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The Influence of Chemical Admixtures on the Fluidity, Viscosity and Rheological Properties of Ultra-High Performance Concrete

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ABSTRACT

To achieve higher strength and better durability, ultra-high performance concrete (UHPC) typically employs a relatively small water-binder ratio. However, this generally leads to an undesired increase in the paste viscosity. In this study, the effects of liquid and powder polycarboxylate superplasticizers (PCE) on UHPC are compared and critically discussed. Moreover, the following influential factors are considered: air-entraining agents (AE), slump retaining agents (SA), and defoaming agents (DF) and the resulting flow characteristics, mechanical properties, and hydration properties are evaluated assuming UHPC containing 8‰ powder PCE (PCE-based UHPC). It is found that the spread diameter of powder PCE is 5% higher than that of liquid PCE. Among the chemical admixtures studied, AEs have the best effect on improving UHPC workability, while DFs have the worst effect. When the addition of AE and SA is 1.25‰ and 14.7% of PCE, paste viscosity reduces by 35% and 19%, respectively compared to the paste with only 8‰ PCE. A low AE dosage (1.25‰) decreases compressive strength by 4.1%, while SA (8.1%) increases UHPC compressive strength by 9.1%. Both AE and SA significantly delay the UHPC hydration process, reducing the hydration heat release peaks by 76% and 27%, respectively.

KEYWORDS

Ultra-high performance concrete; polycarboxylate superplasticizer; air-entraining agent; slump retaining agent; rheological properties

List of Abbreviations

UHPC	Ultra-high performance concrete
PCE	Polycarboxylate superplasticizer
AE	Air-entraining agent
SA	Slump retention agent
DF	Defoamer agent
PCE-based UHPC	UHPC with 8‰ powdered PCE
VMA	Viscosity-reducing admixture
WP	Liquid PCE
PP	Powder PCE



1 Introduction

Concrete was an essential and highly sought-after building material in the construction and civil engineering sectors [1,2]. However, as construction engineering advances, the performance of traditional concrete no longer satisfies the requirements for certain applications [3]. In response, ultra-high performance concrete (UHPC) was developed as a new type of concrete with extremely high compressive strength (exceeding 120 MPa), flexural strength (exceeding 10 MPa), and excellent durability [3]. UHPC has a porosity of less than 1% and typically includes steel fibers to enhance its mechanical properties [4]. These attributes made UHPC an ideal material for long-span bridges [5], high-rise buildings [6], marine engineering [7], railway engineering [8], and structures with specific functions [9,10]. Compared to conventional concrete, UHPC's low water-binder ratio (800 kg/m³) and its multi-scale fine-grained mixture design (with a bulk density of 0.825 to 0.855 N/m³) ensure a dense microstructure, thereby reducing matrix porosity [11–13]. The difference in UHPC's material composition resulted in significantly higher viscosity than that of conventional concrete [14].

The rheological properties of UHPC significantly affected the dispersion and arrangement of matrix particles, influencing their mechanical properties and durability [15]. These properties determined the ease with which cement-based materials can be pumped, formed, and consolidated [16]. UHPC paste typically exhibited shear-thickening behavior [1]. An increase in viscosity can lead to poor UHPC consolidation, resulting in pore defects and affecting overall performance [15]. Semendary et al. [17] demonstrated that when the plastic viscosity was less than 200 Pa·s and the dynamic yield stress was less than 400 Pa, the mixture exhibited good fluidity and pumpability. Yahia [18] evaluated the rheological behavior of high-performance paste mixtures and found a nonlinear relationship between shear stress and strain rate.

Existing research on UHPC indicates that paste rheological properties can be adjusted by modifying the amount of admixture [19–23]. The type of admixture also has an effect on the flow performance of UHPC paste [23–27]. Table 1 shows the influence of different admixture types on concrete flow performance. Polycarboxylate ether (PCE) can improve UHPC paste flow ability, rheology and workability by reducing the water-binder ratio [3]. Compared to other liquid admixtures, PCE has a high water-reducing capacity and excellent dispersibility [28]. Additionally, PCE's molecular structure allows more stable adsorption on cement particle surfaces and good compatibility with different binder materials [29]. Studies found combining two PCEs can reduce the required PCE dose to achieve the same fluidity [28]. Notably, gradually adding PCE can significantly improve its dispersion effect, increasing UHPC fluidity [4]. Some studies have also used viscosity-modifying admixtures (VMAs) to adjust UHPC matrix rheological properties [30]. VMAs maintain low flow resistance by increasing cement pore solution zero shear viscosity and forming associative structures [31]. Sonebi et al. [32] showed that VMAs exhibit shear thinning behavior at low shear rates but shear thickening behavior at high shear rates. However, at a certain PCE amount, increasing VMA dosages can significantly improve UHPC fluidity [32].

Table 1: Influence of different types of chemical admixtures on the slump of high-performance concrete

	Admixture type	W/C	Dosage added (%)		Spread diameter (mm)	Ref.
			Admixture	Fiber		
Fiber-based	PCE-HRWR	0.18	2.00	1.00	185 ± 5	[25]
				2.00	160 ± 5	
				3.00	133 ± 5	
		0.25	1.80	2.0	235 ± 5	[22]

(Continued)

Table 1 (continued)					
Admixture type	W/C	Dosage added (%)		Spread diameter (mm)	Ref.
		Admixture	Fiber		
PCE-HRWR+SRA	0.25	P (1.80)+S (1.00)		245 ± 5	
		P (1.80)+S (2.00)		240 ± 5	
PCE-HRWR	0.18	0.83	2.40	120 ± 5	[26]
SRA		1.00		135 ± 5	
SRA+EA		S (1.00)+E (7.50)		155 ± 5	
PCE-HRWR	0.25	1.5	2.0	215 ± 5	[27]
PCE-HRWR+EA	0.25	P (1.50)+V (2.00)		191 ± 5	
Non-fiber-based PCE-HRWR	0.24	0.10		60 ± 5	[19]
		0.20		312 ± 5	
		0.26		127 ± 5	
		0.20		328 ± 5	
		0.20		210 ± 5	
		2.00		345 ± 5	
PCE-HRWR+VMAs	0.20	P (0.17)+V (0.05)		200 ± 5	[21]
		P (0.24)+V (0.14)		200 ± 5	
		P (0.22)+V (0.27)		200 ± 5	
		P (0.54)+V (0.81)		200 ± 5	
SRA	0.20	0.25		570 ± 5	[23]
PCE-HRWR+SRA	0.20	0.25		585 ± 5	
SRA	0.3	0.50		620 ± 5	[24]
		1.00		605 ± 5	
EA	0.3	5.00		655 ± 5	
		10.00		680 ± 5	

Note: PCE-HRWR is the polycarboxylate ethers high-range water reducer, SRA is shrinkage-reducing admixtures, EA is expansive agents, VMAs is viscosity modifying admixtures and P (1.80)+S (1.00) is mixed with 1.80% PCE-HRWR and 1.00% SRA.

