, 34]. Although a variety of technologies are capable of microstructure determination, a few could be used to observe the sampling of suspension with low light transmittance and in-situ [35, 36]. The FBRM method is advantageous and it could be applied in in-situ observation instead of diluting or sampling from CPB [37]. The FBRM reveals particle conditions, including the chord length distributions (CLD) and change of particle sizes and counts, via measuring the chord length and number of the particles [38]. During the operation of FBRM, a focused laser beam passes over the paste particles at 2 m/s with a rotating laser beam and measure the time duration of laser reflection from one edge to the other of the agglomerate in the scanning-path (Figure 4) [39]. The time is useful for calculation of the chord length of the agglomerates or particles. The mean chord length is used by the FBRM to indicate the mean particle size, $\overline{C}$, which is defined as

$$\overline{C} = \frac{\sum_{i=1}^{k} \left[\left(\frac{n_i}{\sum_{i=1}^{k} n_i} \right) M_i \right]}{\sum_{i=1}^{k} \left(\frac{n_i}{\sum_{i=1}^{k} n_i} \right)} = \frac{\sum_{i=1}^{k} n_i M_i}{\sum_{i=1}^{k} n_i M_i^0} \tag{2}$$

where $\overline{C}$ is the chord length of particle; n_i is the unweighted counts; M_i is the midpoint of an individual channel, and k is the upper channel number [40, 41]. The measurement of particle size covers a range of 0.5 to 1000 μm of the FBRM setup used in the research.

The FBRM experiment equipment is illustrated in Figure 5. The experimental setup includes the FBRM probe, a beaker that contains the CPB, a computer and an experimental bench. With the aim to improve the accuracy of the test results, the probe was placed inside the sample in a direction opposite the flow at a downward angle, and the beaker was fixed to the experimental bench and rotated at 10 rpm along with the bench, so that the probe was not sticking at one point in the sample. After prepared by the high-shearing-type mixer, a portion of the CPB was put into the beaker, and during the experiment the computer recorded every 10 seconds, and each sample was tested for 30 minutes.

3 Results and discussions

3.1 Effects of shear history on rheological properties of CPB

The relationship between yield stress and shear rate as shown in Figures 6-9 was drawn according to the measurements of the experiment (The different groups in each graph are named according to the shear rate in Step-4). Furthermore, the Herschel–Bulkley model parameters were calculated by fitting the experimental data points. The influence of shear history on rheological behaviour of CPB was presented in Table 4, and the values represented the average of two results of duplicate tests. In the subgraph of Figures 6-9, each curve corresponds to a shear rate in Step-4. The influence of shear on rheological behaviour of CPB is manifested by factors such as the aggregation mechanism and mixture composition. As expected, with an increase in solid content, CPB samples tend to reveal a higher viscosity and yield stress, but poorer flowability. A synergistic effect of shear history, solid content, and additives used appeared to control the rheological behavior of CPB, which has been proved in many researches [42, 43]. As can be seen from Table 4, when the shear history of CPB was the same, the yield stress and viscosity of the CPB rise with the increase in the solid volume concentration (an increase in solid volume concentration means a decrease in free water). CPB has different rheological parameters (apparent viscosity and yield stress) under different shear histories, and this trend is amplified in cemented paste back-

Table 4: Influence of different shear histories on Herschel-Bulkley model parameters for CPB.

Sample type	Shear history in Step-4 (s^{-1})	τ_0 (Pa)	K (Pa·s^n)	n (-)	R^2
CPB-A	120	179.75	1.510	1.00	0.97
	240	177.63	1.490	1.00	0.98
	360	174.52	1.488	0.97	0.99
	480	151.17	1.291	0.95	0.99
	600	147.97	1.239	0.90	0.99
	720	155.98	1.312	0.82	0.99
CPB-B	120	153.65	1.044	1.00	0.99
	240	152.76	0.991	0.98	0.98
	360	130.76	0.834	0.93	0.98
	480	128.89	0.739	0.90	0.99
	600	138.45	0.854	0.81	0.99
	720	145.91	0.913	0.75	0.97
CPB-C	120	137.36	0.566	1.00	0.97
	240	130.12	0.528	0.96	0.99
	360	122.73	0.405	0.88	0.98
	480	118.33	0.385	0.85	0.99
	600	133.54	0.531	0.77	0.96
	720	140.51	0.574	0.71	0.99
CPB-D	120	83.50	0.500	1.00	0.97
	240	77.80	0.450	0.92	0.99
	360	65.30	0.350	0.87	0.99
	480	70.10	0.510	0.79	0.98
	600	75.20	0.520	0.70	0.99
	720	87.80	0.542	0.67	0.99

