

Article

Experimental Investigation on Hydrophobic Alteration of Mining Solid Waste Backfill Material

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Abstract: To address the issues of corrosion weakening of solid-waste-based backfill material caused by mine water, a novel hydrophobic solid waste backfill (HSBF) material was developed using polydimethylsiloxane (PDMS) and a silane coupling agent (SCA) as hydrophobic modification additives, and NaOH (SH) and sodium silicate (SS) as alkali activators. Fly ash and slag were chosen as the primary raw solid waste materials. The rheological properties of the hydrophobic-treated backfill slurries were measured, and the resulting physicochemical properties were compared with the unmodified reference group. This study reveals that the fresh HSBF slurry follows a Modified Bingham (M-B) model with shear-thinning characteristics. The addition of PDMS causes an increase in the water contact angle of the hardened HSBF material with F8S2 to up to 134.9°, indicating high hydrophobicity. Morphological observations indicated that PDMS mainly attaches to the inorganic particles' surface through the bridging action of SCA for the hydrophobic modification of the backfill material. The overall strength of the HSBF materials was further ensured via fly ash–slag ratio optimization, and was found to be enhanced up to 98% by increasing slag content from 20% to 50%. This is mainly attributed to the hydration of slag, forming C-S(A)-H gel, which contributes to the increased strength. The novel HSBF material enables the elimination of cement in mine backfilling applications, demonstrating good economic benefits. Its excellent mechanical and hydrophobic properties can not only prevent overburden displacement in goaf areas, but can also mitigate water resource loss from overlying strata and simultaneously reduce the safety risks associated with long-term mine water deterioration.

Keywords: coal-based solid waste; hydrophobic modification; mine solid waste; backfill material; polydimethylsiloxane (PDMS); mine water deterioration mitigation



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1. Introduction

In China, 90% of existing coal mines face challenges such as subsidence in the goaf after mining, structural damage to underground rock layers, and contamination of underground water resources. This significantly impacts human activities and disrupts the natural ecological environment [1]. Concurrently, the coal-fired power generation process generates a substantial amount of fly ash, with a cumulative volume of approximately 4 billion tons and an annual increase of 600 million tons [2,3]. China's blast furnace slag industry research and investment evaluation report (2023 Edition) shows that China's annual blast furnace slag output is 60 million tons, but only 50% of the slag has been effectively utilized. A large number of solid wastes not only occupy ground resources, but also cause

environmental pollution. Utilizing coal mine solid waste to prepare low-cost underground backfill materials is an essential approach to immediately address these issues [4–7].

At present, the research work on mine backfill materials mainly focuses on the basic mechanical properties, solid waste replacing cement as the cementitious material, and the optimal ratio design [8]. By controlling the proportion of fly ash, cement, and soft soil, Ding et al. [9] found that fly ash can give full play to the volcanic ash reaction and significantly improve the material strength under the condition of a certain cement content. Shao et al. [10] pointed out that under the action of lime, blast furnace slag can improve the hydration reaction and increase the strength of concrete. Luo HG et al. [11] found that the compressive strength of backfill prepared with cement, fly ash, and mountain sand in the ratio of 1:4:15 was 8.88 MPa when the age reached 28 d, which met the requirements of filling technology. Furthermore, the inclusion of fly ash in backfill material as the secondary binder gave a promising performance. However, the utilization rate is limited. Most developed materials still rely on cement, resulting in low economic viability and environmental friendliness. Further research is needed on how to improve the utilization rate of solid waste and reduce filling costs while meeting engineering application conditions.

In addition, as a porous hydrophilic medium, the backfill body is vulnerable to erosion by the free water in the goaf and the water flow in the upper aquifer, resulting in damage to the internal structure and a decline in strength [12,13]. Hou et al. [14] found that the seepage water has a significant weakening effect on the compressive strength and elastic modulus of the fractured gangue fly ash cemented backfill. Ngo et al. [15] addressed the effects of various cations in mine water on the deterioration of backfill material. Cations damage the microstructure of backfill material through the ion exchange phenomenon, causing the ejection of tetrahedral calcium. Guo et al. [16] studied the strength characteristics of backfill in acidic mine water environments. The results indicate that under the long-term erosion of acidic mine water, the hydration products inside the material are decomposed, resulting in internal damage. This led to a decrease in strength, affecting the bearing capacity of the filling body, which cannot achieve the goal of long-term control of surface settlement. Therefore, it is necessary to carry out hydrophobic modification on the filling body to solve the aforementioned issues.