The synergistic effect between chemical admixtures was an important consideration [33]. Nehdi et al. [34] observed that adding admixtures further improves the rheological properties of cementitious materials mixed with PCE, compared to those prepared with PCE alone. When PCE and VMA in combination for UHPC, their concentrations needed optimization to obtain the best rheological properties [35]. Additionally, the combination of VMA and PCE can provide varying degrees of robustness [36]. Fares et al. [37] found that the effect of PCE and VMA in the cement matrix depended on their order of addition and the critical PCE/VMA ratio. When VMA was added first, paste fluidity mainly depended on the water-binder ratio. When VMA was added after PCE, the paste flow affected significantly improved. Yin et al. [38] discussed the feasibility of grouting with waste glass powder (WGP), PCE, and VMA. The fresh state of cement-based materials was closely related to the WGP, PCE, and VMA dosages. When the WGP, PCE, and VMA dosages were 15%, 0.115%, and 0.03%, respectively, the pseudoplastic index was the smallest. Huang et al. [39] introduced a rosin resin-type air-entraining agent based on PCE and VMA.

With increasing PCE and AE dosages, the plastic viscosity of self-compacting concrete gradually decreases. Lazniewska-Piekarczyk [40] analyzed the effects of air-entraining admixtures, PCE, and VMA, highlighting that the VMA type affects the fluidity of high-performance self-compacting concrete. Although different admixture types can improve the rheological properties of cement-based materials, a research gap exists in their application effects and synergistic improvement effects on UHPC [41,42].

In this study, the effects of powder and liquid PCE on UHPC paste rheological properties were compared and powder PCE was selected to prepare low-viscosity and high flow UHPC with air-entraining agents (AE), defoaming agents (DF) and slump retaining agents (SA), respectively. The effects of PCE, AE, SA and DF dosages and mixed types on flow properties, viscosity, rheological properties, mechanical properties and hydration process were studied. This study is expected to provide a theoretical reference for designing and preparing low-viscosity and high-flow UHPC admixtures.

2 Raw Materials and Test Methods

2.1 Raw Materials

The cementitious material employed in this study was sourced from Wuhan Huaxin Cement Co., Ltd. (China), and its chemical composition is detailed in Table 2. The aggregate used was quartz sand, acquired from Wuhan, Hubei. The superplasticizer utilized in this study was a polycarboxylate superplasticizer (PCE), purchased in Wuhan, Hubei Province. Two forms of PCE are depicted in Fig. 1. The water-reducing rates of the PCE is presented in Table 3, with the liquid PCE exhibiting a water-reducing rate of 30.1% and the powder PCE achieving a rate of 52%. The air-entraining agents (AE), slump retaining agents (SA), and defoaming agents (DF) used in this study were all manufactured in Wuhan City, Hubei Province. The AE was anionic surfactant; the SA was polycarboxylate-based slump retaining agent; and the DF was polyether-based defoaming agent.

Table 2: Chemical composition of PCE (wt%)

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	TiO ₂	Na ₂ O	MnO
PC	58.22	25.03	6.36	3.18	2.39	2.29	0.98	0.471	0.448	0.128

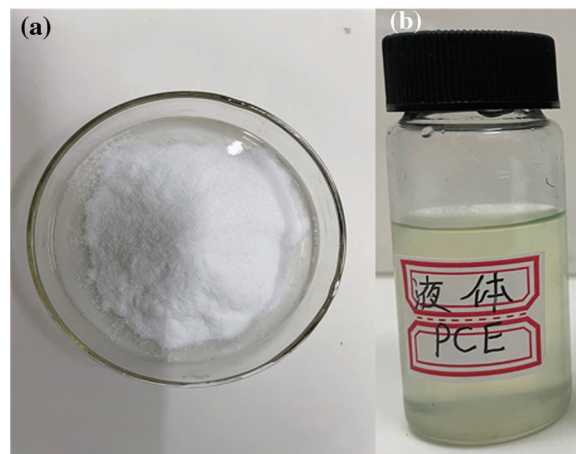


Figure 1: Two different forms of PCE. (a) Powder and (b) Liquid

Table 3: Chemical parameters of PCE

	Cl ⁻ (%)	Alkali content (%)	Water reducing rate (%)
Liquid PCE	0.03	3.75	30.1
Powder PCE	–	–	52

2.2 Mix Proportion Design of PCE and Admixture System

The quality of the solid and UHPC admixtures used in this study is presented in Tables 4 and 5. For all mixtures, the mass ratios of water to binder (w/b) and binder to quartz sand were maintained at 0.175 and 1.1, respectively [43,44]. The total water used consisted solely of tap water. The w/b ratio was kept at 0.175 to investigate the diffusion flow, slump, hydration kinetics, and strength of the paste [45]. The dosage of PCE was determined based on the binder mass, while the dosages of the other additives were based on the PCE mass [46]. The paste was mixed for approximately 8 min using a 5-liter mixer. The mixing procedure included 30 s of dry mixing, followed by 180 s for adding the chemical admixtures and water, then 150 s of mixing at low speed, and finally 120 s at medium speed [45].

Table 4: The UHPC mix ratio with different forms of PCE

Sample	Binder (g)	Quartz sand (g)	Water (g)	Powder PCE	Liquid PCE
PP-0	1000	909.1	175	6‰	–
PP-1	1000	909.1	175	8‰	–
PP-2	1000	909.1	175	10‰	–
WP-0	1000	909.1	175	–	6‰
WP-1	1000	909.1	175	–	8‰
WP-2	1000	909.1	175	–	11‰

Note: “PP” and “WP” represent powder PCE (PP) and liquid PCE (WP), respectively. The “0” and “1” indicate that the dosages of PCE is 6‰ and 8 ‰, respectively. “PP-2” and “WP-2” represent the dosages of 10‰ powder PCE and 11‰ liquid PCE, respectively.

Table 5: Different types of admixture UHPC mix ratio

Sample	Binder (g)	Quartz sand (g)	Water (g)	PCE (g)	AE (g)	SA (g)	DF (g)
Re	1000	909.1	175	8	–	–	–
AE-1	1000	909.1	175	8	0.01	–	–
AE-2	1000	909.1	175	8	0.03	–	–
AE-3	1000	909.1	175	8	0.05	–	–
SA-1	1000	909.1	175	7.575	–	0.425	–
SA-2	1000	909.1	175	7.4	–	0.6	–
SA-3	1000	909.1	175	7.175	–	0.825	–
SA-4	1000	909.1	175	6.975	–	1.025	–
DF-1	1000	909.1	175	7.95	–	–	0.05
DF-2	1000	909.1	175	7.9	–	–	0.1
DF-3	1000	909.1	175	7.85	–	–	0.15

1) The UPHC mix proportion design of different forms of PCE

To assess the impact of different forms of PCE on the viscosity and strength of UHPC, we initially investigated the influence of powder and liquid PCE on the properties of UHPC paste. The specific ratios are detailed in [Table 4](#). The dosages of powdered PCE were established at 6‰, 8‰, and 10‰ of the cement mass, while the dosages of liquid PCE were set at 6‰, 8‰, and 11‰ of the water mass. An experimental group with an 8‰ dosage of PCE was designated as the control group.