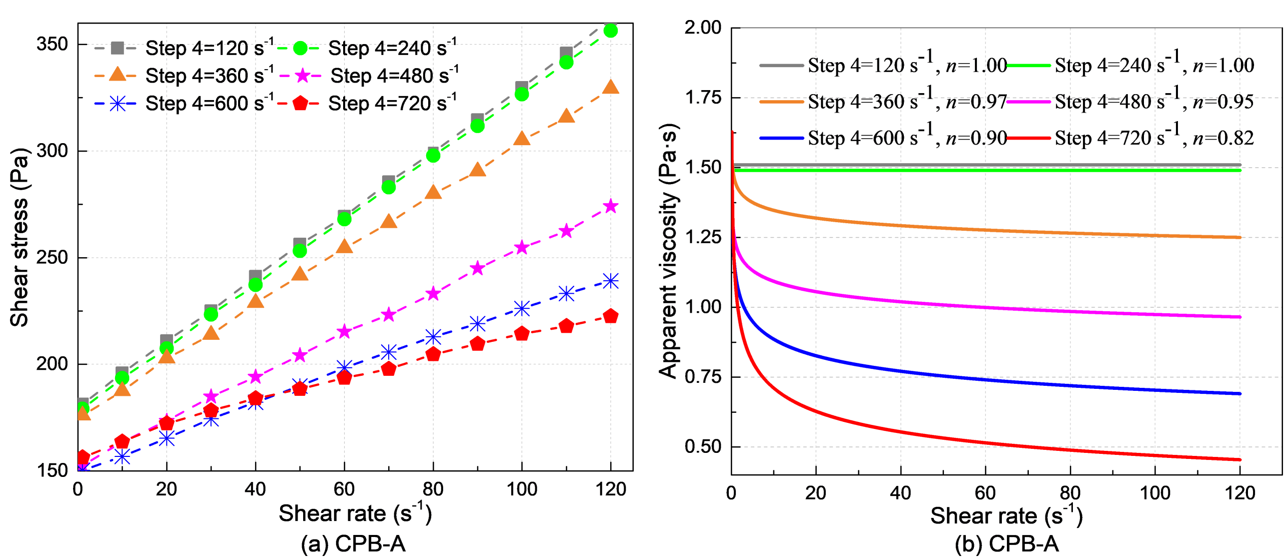


Figure 6: Effect of shear on flow curve behavior of CPB-A.

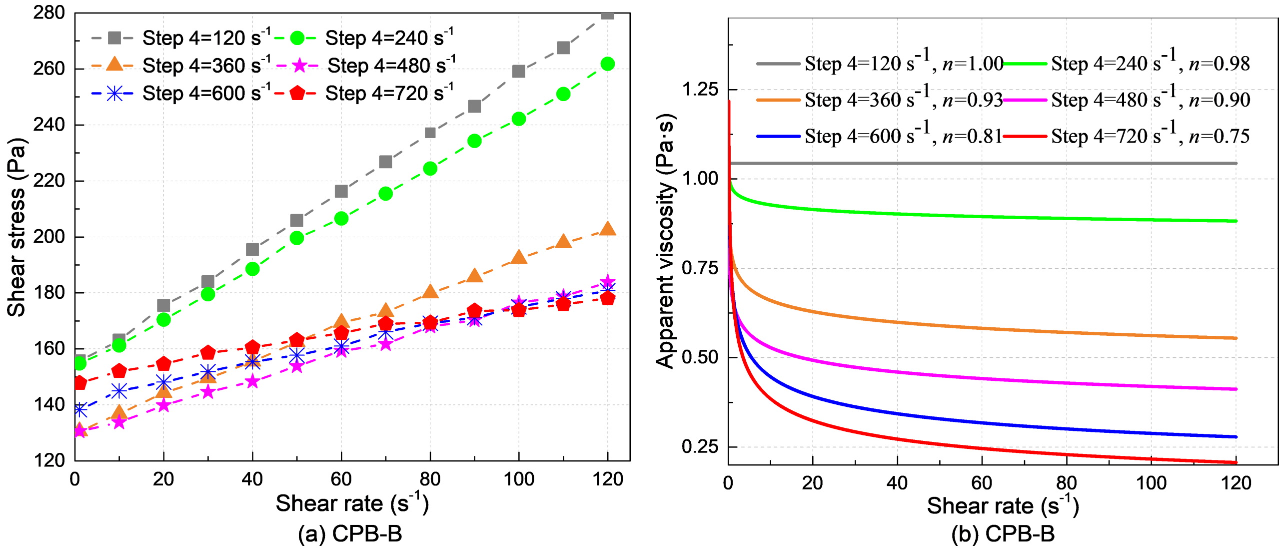


Figure 7: Effect of shear on flow curve behavior of CPB-B.