Numerous scholars have conducted in-depth research on the hydrophobic modification of building concrete. For building concrete, the most commonly used hydrophobic modification methods are surface coating, hydrophobic treatment, and the addition of hydrophobic agents. [17] Sobolev and Batrakov [18] have shown that polyethylhydrosiloxanes and polymethylhydrosiloxane groups can form hydrophobic voids in concrete by releasing hydrogen. Wong et al. [19] performed hydrophobic modification of cement mortar by PDMS, and the results showed that the concrete surface modified by PDMS was superhydrophobic, with a contact angle of 157.3° and a sliding angle of 8.7° . Wang et al. [20] coated SiO_2 nanoparticles by introducing a siloxane monomer to form a complex network particle structure to achieve hydrophobic modification of SiO_2 nanoparticles, and then mixed them with polymethylhydrosiloxane to prepare a superhydrophobic coating to improve the hydrophobic performance of concrete. Flores Vivian et al. [21] synthesized a superhydrophobic coating using polymethylhydrosiloxane, kaolin, and polyvinyl alcohol fibers, with a water contact angle of 156° , which significantly improved the hydrophobicity of concrete. The above studies show that silane is a potential additive for the hydrophobic modification of cement concrete. To the best of our knowledge, there are still few studies on the hydrophobic modification of mine filling materials. Wang et al. [22] used silicone rubber (RTV) as a hydrophobic additive for the interior of concrete, and the modified concrete surface and all sections exhibited superhydrophobicity.

Therefore, this paper is the first to study the hydrophobic backfill material in mines. A hydrophobic backfill material was developed using fly ash–slag as the raw materials and activated by alkali additives. PDMS and SCA were chosen as the hydrophobic agents. The effects of PDMS hydrophobic modification and fly ash–slag ratio optimization on rheological and mechanical properties were equally measured. The underlying mechanisms

were investigated using morphological analyses. The success of this work then provides a promising method to mitigate mine water deterioration, and simultaneously improves the economic viability of the backfill application.

2. Materials and Methods

2.1. Experimental Raw Materials

The Class F fly ash used in this study was sourced from a coal-fired power plant in Zhengzhou, Henan Province, China. The S95 slag used in the experiments was acquired from Gongyi City, Henan Province. The particle size distribution tests were carried out on fly ash and slag, respectively, and the results are shown in Figure 1 and Table 1. The average particle size of both slag and fly ash is less than 20 μm . The test results of the oxide composition of fly ash and slag are shown in Table 2. The results show that fly ash is mainly composed of SiO_2 and Al_2O_3 (the total content is greater than 85%), and the slag is mainly composed of CaO , SiO_2 , and Al_2O_3 (the total content is more than 80%). Because the hydration reaction of fly ash and slag is similar to that of cement, they were chosen as aggregates for the filling material [23].

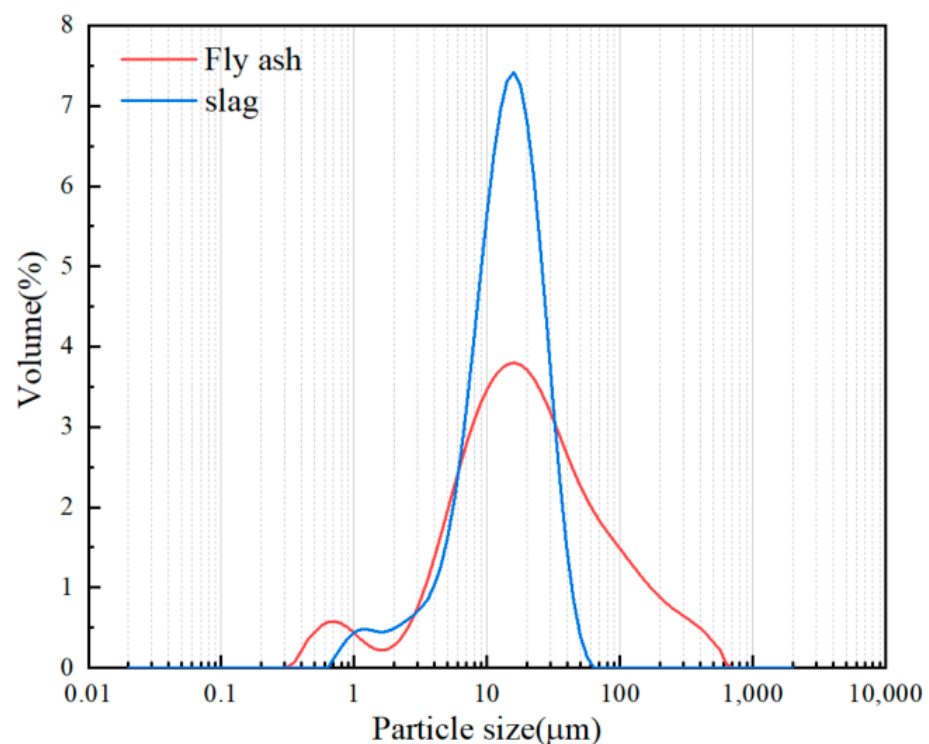


Figure 1. Particle size distribution of fly ash and slag.

Table 1. Physical properties of raw materials.