2) The UPHC mix proportion design of chemical admixtures

Based on the PCE tests, we carried out chemical admixture tests, with specific combinations shown in [Table 5](#). We selected the air-entraining agent (AE), slump retaining agents (SA) and defoaming agents (DF) for this study. The AE dosages were set at 1.25‰, 3.75‰ and 6.25‰ of the PCE mass. The SA was added to replace the PCE, with substitution masses of 0.425, 0.6, 0.825 and 1.025 g, respectively. The DF was mixed internally to replace the PCE, with masses of 0.05, 0.1 and 0.15 g, respectively. The experimental group with an 8‰ powder PCE dosage served as the control group.

2.3 Specimen Preparation Methods

The concrete block forming method adhered to the Chinese standard GB/T 50080-2016 [47]. The paste test block preparation followed the requirements of GB/T 8007-2000 [48]. All test blocks were placed in a standard curing room (20°C, 95% humidity) for 24 h. Subsequently, the molds were removed and the blocks continued curing until the designated testing age.

2.4 Test Methods

2.4.1 Compressive Strength

For the compressive strength test, specimens measured 100 mm × 100 mm × 100 mm, with a loading rate of 1.2 to 1.4 MPa/s. Six specimens with the same mix ratio were tested for compressive strength, with the average value taken as the final result [49]. The deviation between the measured and average values did not exceed 15% and the final result was accurate to 0.1 MPa.

2.4.2 Fluidity

The slump test was conducted using a slump cylinder with a base diameter of 100 mm, a top diameter of 200 mm and a height of 300 mm [19]. The test site was ensured to be dry and debris-free. Concrete was filled in three layers, each compacted by vibrating 25 times with a rod from the outside to the inside along the cylinder wall. The surface was flattened using a funnel to ensure smoothness. Afterward, the cylinder was lifted, allowing the concrete to collapse. The slump was calculated by subtracting the height of the highest concrete point from the cylinder height (300 mm).

2.4.3 Viscosity Test

Due to the high viscosity characteristics of UHPC, this study innovatively applied the asphalt viscosity test method, using Brookfield viscosity as the characterization index. The largest rotor (No. 6) was selected and the speed was fixed at 20 rpm to ensure test accuracy and comparability.

2.4.4 Rheological

The rheological properties were tested using an RST-SST touchscreen rheometer (Bolefeld Company, USA). Instrument parameters were: torque 100 mN·m, torque resolution 0.15 μN·m and a rate range of 0.01–1300 rpm. The paste was tested at a constant shear rate, sheared at 100 s⁻¹ for 480 s and then stopped [50]. Results were fitted using the Herschel-Bulkley model, as shown in [Eq. \(1\)](#).

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (1)$$

where τ represents the shear stress, τ_0 denotes the yield stress, K is the consistency coefficient, γ is the shear rate and n is the flow index.

2.4.5 Hydration Heat

Isothermal calorimetry analysis of the mixture was performed at 20°C using a TAM Air isothermal calorimeter. A total of 8 g of paste samples were uniformly stirred and injected into a sealed plastic ampoule, then measured for 120 h.

3 Results and Discussion

3.1 Flowability of UHPC Paste

3.1.1 Different Forms and Dosage of PCE

Fig. 2 depicts the effects of different types and concentrations of polycarboxylate Ether (PCE) on the fluidity of UHPC paste. It can be observed from Fig. 2 that powder PCE (PP) significantly improved the fluidity of fresh UHPC paste compared to liquid PCE (WP), suggesting that powder PCE was more suitable for the UHPC material system studied. When the flow time was 30 s, the fluidity measurements for the PP-6%, PP-8%, PP-10%, WP-6%, WP-8% and WP-11% paste was 280, 287, 295, 265, 271 and 285 mm, respectively. It was evident that increasing the PCE dosages gradually enhanced the fluidity of UHPC. Both excessively low and high fluidity can negatively impact the performance of building structures. Therefore, for further studies on the influence of air-entraining agents (AE), slump retaining agents (SA) and defoaming agents (DF) on the basic properties of UHPC, PP-8% was chosen as the control group.

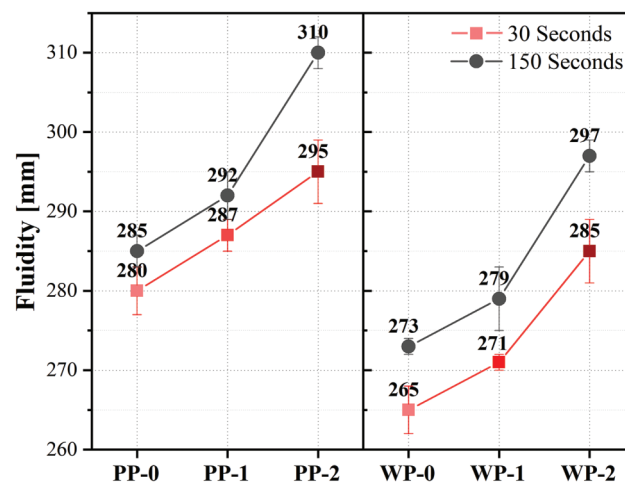


Figure 2: The influence of different forms and dosages of PCE on the fluidity of UHPC paste

3.1.2 Different Dosages of AE, SA and DF

Fig. 3 depicts the effect of AE on the fluidity of UHPC paste. Upon adding AE, the fluidity initially increased and then decreased, but all experimental groups exhibited higher fluidity than the control group, particularly AE-1, which increased by 9.4% in fluidity. Low-dosage AE significantly enhanced the fluidity of the paste by introducing tiny bubbles, reducing direct particle contact and facilitating flow [24]. However, excessive AE can cause paste agglomeration, reducing fluidity.

Fig. 4 demonstrates the effect of SA on the fluidity of UHPC paste. After adding SA, fluidity initially decreased and then increased. Compared to the control group, the fluidity of SA-2 decreased by 4.3%. With increased SA dosages, fluidity rose, particularly in SA-4, which was 6% higher than the control group. Both

SA and PCE operate in a similar manner in cementitious materials, facilitating the dispersion of cement particles and inhibiting aggregation through electrostatic repulsion, steric hindrance, and hydration control [51–53]. Additionally, slump retaining agents commonly include retarders that prolong concrete setting time [52].