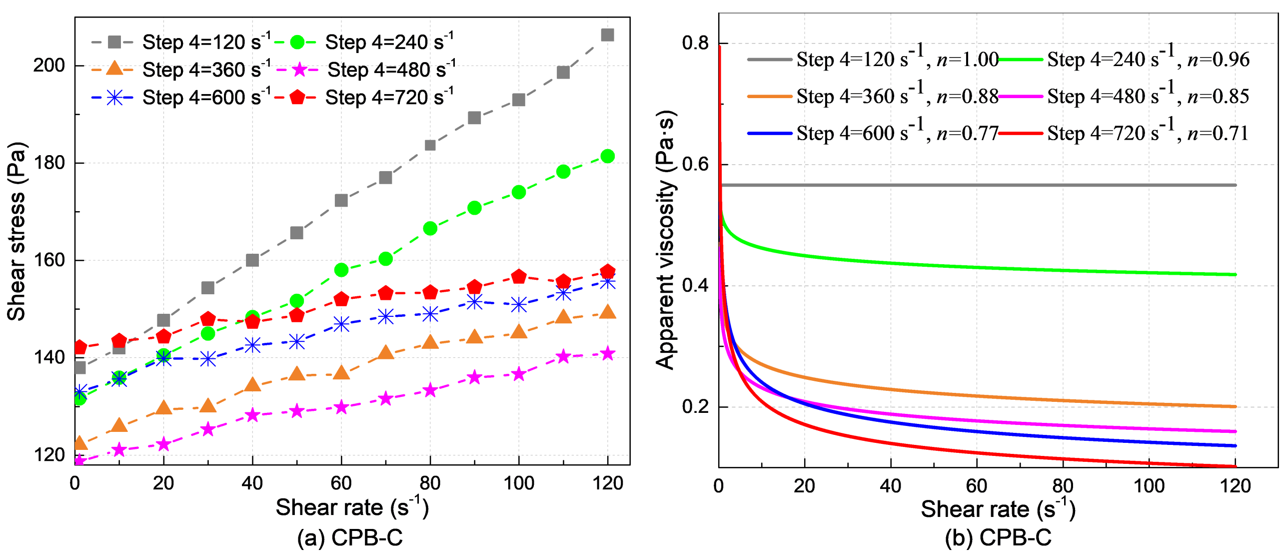


Figure 8: Effect of shear on flow curve behavior of CPB-C.

fill with increasing cement content and containing superplasticizer.

As shown in Figures 6-9, the rheological parameters of each sample did not differ significantly when the CPB was subjected to a relatively low shear rate (before reaching 240 s^{-1}). The shear history seemed to exert no effect on the rheological properties of CPB. However, when CPB underwent a more intense shear history that the shear rate in Step-4 exceeding 240 s^{-1}, the rheological parameters decreased with an increase in shear rate in some CPB samples and the paste presented shear thinning characteristics. As it was found in the field where the CPB was prepared by a higher mixing speed, and thus had better fluidity than in laboratory experiment.

On the other hand, when CPB underwent high shear rate (exceeding 480 s^{-1} in this research), the rheological parameters (yield stress τ_0 and consistency index K) generally increased and the CPB had shear thickening characteristics. Such non-Newtonian flow behavior of paste is thought to be caused by changes in particle arrangements. Compared with Newtonian fluids, such as water, the rheological behavior of CPB is complicated under different shear histories as tiny particles are suspended in the liquid.

However, the rheological curves in Figures 6-9 of all CPB samples conform to Bingham fluid or pseudoplastic fluid ($n \leq 1$), and the flow index (n) decreases under a shear history of increasing shear rate. The phenomenon