Property	Fly Ash	Slag
D_{10}^a	31.73	33.9
D_{30}	67.54	91.68
D_{50}	77.78	99.46
D_{60}	81.83	99.86
D_{90}	86.93	100
C_u^b	2.58	2.95
C_c^c	1.76	2.48
U^d	0.12	0.001
Specific surface area	0.88	0.99

Notes: ^a D_x represents the percentage of x% volume of particles with a diameter less than D_x in μm ; ^b coefficient of uniformity ($C_u = D_{60}/D_{10}$); ^c coefficient of curvature ($C_c = D_{30}^2/(D_{60} \times D_{10})$); and ^d uniformity of gradation ($U = (D_{90} - D_{60})/D_{50}$).

Table 2. Chemical composition of raw materials.

Oxides	Fly Ash	Slag
CaO	2.08	39.99
SiO ₂	53.43	26.92
Al ₂ O ₃	31.93	16.26
Fe ₂ O ₃	3.36	0.99
K ₂ O	1.29	0.51
TiO ₂	1.18	1.14
MgO	0.53	9.93
SO ₃	0.53	2.12
P ₂ O ₃	0.18	0.05
Others	5.16	2.62
Minerals	Mullite, quartz, and hematite	Melilite, pyroxene, and plagioclase

Polydimethylsiloxane (PDMS, purity 99%), obtained from Jiangsu Suqian, and silane coupling agent (SCA, Irvine, CA, USA, model KBM-403, purity 99%), from Shin-Etsu Chemical Co., Ltd., Tokyo, Japan, were used as hydrophobic modification additives. Silicate additive (SA, purity 99.9%) was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. PDMS is a polymer composed of small organic siloxane molecules, which has good thermal stability and hydrophobicity. The hydrolyzable group X in the coupling agent only serves as a bridge transition, bonding organic polymers (PDMS) with inorganic materials such as slag and fly ash, with little impact on the properties of the material itself [24]. Therefore, PDMS and SCA were chosen as hydrophobic agents.

2.2. Preparation

To investigate the mechanisms of the hydrophobicity and hydration evolution of the high-strength hydrophobic solid waste backfill (HSBF) material, various mixtures of fly ash and slag were formulated under predetermined concentrations of SS, SH, and hydrophobic agents PDMS and SCA. The formulation details are presented in Table 3. The preparation of mortar samples followed the Chinese standard (GB/T17671-2021) [25]. Prior to formulation, the dry components of fly ash and slag were thoroughly mixed. Subsequently, SS and SH were dissolved in tap water and mechanically stirred at 500 rpm for 10 min at room temperature to form a 10 wt% SS and 5 wt% SH mixed solution. The fly ash–slag mixture with the prepared solution was transferred to the reactor and stirred at 1000 rpm for 5 min. Simultaneously, the PDMS base solution and curing agent were mixed at a ratio of 10:1, and 2% of SCA based on the mass of the PDMS was added. This mixture underwent a thorough mixing and reaction at 500 rpm for 3 min at room temperature. The obtained hydrophobic solution was added to the mortar and stirred at 1000 rpm for 5 min to achieve the hydrophobic mortar.

Table 3. Formulation of backfill material.

Solid-Liquid Ratio	Solid Ratio (Fly Ash–Slag)	Na ₂ SiO ₃ and NaOH Solution Concentration	PDMS Main Agent	KBM-403 SCA
5:2	9:1	SS 10 wt%/SH 5 wt%	1 wt% of solid mass	2 wt% of PMDS
	8:2			
	7:3			
	6:4			
	5:5			

2.3. Experimental Methods

The performance of HSBF as a backfilling material was investigated through systematic experiments. The entire experimental process is illustrated in Figure 2.