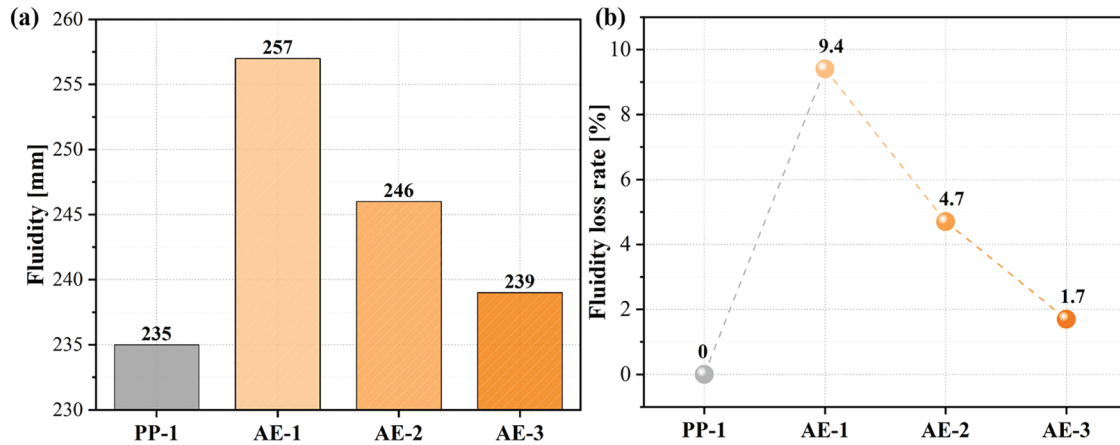


Figure 3: The influence of air-entraining agents (AE) on (a) fluidity and (b) fluidity loss ratio of UHPC paste

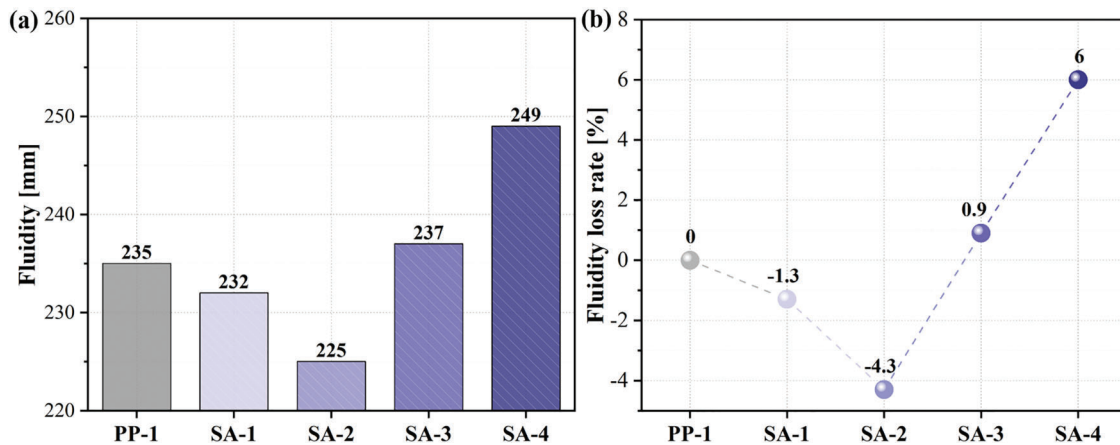


Figure 4: The influence of slump retaining agents (SA) on (a) fluidity and (b) fluidity loss ratio of UHPC paste

Fig. 5 depicts the effect of DF on the fluidity of UHPC paste. The fluidity progressively decreased with the addition of DF. The fluidity measurements for the control, DF-1, DF-2 and DF-3 were 235, 230, 224 and 217 mm, respectively. DF-3 exhibited a 7.7% decrease in fluidity compared to the control group, indicating a significant negative effect. The low surface tension of DF reduced the air content and enhanced the friction between paste particles, thereby diminishing fluidity [54].

Based on these findings, DF had the most substantial negative impact on UHPC paste performance. Lower dosages of AE were found to improve fluidity, while higher dosages of SA had an effect similar to

that of lower dosages of AE. Consequently, in subsequent work, we focused on the effects of the AE and SA on the basic properties of UHPC.

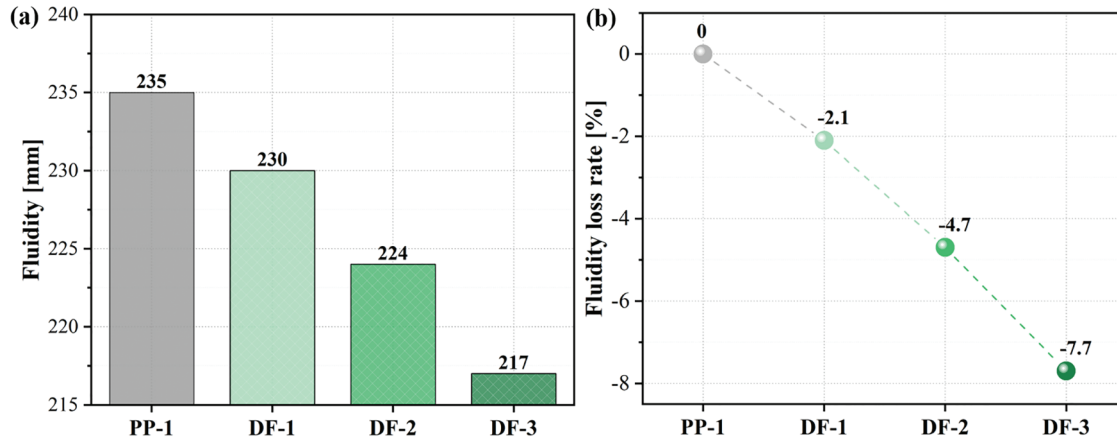


Figure 5: The influence of defoaming agents (DF) on (a) fluidity and (b) fluidity loss ratio of UHPC paste

3.2 Viscosity Properties of UHPC Paste

3.2.1 Different Dosages of PCE and AE

To assess the effect of additives on UHPC viscosity, we tested the viscosity of UHPC paste. Fig. 6 illustrates the impact of PCE and AEs on UHPC viscosity. Fig. 6a indicates that powder water reduces markedly decrease UHPC viscosity. Fig. 6b demonstrates that increasing the dosage of AE initially led to a decrease in viscosity, followed by an increase. All experimental groups exhibited lower viscosity than the control group, with AE-1 achieved a 35% reduction. Zhang et al. [55] reported that incorporating 10% of 4 μm limestone powder decreased UHPC plastic viscosity by 22.8%, while Li et al. [56] found that adding 15 wt% bentonite increased it by 16%. The dosage of AE enhanced surface adsorption and foam height, thereby improving dispersibility. Nonetheless, excessive AE increased paste air content, raising viscosity due to increased contact area between paste particles [31].