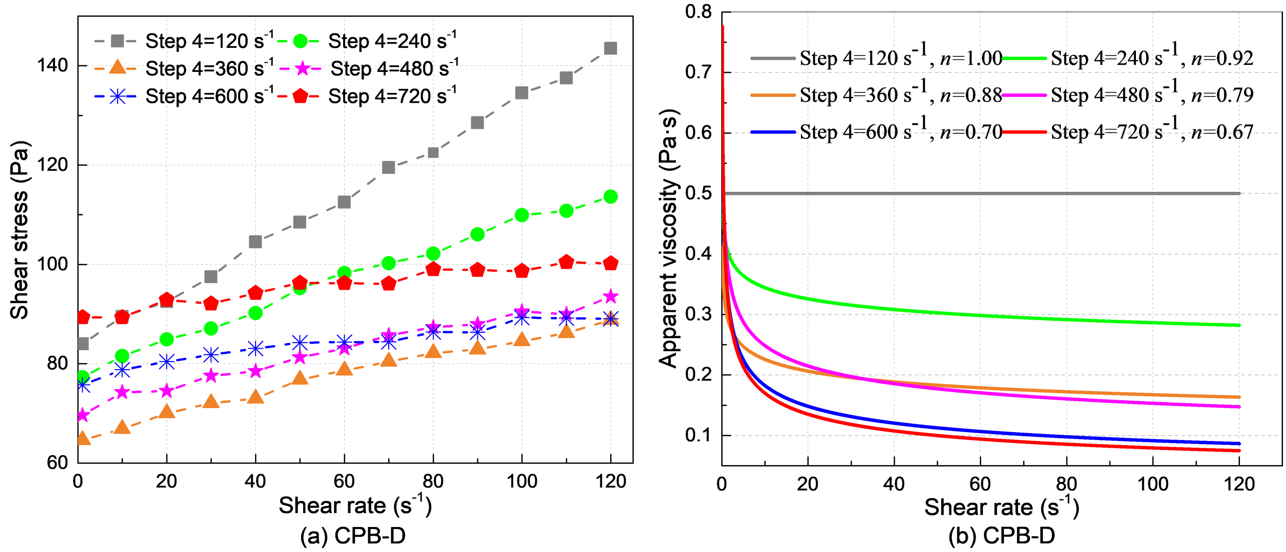


Figure 9: Effect of shear on flow curve behavior of CPB-D.

is believed to be caused by the shear action of the rheological test process which breaks the microstructure of the paste and leads to the decrease of the apparent viscosity. Therefore, it could be considered that the paste microstructure becomes more fragile after undergoing strong shear action (such as high mixing intensity). It is generally believed in some previous studies that CPB conforms to Bingham fluid [44], and it is true when the shear rate (shear history) is relatively low, but not only and not always. Previous studies of the rheology of CPB have inconsistently demonstrated shear thinning or shear thickening. One of the important reasons for these different and even opposite conclusions is that, as explained by the authors herein, the shear history effects, which play an important role in rheological properties of CPB, have been ignored.

3.2 Microstructural change of CPB

The results of FBRM test, shown in Figures 10-13, include two aspects, one is the number of particles detected in real time (see plot (a) in Figures 10-13), and the other is the average string length of agglomerates or particles (see plot (b) in Figures 10-13). It could be seen that the mean chord length of agglomerates or particles of CPB prepared with a final shear rate of 720 s^{-1} was generally longer than that of CPB produced at a less than 480 s^{-1} final mixing, and the number of particles tended to decline. In addition, the behavior of CPB with SP was different from that without when produced by different shear histories. The CPB containing SP was more sensitive to shear history as SP helped to disperse agglomerates, so CPB-D tended to contain a larger number of fine particles. This means that the samples experiencing different shear histories have different microscopic structures.

For CPB at low speed in Step-4, although the average string length of agglomerates or particles is in a relatively stable state, the experimental data obtained was relatively inconsistent because of the interference of large particles. With an increase in the shear rate (not exceeding 480 s^{-1} in this research), the particle size declined because this level of shear rate contributed to particle dispersion. A high shear rate of 720 s^{-1} in Step-4 results in a decrease in the number of particles and increase in the mean chord length of particles. Therefore, it could be revealed that under intermediate shear rate, more small particles were scattered in the CPB compared to that under a low shear rate. However, when undergoing high shear rate, the average particle size increases with time gradually, and high shear rate history promotes the flocculation of particles. Further analysis shows that the mean chord length curve first increases and then stabilizes, of which the increase process is called the agglomeration period [45]. As shown in Table 5, the agglomeration period is sensitive to the shear history.

Inspired by a method described by Ferron, the relationship between the particle size (the mean chord length) and time gradient is used to determine the agglomeration rate [46]. The agglomeration rate is used as a measure to estimate the change of the microstructure of CPB, shown in Equations 3.

$$\varepsilon = \frac{\overline{C}}{t} \tag{3}$$

Where ϵ is the agglomeration rate of CPB; $\overline{C}$ is the chord length of particle; t is the time gradient.