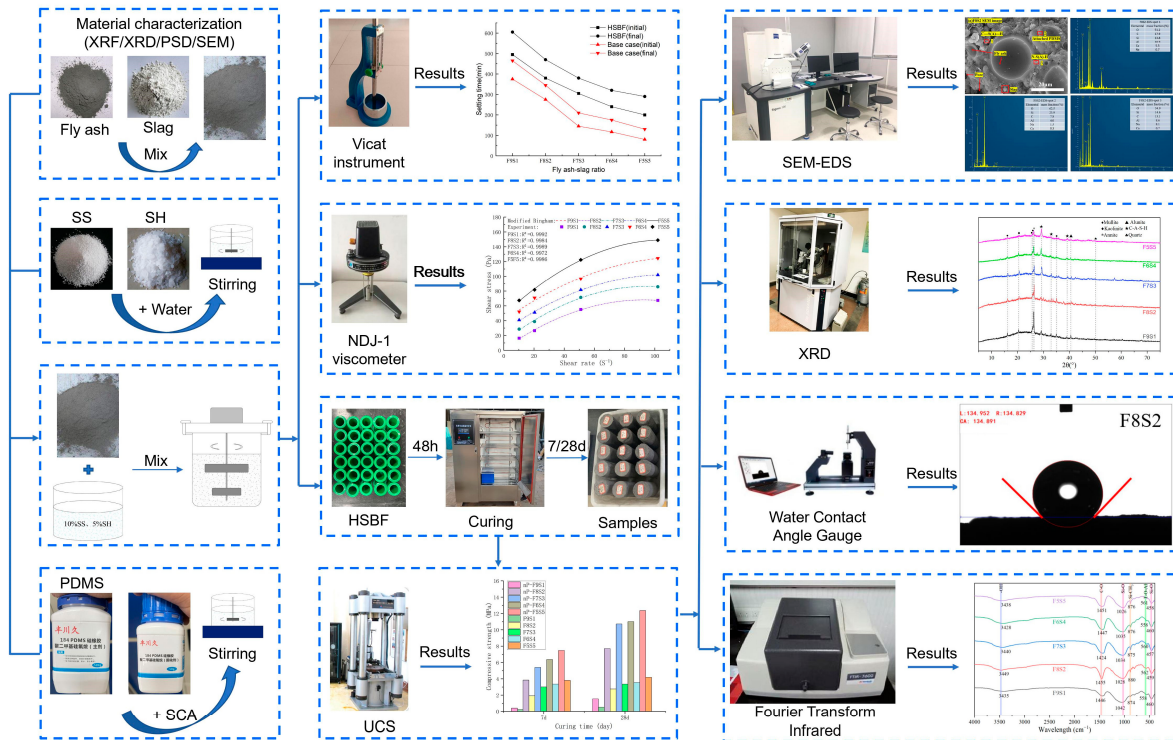


Figure 2. Experimental flow chart.

2.3.1. Rheological Test

The rheological properties of fresh HSBF paste were measured by NJ-1 viscometer. The tests were carried out in two approaches: (1) Yield stress and viscosity were determined in a controlled mode, where shear rate increased linearly from 1 to 100 s^{-1} . After that, the paste was allowed to stand for 2 min. (2) Thixotropy was determined in descending mode, where shear rate first increased linearly from 1 to 100 s^{-1} . Then, shear rate decreased linearly from 100 to 1 s^{-1} .

2.3.2. Setting Time Test

According to ASTM C150 standards [26], the setting times of the HSBF material was tested using an ISO Vicat apparatus. For the initial setting time test, measurements were taken every 5 min. The initial setting state was achieved when the initial setting needle sank to a depth of 4 ± 1 mm from the bottom plate. After completing the initial setting time measurement, the test mold was flipped 180° for the final setting time test. During the approach to the final setting, measurements were taken every 15 min. The final setting state was reached when the final setting needle penetrated the specimen by 0.5 mm.

2.3.3. Uniaxial Compressive Strength (UCS) Test

The backfill material used in mine goaf requires a specific strength to support the overburden and prevent the overlying strata from sinking. The uniaxial compressive strength of the specimens at curing ages of 7 d and 28 d was tested using a WDW-300 electronic universal testing machine with a loading speed of 0.1 mm/min, as outlined in reference [27]. All experiments were repeated 3 times, and the average value of the three tests was recorded as the final strength of the backfilling material at the respective age.

2.3.4. XRD and SEM Analyses

X-ray diffraction (XRD) and scanning electron microscopy (SEM) experiments were conducted on the HSBF material to discover the mechanisms of hydrophobicity and hydration evolution. After UCS experiments, the broken samples were collected and soaked in anhydrous ethanol for 12 h, followed by drying and grinding into powder with a particle

size below 200 mesh. A Rigaku Ultimate IV X-ray diffractometer was employed for the XRD experiment, with a scanning range from 5° to 90° and a scanning speed of 5°/min. For SEM testing (Instrument Model: Hitachi Regulus 8100, Tokyo, Japan), the same samples were used, but surface gold spraying was performed to reduce the interference of negative charges on imaging [28].

2.3.5. Water Contact Angle Test

The water contact angle test was carried out to evaluate the hydrophobicity of the HSBF material. The contact angle between the sample surface and a water droplet was measured using 2 cm × 2 cm specimens from the samples collected in the UCS experiments. The water contact angle tests were conducted using the contact angle measurement instrument (Instrument Model: Shengding SDC350K, Dongguan, China). A high contact angle reflects the hydrophobic nature of the material, while a low contact angle indicates hydrophilicity [29]. The contact angle provides valuable insights into the wetting properties of the backfill material surface.

2.3.6. FTIR Spectroscopy Analysis

The samples obtained after the UCS experiment were dried and ground into a powder of less than 200 meshes. The experiment was carried out using a FTIR spectrometer (Instrument Model: Thermo Scientific™ Nicolet™ iS50, Waltham, MA, USA) in the scanning range of 4000~400 cm⁻¹, with an optical resolution of 4 cm⁻¹.