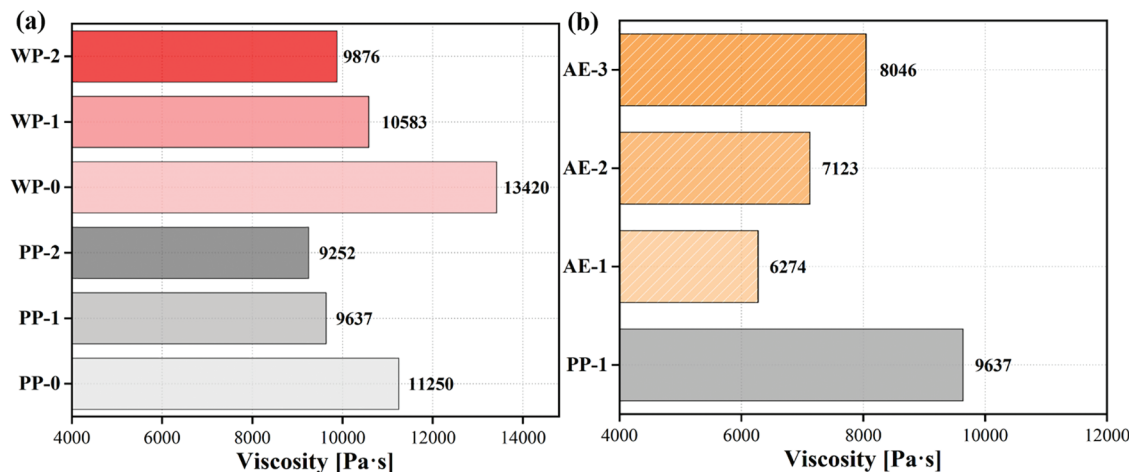


Figure 6: The influence of (a) PCE and (b) air-entraining agents (AE) on the viscosity of UHPC

3.2.2 Different Dosages of SA and DF

Fig. 7 displays the influence of SA and DF on the viscosity of UHPC paste. As shown in Fig. 7a after adding SA, the viscosity of UHPC paste showed a trend of increasing first and then decreasing [51]. The viscosity of SA-2 increased by 7.5% compared with the control group, while the viscosity of SA-4 decreased by 18.7% compared with the control group. The addition of higher dosages of SA significantly reduced the viscosity of UHPC paste. This effect can be attributed to the high dosages of SA, which facilitate the redispersion and dilution of fine powder agglomerates in the concrete, thereby lowering the viscosity of the UHPC paste. This observation aligns with the trend of paste fluidity changes observed after the addition of SA [57]. As shown in Fig. 7b, the viscosity of UHPC paste increased after adding DF and the viscosity values of all test groups were higher than those of the control group. With the increase of DF dosages, the viscosity of UHPC paste continued to increase, especially in the DF-3, where the viscosity reached 14,526 Pa·s, which was 51% increase over the control group. The addition of DF had a pronounced negative effect on the viscosity of the paste. The primary function of DF was to reduce the air content in the concrete, which increased the contact surface between the paste, enhanced the cohesion between the paste and increased the viscosity of the paste [58].

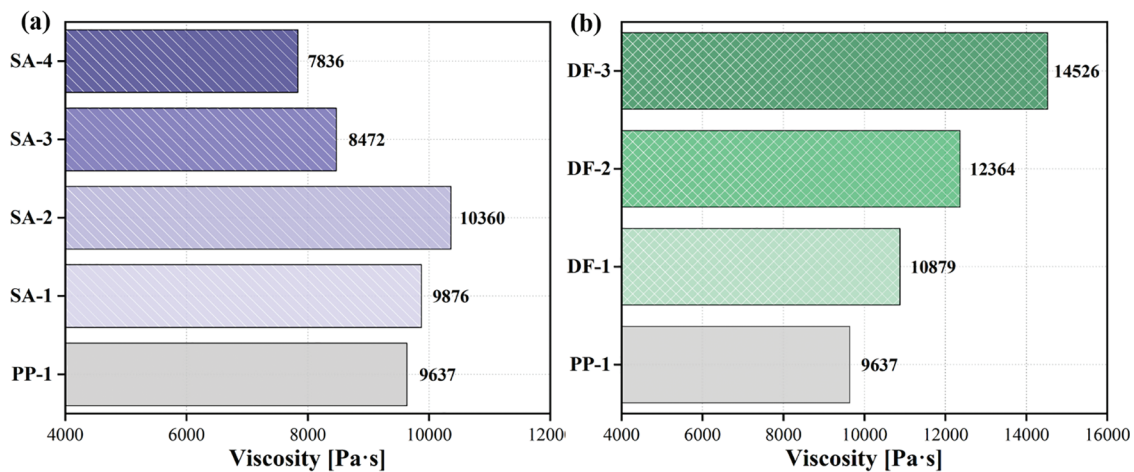


Figure 7: The influence of (a) slump retaining agents (SA) and (b) defoaming agents (DF) on the viscosity of UHPC

3.3 Rheological Properties of UHPC Paste

3.3.1 Different Dosages of AE

To assess the viscosity reduction effect of AE, we conducted rheological tests on UHPC paste. Fig. 8 depicts the impact of AEs on the rheological properties of UHPC. The test results for the groups were well-fitted to the H-B model, with correlation coefficients exceeding 0.99. Specific rheological parameters are shown in Table 6. Fig. 8a indicates that with increasing AE dosages, the shear stress of UHPC paste initially decreases and then increases. Table 6 shows that the yield stress increases as the AE dosage is increased. Fig. 8b indicates that UHPC viscosity follows the similar trend, with AE-2 exhibiting the lowest apparent viscosity. High AE dosages reduced viscosity by increasing air content and bubble volume proportion, enhancing plastic viscosity [59]. Fig. 8c demonstrates a strong correlation between static yield strength and apparent viscosity after adding AE.