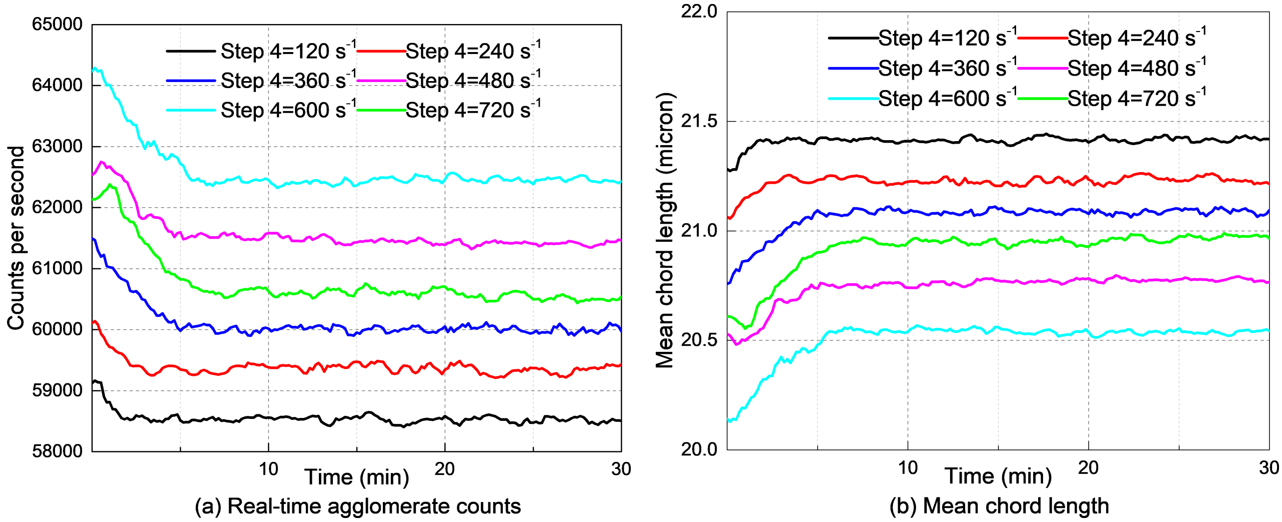


Figure 10: Effect of shear history on fresh state agglomerate condition for CPB-A.

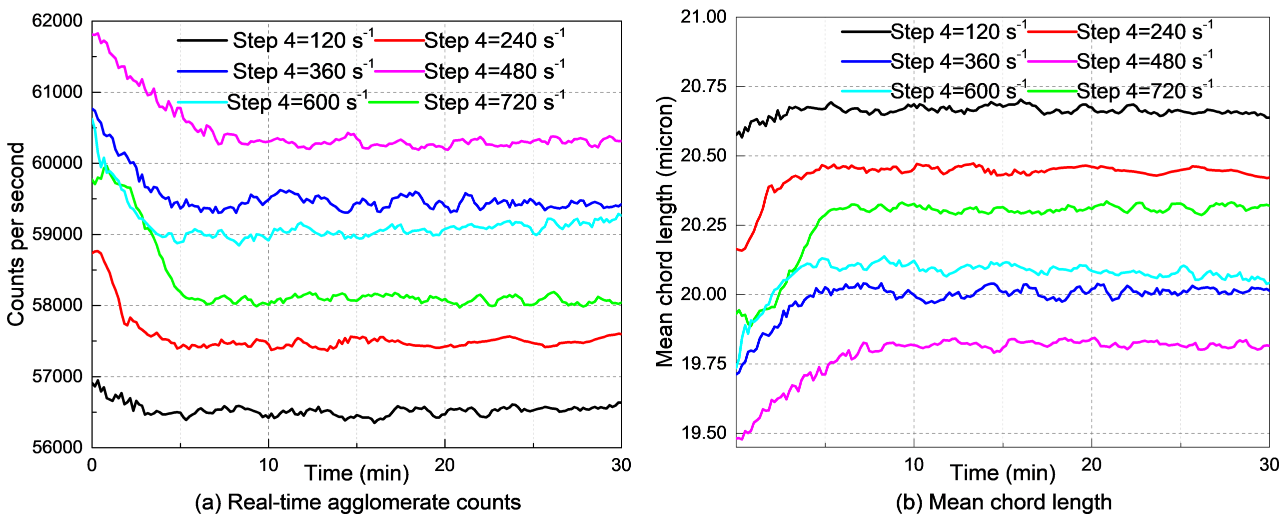


Figure 11: Effect of shear history on fresh state agglomerate condition for CPB-B.