3. Results and Discussion

3.1. Rheological Properties

3.1.1. Yield Stress and Viscosity

The backfill material prepared with fly ash and slag essentially belongs to non-Newtonian fluids, similar to mortar and cementitious materials. Typically, their rheological properties can be characterized by representative models such as the Bingham model, the Modified Bingham (M-B) model, and the Herschel–Bulkley (H-B) model [30,31]. The experimental measurements were fitted to the mentioned models, and the fitting results are shown in Figure 3. The rheological curves of the fresh slurry agreed with the H-B and M-B models. The formula for the H-B model is given as follows [32]:

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

In the equation, τ represents shear stress; τ_0 is the yield stress; K is the consistency index; and n is the flow behavior index. When $n > 1$, the material exhibits shear-thickening characteristics, known as an expansive plastic fluid; when $n < 1$, the material shows shear-thinning characteristics, referred to as pseudoplastic fluid; and when $n = 1$, the material follows the Bingham model [33]. The regression equation and rheological parameters for the fitted H-B model are shown in Table 4.

Table 4. Fitting results of the Herschel–Bulkley model for backfill slurry.

	Model	Fitting Result	τ_0 (Pa)	K	n	R^2
F9S1	H-B	$\tau = -125.88 + 102.09\dot{\gamma}^{0.14}$	−125.88	102.09	0.14	0.9895
F8S2		$\tau = -64.31 + 55.12\dot{\gamma}^{0.22}$	−64.31	55.12	0.22	0.9894
F7S3		$\tau = -24.51 + 31.84\dot{\gamma}^{0.3}$	−24.51	31.84	0.3	0.9918
F6S4		$\tau = -27.92 + 42.41\dot{\gamma}^{0.28}$	−27.92	42.41	0.28	0.9991
F5S5		$\tau = -32.77 + 52.5\dot{\gamma}^{0.27}$	−32.77	52.5	0.27	0.9920
nP-F9S1		$\tau = 3.99 + 3.8\dot{\gamma}^{0.76}$	3.99	3.8	0.76	0.9990
nP-F8S2		$\tau = 15.8 + 3.29\dot{\gamma}^{0.8}$	15.8	3.29	0.8	0.9921
nP-F7S3		$\tau = 37.22 + 1.57\dot{\gamma}^{0.96}$	37.22	1.57	0.96	0.9930
nP-F6S4		$\tau = 38.57 + 3.7\dot{\gamma}^{0.8}$	38.57	3.7	0.8	0.9866
nP-F5S5		$\tau = 45.1 + 6.5\dot{\gamma}^{0.69}$	45.1	6.5	0.69	0.9987