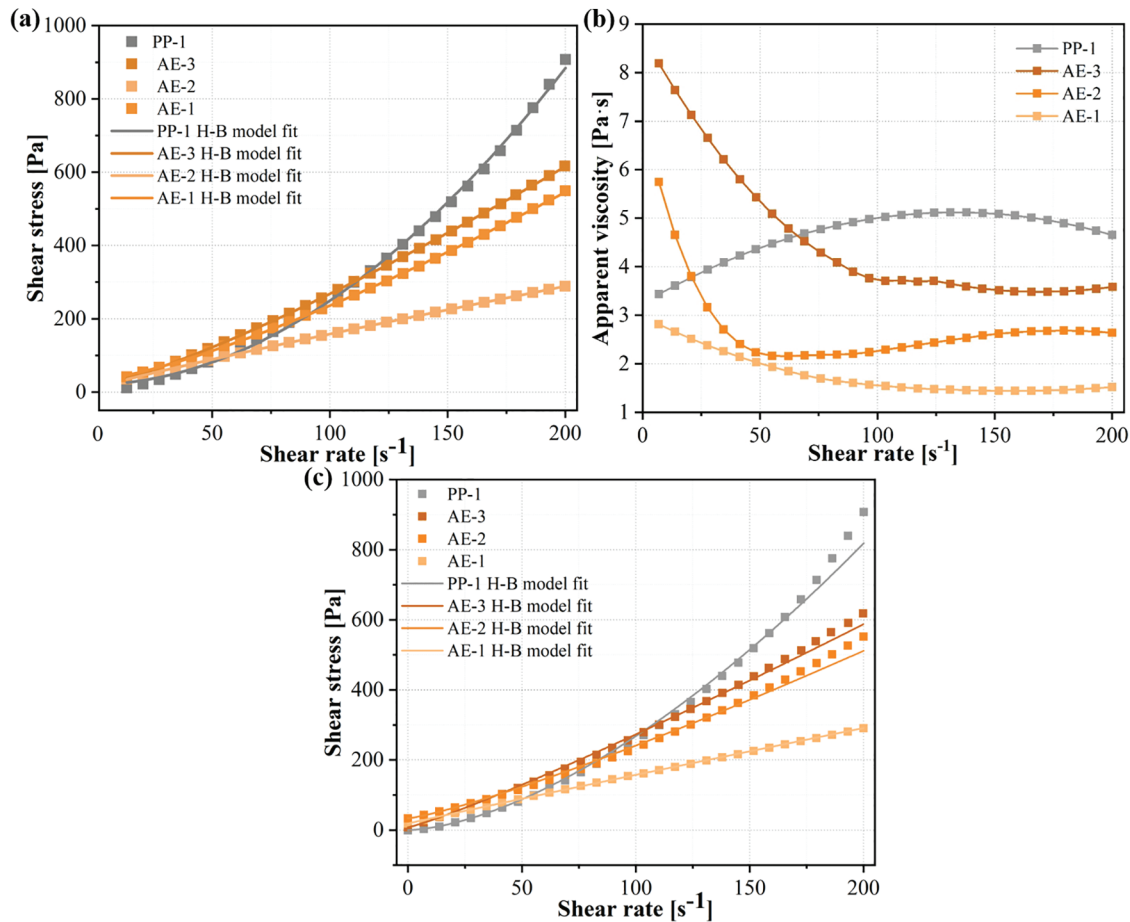


Figure 8: Air-entraining agents (AE) effect on UHPC (a) yield stress, (b) apparent viscosity and (c) correlation between static yield strength and apparent viscosity

Table 6: The H-B model rheological parameters of UHPC paste with air-entraining agents (AE)

Sample	τ_0 (Pa)	K	n	R ²
PP-1	20.89799	0.03325	1.91819	0.99876
AE-1	10.47300	2.22271	0.91151	0.99997
AE-2	16.66841	0.78543	1.25252	0.99982
AE-3	30.94276	0.45161	1.32843	0.99999

3.3.2 Different Dosages of SA

Fig. 9 shows the effect of SA on UHPC rheology. Fig. 9a reveals that increasing SA dosages initially increases and then decreases shear stress. Under the same shear rate, SA-2 exhibited the highest shear stress, while SA-4 showed the lowest. Fig. 9b indicates that both control and experimental groups exhibited increased apparent viscosity with shear rate. SA-2 had the highest apparent viscosity, while SA-4 had the lowest. Rheological data fitting results aligned with the H-B model, with correlation coefficients

exceeding 0.99. Specific rheological parameters are shown in Table 7. The yield stress of SA-2 was the lowest, while SA-4's was the highest. Fig. 9c shows a strong correlation between static yield strength and apparent viscosity after adding SA.

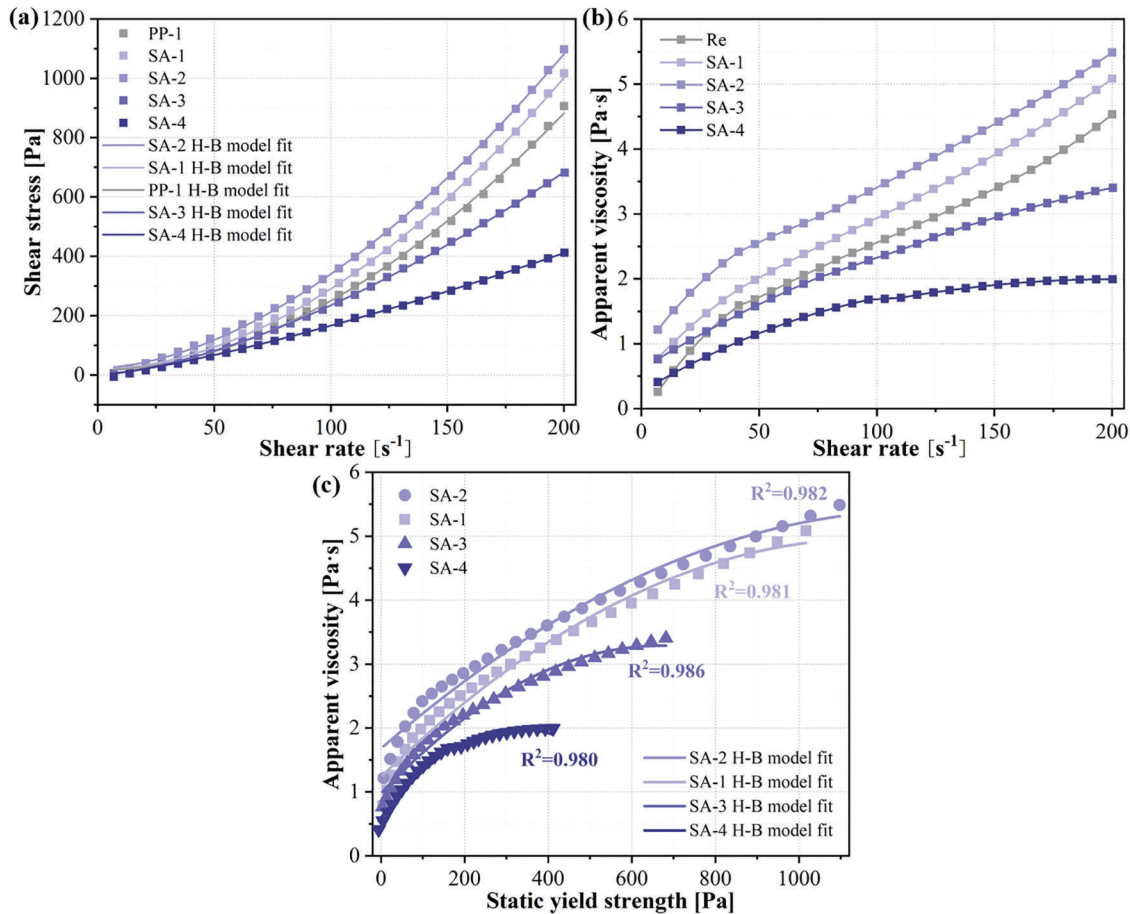


Figure 9: Slump retaining agents (SA) effect on UHPC (a) yield stress, (b) apparent viscosity and (c) correlation between static yield strength and apparent viscosity

Table 7: The H-B model rheological parameters of UHPC paste with slump retaining agents (SA)