Table 5: Influence of shear history on the agglomeration period.

Sample type	Shear history in Step-4 (s^{-1})					
	120	240	360	480	600	720
CPB-A	170±10 s	280±40 s	360±20 s	390±30 s	490±20 s	510±30 s
CPB-B	190±20 s	320±20 s	360±10 s	400±10 s	440±40 s	460±20 s
CPB-C	260±10 s	350±30 s	360±20 s	400±10 s	420±30 s	450±10 s
CPB-D	310±30 s	360±20 s	370±10 s	380±20 s	390±10 s	430±30 s

According to the description of the method, if the slopes of the agglomeration rate curves of the two samples (of same FBRM test methods and mixture compositions) are the same, we can consider that the microstructural response to the shear history is similar of the two samples. And the agglomeration rate can reflect the strength of the interaction between particles in the CPB. To make the data more precise, the agglomeration rate was calculated by using the mean chord length over a time frame (1 min in this research). The sign of the rate represents the occurrence of aggregation or breakdown, where positive signs represent agglomeration/flocculation. Based on this idea, the

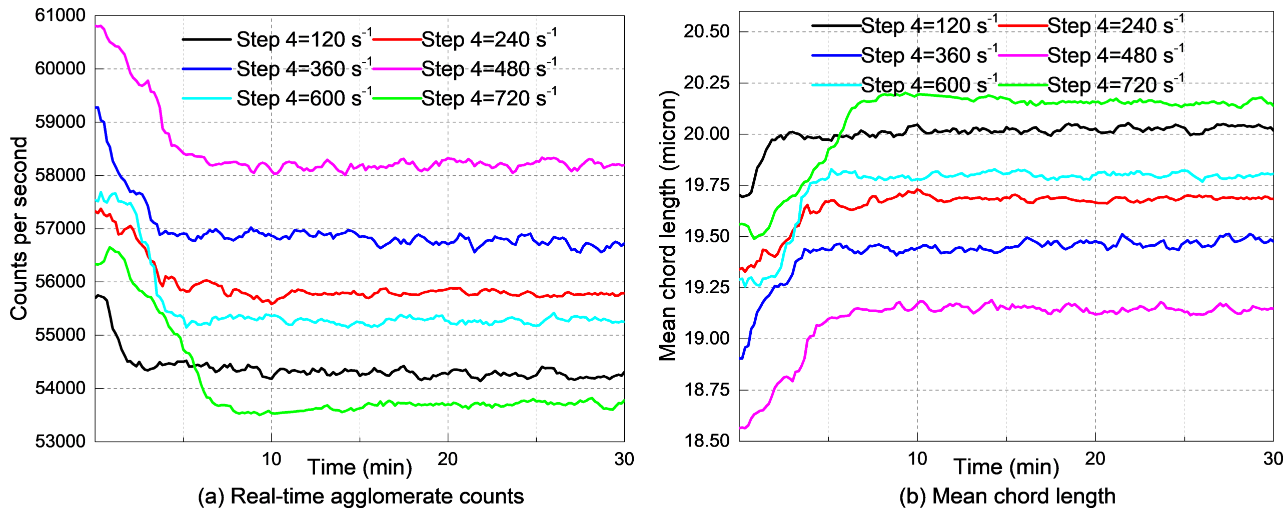


Figure 12: Effect of shear history on fresh state agglomerate condition for CPB-C.