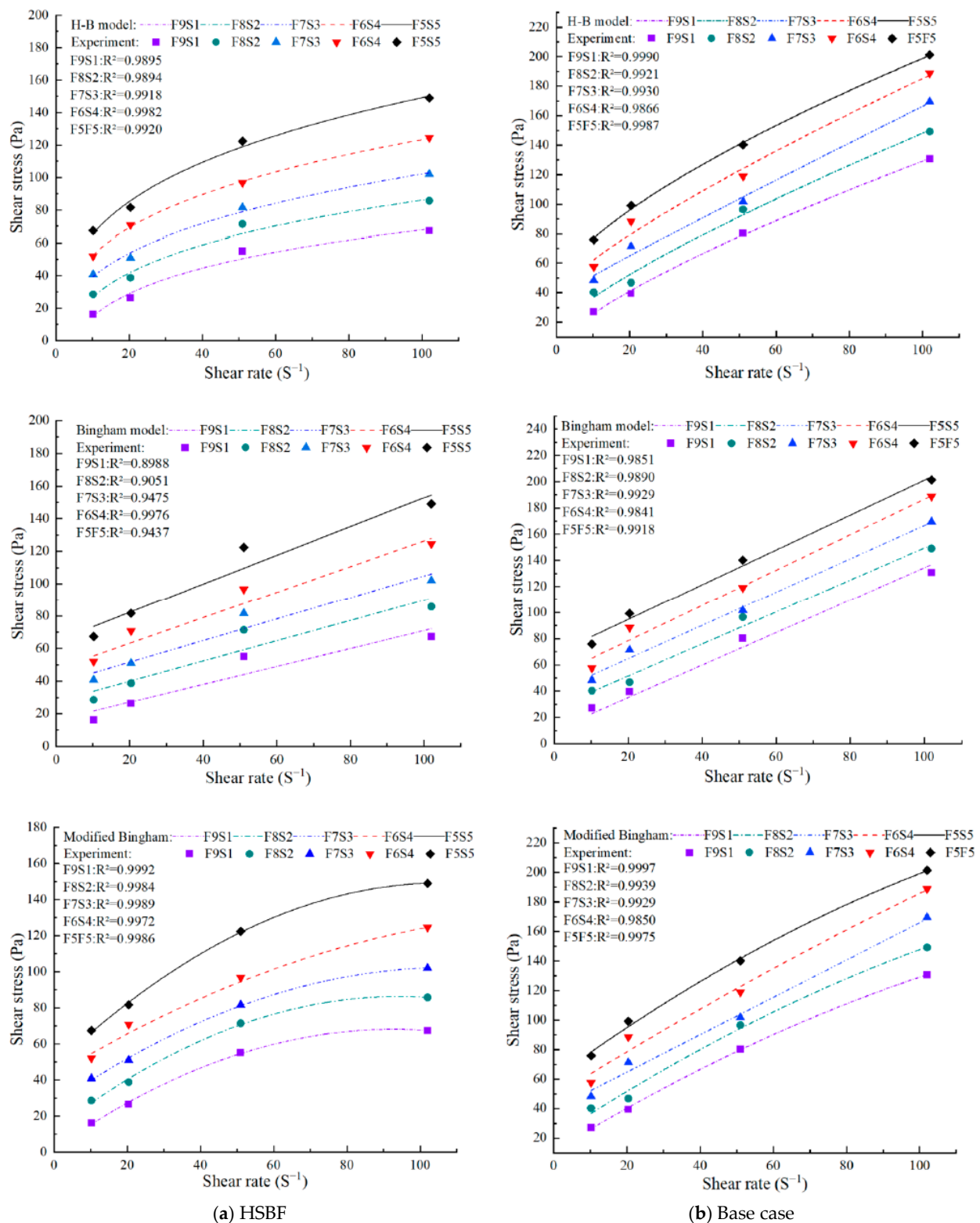


Figure 3. Shear stress against the shear rate (a) HSBF (b) Base case.

Table 4 shows that the flow behavior index (n) for the backfill slurry is less than 1, indicating that the backfill slurry essentially exhibits shear-thinning characteristics. However, the fitted yield stress is negative for the PDMS-modified backfill slurry, which contradicts the nature of yield stress. Therefore, the H-B model is not suitable for describing the rheological properties of the hydrophobic backfill slurry.

The equation and fitting results of the M-B model are shown in Equation (2) [34] and Figure 3, respectively. It can be observed that the shear stress is positively correlated with the applied shear rate. At the same shear rate, the shear stress gradually increased with the concentrated slag. Compared to the spherical and granular shape of fly ash, slag has a more irregular particle shape. The addition of slag increased the specific surface area and interactions between particles, leading to particle aggregation and adversely affecting the rheological properties of the slurry [35]. After the addition of PDMS, the rheological performance of the slurry still showed a positive correlation. However, the increase in shear stress became less significant when the shear rate exceeded 51 s^{-1} . Compared to the reference group, PDMS inclusion led to a better flowability of the fresh backfill slurry at higher shear rates. This was plausibly due to the surface action of PDMS between slurry particles.

$$\tau = \tau_0 + \eta\dot{\gamma} + c\dot{\gamma}^2 \quad (2)$$

In the equation, η is the rheological index, Pa·s; c is the correction factor. The regression equation and rheological parameters of the fitted M-B model are shown in Table 5. When using the M-B model, the fitting coefficients of the rheological curves for each group of samples were above 0.98. The fitting coefficients of the samples with added PDMS were above 0.99, indicating a high correlation. Therefore, the M-B model is more suitable for describing the rheological characteristics of hydrophobic backfill materials.

Table 5. Fitting results of the Modified Bingham model for filling slurry.

	Model	Fitting Result	τ_0 (Pa)	η (Pa·s)	c	R^2
F9S1	M-B	$\tau = 1.76 + 1.43\dot{\gamma} - 0.008\dot{\gamma}^2$	1.76	1.43	−0.008	0.9987
F8S2		$\tau = 12.09 + 1.57\dot{\gamma} - 0.008\dot{\gamma}^2$	12.09	1.57	−0.008	0.9972
F7S3		$\tau = 26.29 + 1.41\dot{\gamma} - 0.007\dot{\gamma}^2$	26.29	1.41	−0.007	0.9989
F6S4		$\tau = 40.37 + 1.44\dot{\gamma} - 0.006\dot{\gamma}^2$	40.37	1.44	−0.006	0.9932
F5S5		$\tau = 47.81 + 1.91\dot{\gamma} - 0.009\dot{\gamma}^2$	47.81	1.92	−0.009	0.9992
nP-F9S1		$\tau = 11.25 + 1.52\dot{\gamma} - 0.003\dot{\gamma}^2$	11.25	1.52	−0.003	0.9996
nP-F8S2		$\tau = 20.41 + 1.63\dot{\gamma} - 0.004\dot{\gamma}^2$	20.41	1.63	−0.004	0.9939
nP-F7S3		$\tau = 39.41 + 1.27\dot{\gamma} - 0.005\dot{\gamma}^2$	39.41	1.27	−0.005	0.9930
nP-F6S4		$\tau = 48.13 + 1.55\dot{\gamma} - 0.002\dot{\gamma}^2$	48.13	1.55	−0.002	0.9850
nP-F5S5		$\tau = 60.23 + 1.81\dot{\gamma} - 0.004\dot{\gamma}^2$	60.23	1.81	−0.004	0.9975

The yield stress is the minimum shear stress required for the slurry to flow. A comparison reveals that the yield stress of the backfill slurry increased with the addition of slag. For example, the yield stress of nP-F9S1 and nP-F5S5 increases from 11.25 Pa to 60.23 Pa. The increase in yield stress was attributed to the larger specific surface area and irregular particle shape of the slag, allowing it to absorb more free water. As described in the document in [36], the adsorption of water molecules leads to particle stacking, resulting in an increase in inter-particle interactions. Thus, yield stress increases.