Sample	τ_0 (Pa)	K	n	R^2
PP-1	20.89799	0.03325	1.91819	0.99876
SA-1	18.72532	0.05249	1.85673	0.99933
SA-2	23.53622	0.10347	1.74259	0.99944
SA-3	1.89353	0.18432	1.55061	0.99992
SA-4	2.22387	0.40578	1.30607	0.99926

3.4 Hydration Heat of UHPC Paste

3.4.1 Different Dosages of AE

Fig. 10 demonstrates the impact of AE on the hydration heat of ultra-high-performance concrete (UHPC). The incorporation of AE resulted in a rightward shift of the hydration exothermic peak for UHPC, markedly delaying the hydration exothermic process. As depicted in Fig. 10a, the control group's hydration exothermic peak occurred at 24 h, whereas the AE group's peak was observed at 90 h. Kubissa et al. [60] reported a 33% delay in the peak of hydration heat release when 0.1 and 0.2 wt% AE were added to concrete. Similarly, Qin et al. [61] found that both PCE and AE delayed the hydration reaction time by approximately 35%. Zhang et al. [62] observed that AE dosages ranging from 0 to 0.2 wt% inhibited the hydration reaction time of cement. With AE addition, the peak value of hydration heat release in UHPC significantly decreased. For the control group, the peak was 1.65 mW/g, while for the AE group, it was 0.4 mW/g. Increasing AE dosages further reduced the peak value, though the differences were minimal. According to Fig. 10b, AE addition also drastically reduced the cumulative heat release of UHPC, with the AE group's cumulative heat release being one-third that of the control group. Increasing AE dosages had little effect on cumulative heat release. AE reduced the surface tension of the concrete system, introducing more tiny bubbles, which buffered the cement hydration process [63].

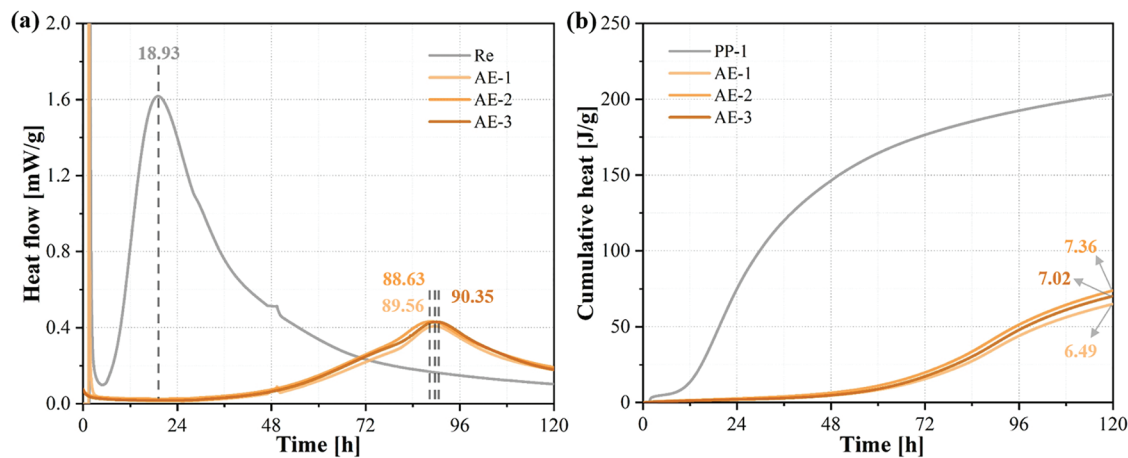


Figure 10: The influence of air-entraining agents (AE) on the (a) Heat flow and (b) cumulative heat of UHPC

3.4.2 Different Dosages of SA

Fig. 11 depicts the effect of SA on the hydration heat of UHPC. Fig. 11a showed that increasing SA dosages decreased the exothermic peak and delayed the hydration process. The control group's peak appeared at 24 h, whereas the SA group's peak appeared at 48 h, with SA-4 peaking at 60 h. Massarweh et al. [64] found that using 0.03, 0.05 and 0.08 wt% SA delayed the water exothermic peak by 23%, 31% and 46%, respectively. The peak values of hydration heat release for SA-1, SA-2 and SA-3 were similar, but they decreased significantly for SA-4, possibly due to the negative effect of excessive SA on UHPC hydration performance. From Fig. 11b, it is evident that SA incorporation reduced the cumulative heat release of UHPC. All SA groups had lower cumulative heat release than the control group, with SA-2 having a relatively high cumulative heat release. Compared to Fig. 10a, the hydration exothermic peak of UHPC with SA addition was relatively higher, possibly due to the chemical composition and effect of SA being similar to PCE [46].

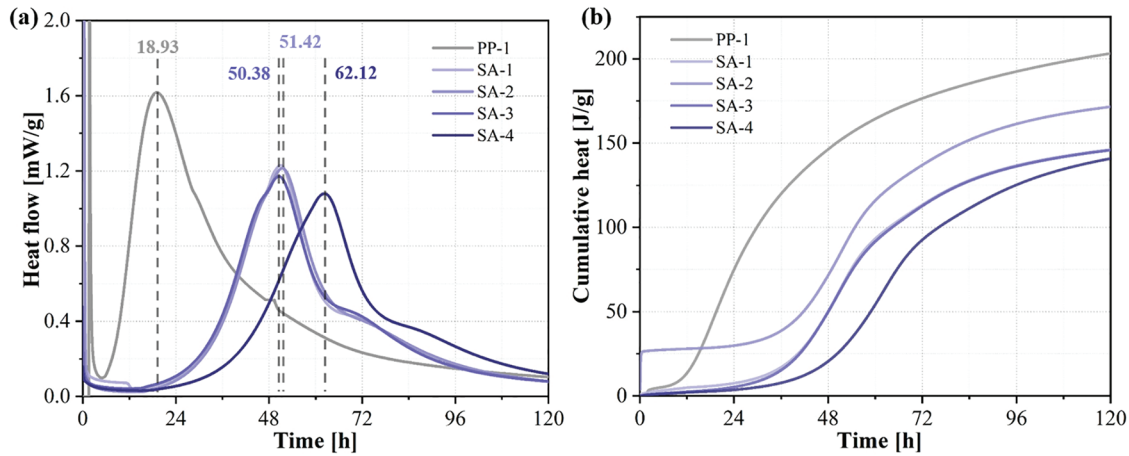


Figure 11: Effect of slump retaining agents (SA) on the (a) Heat flow and (b) cumulative heat of UHPC

3.5 Hydration Heat of UHPC Paste

3.5.1 Different Dosages of PCE and AE

Fig. 12 shows the effects of PCE and AE on the compressive strength of UHPC. In Fig. 12a, the compressive strength of UHPC with powder PCE was higher than that with liquid PCE. Notably, when the powder PCE dosage was 8%, the 28-day compressive strength of UHPC reached 117.2 MPa. However, further increasing the powder PCE dosage reduced compressive strength. Fig. 12b indicates that the compressive strength of UHPC at various ages was lower than that of the control group after AE addition. As AE dosages increased, UHPC strength further decreased. The 28-day compressive strength of AE-1 was 112.4 MPa, 4% lower than the control group, while AE-3 was 89.7 MPa, 23% lower. This suggested that AE significantly influenced UHPC compressive strength, with higher AE dosages weakening mechanical properties [65]. The effect was mainly due to AE altering the pore structure of concrete, including pore size and distribution, affecting compressive strength.