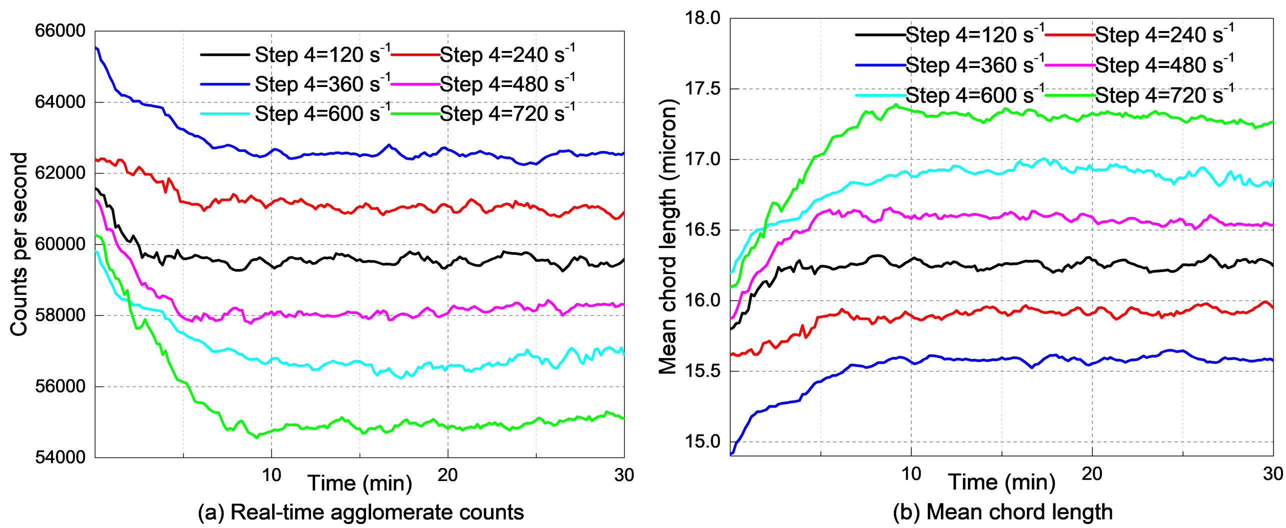


Figure 13: Effect of shear history on fresh state agglomerate condition for CPB-D.

agglomeration rate of the CPB was calculated on the results of FBRM tests at the agglomeration period, shown in Figure 14.

It could be seen that the CPB prepared at higher shear rate had stronger agglomeration. CPB-D (with SP) is more sensitive to shear history than CPB-C (without SP). But on the other hand, with an increase in the size of agglomerates, breakage is more likely to occur since the probability of finding flaws (*i.e.* weaker bonds) also increase. This mechanism induced the formation of agglomerates, and it could be seen that these large agglomerates were unable to resist breakdown under shear action during the rheology properties test. It is in accordance with the general trends shown in the rheology properties test, and is in agreement with the research of Wang *et al.* [47, 48] which observed the flowability of CPB could be improved by using plasticizer. In some literature, researchers believed that both shear thinning and shear thickening belonged to the scope of thixotropy of CPB [49, 50]. The authors herein think that this is a controversial point of view, and the microstructural differences between the two performances should be further studied to verify the viewpoint.

The non-Newtonian flow behavior of suspensions such as CPB is thought to be caused by changes in particle arrangements under different shear histories. In order to investigate this problem, some researchers have made direct measurements on particle arrangements in samples [51, 52]. For example, elegant Cornell experiment from the particle-scale revealed that the suspension rheology characteristics were due to the interaction of particles [53], and the structural changes on the other hand. It is generally believed that shear thinning is caused by the

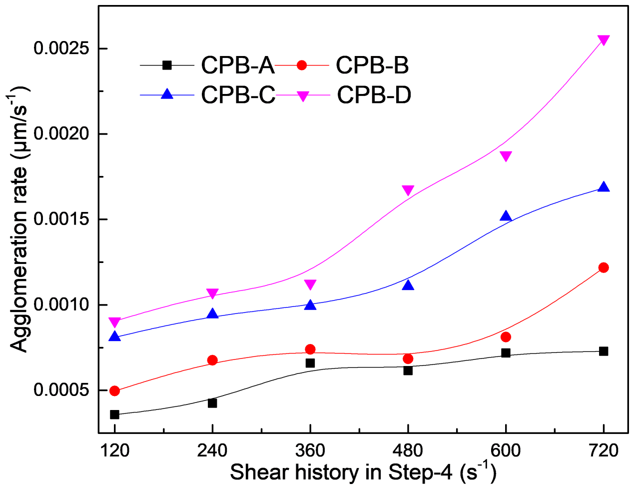


Figure 14: Approximated agglomeration rate in different CPBs prepared at different shear histories.

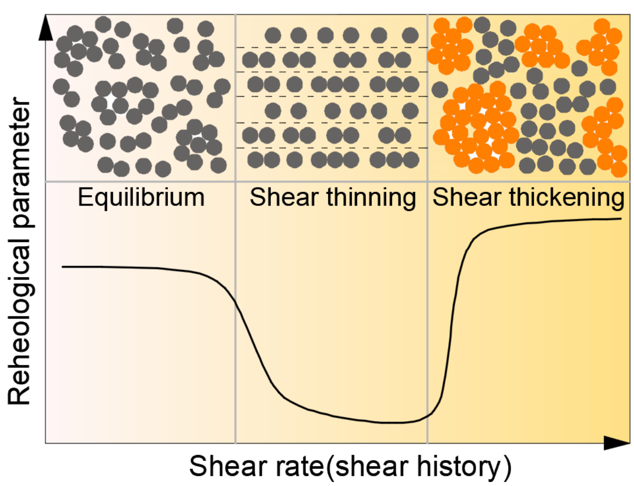


Figure 15: The change in the microstructure of CPB explains the transition to shear thinning and shear thickening. Figure based on Ref. [55].