The addition of PDMS significantly reduces the yield stress of the backfill slurry. For instance, the yield stress of nP-F5S5 decreased from 60.23 Pa to 47.81 Pa, and nP-F9S1 decreased from 11.25 Pa to 1.76 Pa when compared to F5S5 and F9S1, respectively. The reduction might be attributed to PDMS forming as a barrier between particles, reducing intermolecular interactions. The respected yield stress was thus decreased. As discussed in the literature [37], the strong chemical bonding inherent within siloxane (−Si−O−) networks, as well as their thermal stability, promotes inertness against chemical attack. Hence, PDMS works as a protective coating on fly ash and slag particles. Another reason is that during the alkali activation of fly ash and slag, C−S(A)−H gel is formed [38,39]. The forming gel binds the surrounding particles, causing particle aggregation and an increase in slurry viscosity [40]. The addition of PDMS suppressed the early formation of C−S(A)−H gel, resulting in lower viscosity and a significant reduction in yield stress [41].

To ensure the slurry transportation in pipeline, the yield stress of the fresh backfill slurry should be controlled within 200 Pa [42]. The yield stress of the hydrophobic backfill slurry was below 50 Pa, indicating good pumpability.

3.1.2. Thixotropy Analysis

Thixotropy refers to the property of a material where its internal structure undergoes destruction after shear but rebuilds when shear stops or slows down [43]. The thixotropic hysteresis loop typically consists of ascending and descending curves. The ascending curve represents the process of reduced internal viscosity during shear, while the descending curve represents the rebuilding of the internal structure. The thixotropic properties of materials are often evaluated by calculating the area between the ascending and descending curves [44]. The thixotropic study of hydrophobic backfilling materials is shown in Figure 4.

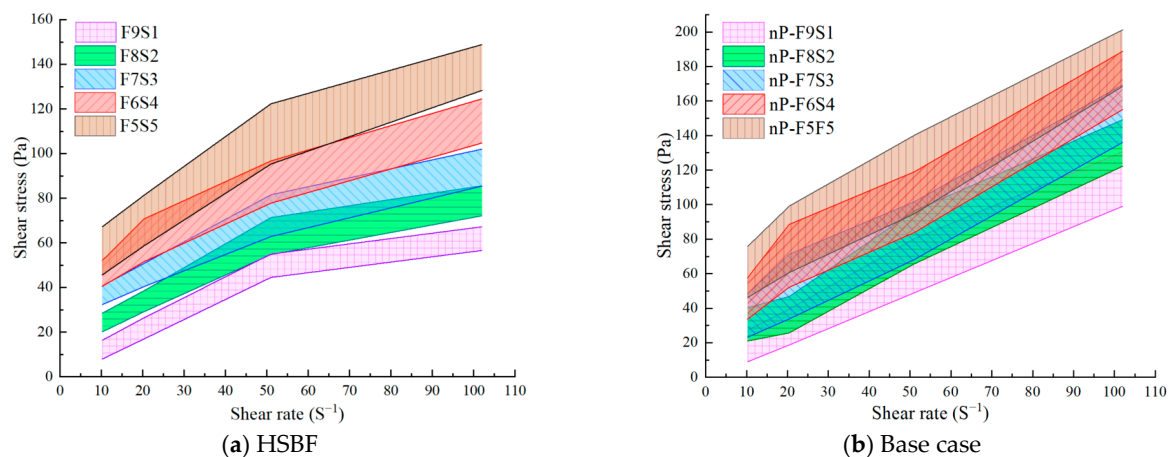


Figure 4. Thixotropy characteristics of the backfill slurry (a) HSBF (b) Base case.

As observed, regardless of the addition of hydrophobic agents, the thixotropic loop gradually increases with the addition of slag, indicating that slag has a significant effect on the thixotropic properties of the material. This is because the activity of slag is greater than that of fly ash [45], the hydration products are physically wrapped, and there is surface adsorption, chemical precipitation, etc. [46,47], so heavy metal ions are bound in the solidified body of slag, which promotes the interaction between particles. The internal structure of the high-slag-content slurry was more likely to undergo destruction and rebuilding during the shearing process, leading to an increase in thixotropic behavior.