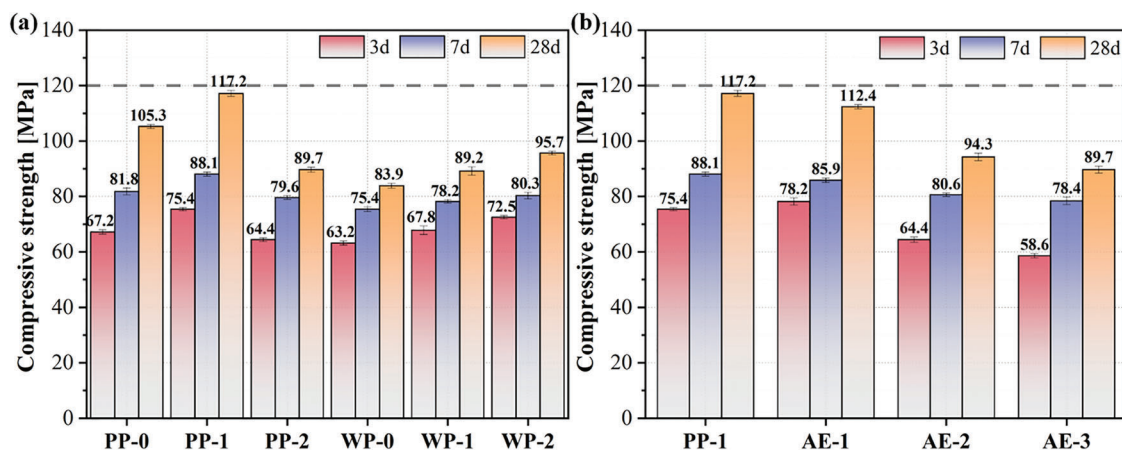


Figure 12: Effect of (a) PCE and (b) air-entraining agents (AE) on the compressive strength of UHPC

3.5.2 Different Dosages of AE and SA

The effect of SA and DF on the compressive strength of UHPC is shown in Fig. 13. It can be found from Fig. 13a that the compressive strength of UHPC increased first and then decreased after the addition of SA.

The compressive strength of UHPC was improved when an appropriate amount of SA was added. Good fluidity made UHPC paste uniformly hydrated, thus forming a more uniform microstructure [24]. When the dosages of SA were too high, the compressive strength began to decrease. When the quality of the SA was controlled at about 1‰ of the cementitious material, the mechanical properties of UHPC could be improved. The main function of the SA was to maintain the slump of the concrete and it will also have a certain impact on the final strength development of the concrete. Some studies have pointed out that the SA may have a certain adverse effect on the early strength of concrete, but it had little effect on the strength after 28 days or longer.

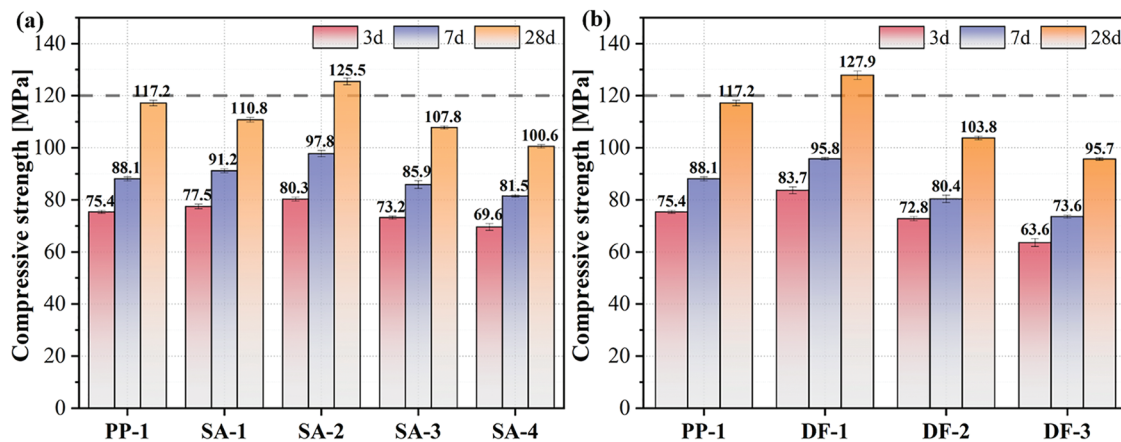


Figure 13: Effect of (a) slump retaining agents (SA) and (b) defoaming agents (DF) on the compressive strength of UHPC

Fig. 13b demonstrated that increasing DF dosages initially increases and then decreases UHPC compressive strength. DF-1 exhibited the best mechanical properties, with a 28-day compressive strength of 127.9 MPa, 9% higher than the control group. However, excessive DF dosages decrease compressive strength, with DF-3 being 18% lower than the control group. Studies indicate a correlation between bubble content and concrete strength [54]. DF reduces bubble content, enhancing strength, but excessive DF causes supersaturation, negatively affecting UHPC strength [58].

4 Conclusions

This study compared the effects of liquid and powder polycarboxylate superplasticizer (PCE) and evaluated the impact of air-entraining agents (AE), slump retaining agents (SA) and defoaming agents (DF) on the flow characteristics, mechanical and hydration properties of PCE-based UHPC. The following conclusions were drawn:

1. Under the same dosage, UHPC with powder PCE exhibited higher flow and mechanical properties than with liquid PCE. At 8‰ powder PCE, the 28-day compressive strength reached 117.2 MPa, 31% higher than with liquid PCE.
2. AE significantly improved the flow and mechanical properties of PCE-based UHPC paste, though this effect diminished with increased dosage. At 1.25‰ AE dosages, UHPC exhibited fluidity of 257 mm, viscosity of 6274 Pa·s and 28-day compressive strength of 112.4 MPa.
3. Increasing SA dosages initially decreased and then increased the flow characteristics of PCE-based UHPC paste. At 14.69‰ PCE (SA-4), UHPC fluidity was 249 mm and viscosity was 7836 Pa·s. Although DF improved compressive strength, it reduced paste fluidity.

4. Both AE and SA delayed the hydration heat release process of PCE-based UHPC paste, with AE having a more significant effect. The hydration heat peak for AE was about 0.4 mW/g, whereas for SA, it was about 1.2 mW/g. AE and SA dosages had minimal effects on the hydration process.
5. For high early strength, reduce AE and SA dosages while increasing powder PCE. For high fluidity, moderately increase AE and SA, controlling powder PCE dosages.

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Availability of Data and Materials: The data used to support the findings of this study are available from the corresponding author upon request.

Ethics Approval: Not applicable.

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