attraction between particles, steric (solid particle) repulsion and electrostatic potential, and shear thinning can occur in CPB suspensions with a microstructure that is either loose interconnection (attractive forces of interparticles) or random [54]. The sketch of shear thinning and shear thickening for CPB suspensions is shown in Figure 15, the microstructure evolution of CPB gives explanation to the transitions to shear thinning and shear thickening. With an increase in the shear rate of shear history, agglomeration is dispersed into smaller particles and random collisions among particles become organized in the shear flow, reducing the yield stress and viscosity.

However, the rheological parameters do not always decrease with the increase of shear rate. On the contrary, when the shear rate exceeds a certain threshold value, the rheological parameters gradually increase due to shear thickening. Although this kind of phenomenon rarely occurs in conventional mixing methods, sufficient attention should be paid to the problem of excessive mixing, especially when high shear mixers are used [56]. Researches have shown that the chemical and physical qualities of the suspension system changed once the shear history differed [57, 58]. Intense shear of CPB promoted the aggregation (red, in Figure 14) of particles. Dongyeop Han *et al.* believe that this is related to the shrinking electric layer of particle, which increases the interaction between particles [59]. On the other hand, strong shear thickening in CPB can result in a nearly discontinuous jump (a few orders of magnitude) in rheological parameters, also known as the shear-blocking phenomenon, which was found in some rheological tests [60]. This has been attributed to that particles in a strong flow are difficult to flow around each other and push against boundaries. One outstanding question is whether there is any connection between the shear blocking and shear-induced network structure for shear thickening. A possible speculation is that aggregations (red, in Figure 15) of particles eventually become big enough to stride leap the system and jam.

In this research, the shear rate of mixing of CPB (no SP) is considered to be acceptable between 240 s^{-1} and 480 s^{-1}. Below 240 s^{-1} or above 480 s^{-1} is considered to be a low shear rate or a high shear rate. Shear-induced flocculation in concentrated suspensions is a well-studied and known phenomenon [61, 62]. This is especially common in weakly stabilized dispersions, hence shear history may disperse weak network structures in suspension, then applied shear causes agglomeration and shear thickening. The shear history is an important factor affecting the rheological characteristics of CPB. Therefore, the variation between shear thinning, Newtonian and shear thickening is regarded to be related to the evolution of particle arrangements. It needs to be specially pointed out that whether shear thinning belongs to a kind of thixotropic phenomenon is not the goal of this study (this kind of phenomenon is reversible). Instead, it can be confirmed that shear thickening of CPB is related to the shrinkage of the electric double layer, which is an irreversible change, so a possible speculation is that the shear thickening of CPB may not be a thixotropic phenomenon. This hypothesis remains to be directly proven by more experiments in further researches, for instance, zeta potential measurements.

4 Conclusion

The effect of the shear history on the microstructural development and rheological behavior of CPB was evaluated using FBRM and rheometer. The results of this study can help us to understand the mechanism of shear history effects on the rheological behavior of CPB. The evolution of particle arrangement of paste is the key to explaining the complex rheological behavior. The shear history of the sample must be fully considered when studying the rheological behavior of CPB. Besides, regardless of the shear rate of sample preparation, the CPB with SP tended to be more sensitive to the shear history than that without SP.

CPB as a particularly concentrated suspension may present several kinds of rheological behaviors, depending on material properties and the shear history. Shear thinning is caused by the attraction between particles, steric (solid particle) repulsion and electrostatic potential; and shear thinning occurs in CPB suspensions with microstructure that is either loose interconnection or random. With an increase in shear rate (the shear rate between 240 s^{-1} and 480 s^{-1} in Step-4 in this research), random collisions among particles come to being organized in the flow, lowering the yield stress and viscosity (shear thinning), and it is advantageous for pipe transportation of CPB.

Higher shear rates (shear rate higher than 480 s^{-1} in Step-4 in this research), promote the aggregation of particles. The average string length of agglomerates or particles in the sample increases with time and a surge in yield stress and viscosity of CPB (shear thickening). Although this is not a common phenomenon in CPB technology, sufficient attention should be paid to the problem of over mixing, especially when high shear mixers are used.

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