With the addition of PDMS, the thixotropic behavior significantly decreased. Due to the bridging effect of SCA, PDMS can be connected to inorganic molecules such as slag and fly ash [7]. PDMS then reduces molecular aggregation, lowering interactions between molecules. Therefore, the destruction and rebuilding of particles are reduced during shearing, resulting in decreased thixotropic behavior.

3.2. Setting Time

The setting times were measured, and the results are shown in Figure 5.

It can be observed that the slag content and the addition of hydrophobic agents significantly influenced the setting times. The initial setting times of nP-F9S1 and nP-F5S5 are 375 min and 80 min, with final setting times of 465 min and 130 min, respectively. The addition of slag led to a significant reduction in the setting time. This is attributed to the higher reactivity of slag compared to fly ash [48]. The early hydration reactions involving slag result in the formation of C-S(A)-H colloids and calcium aluminate phases (Aft), creating a dense skeleton structure. This not only effectively enhances the strength of the specimens but also shortens the setting time. The setting time for samples with PDMS decreased. The initial setting times for F9S1 and F5S5 are 495 min and 200 min, with final setting times of 605 min and 290 min, respectively.

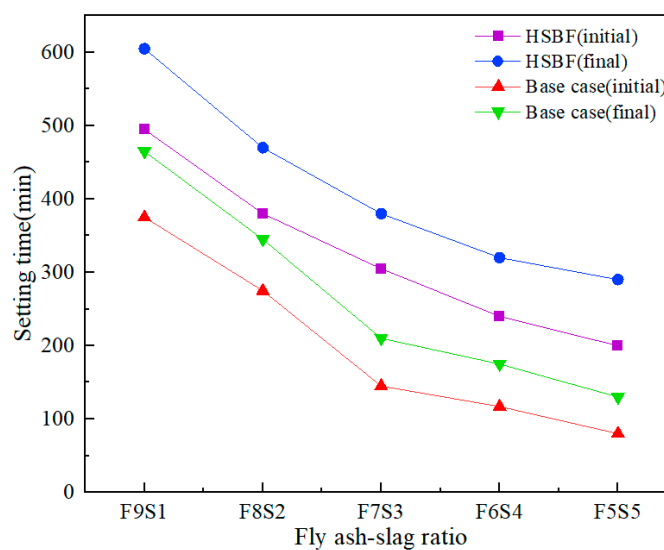


Figure 5. Setting time of backfill samples.

For the reference group, without adding hydrophobic agents, the setting time undergoes a turning point around nP-F7S3, and the rate of reduction slows down after nP-F7S3. This is due to the lower reactivity of fly ash in nP-F9S1 and nP-F9S1. So, a longer reaction time is required. This phenomenon significantly weakens after the addition of PDMS, because PDMS hinders the hydration reaction, which inhibits the aggregation of molecules and the adsorption of molecules by gels [49]. Due to the action of PDMS, the interval between the initial and final setting times of the hydrophobic slurry increased by 2 h on average compared to the reference group.

Considering the impact of transportation distance, the setting time should not be too short. Generally, the transportation distance from the mixing station to the void filling area exceeds 2 km, with a transportation duration over 2 h [50]. The hydrophobic backfill materials can meet these requirements.

3.3. UCS Development of the Backfill Samples

The UCSs of HSBF materials were plotted against the reference sample, as shown in Figure 6.

As expected, the mechanical properties of the backfill material increased with curing time. The hydration reaction is a continuous process, and as the curing time extends, the gel material produced by the hydration reaction continues to increase, aggregating the particles together and enhancing the mechanical performance.

The introduction of PDMS weakens the strength of hydrophobic samples compared to the control group. As shown in Figure 6, the UCS of hydrophobic samples is reduced by approximately 50% compared to the control group after 7 d of curing. After 28 d of curing, the UCS is reduced by around 65%. In the control group without PDMS, hydration reactions continue, and the UCS of the samples steadily increases with prolonged curing time. PDMS in hydrophobic samples chemically couples to the molecular surfaces of slag and fly ash through the SCA, inhibiting subsequent hydration reactions. Therefore, the strength of hydrophobic samples is weakened compared to the control group, and the degree of reduction increases with extended curing time.

From Figure 7, it can be observed that the UCS of the samples increases with the increasing slag content. The UCSs of F9S1 were 0.21 MPa and 0.53 MPa after 7 d and 28 d of curing, respectively. The F9S1 sample carried a higher fly ash content, which was mainly composed of illite and quartz. Since illite crystals are generally less reactive, they thus make fly ash less effective for producing binding agents than slag [51], resulting in lower mechanical performance. The addition of slag improves the mechanical properties of the hydrophobic backfill material. The UCS at 28 d for F8S2 was 2.75 MPa, while that

of F5S5 was 4.19 MPa. This improvement is attributed to the alkali-activated reaction of slag, forming a dense Si-O-Al three-dimensional network structure. Furthermore, a large amount of Ca^{2+} accompanies the formation of a substantial amount of hydrated calcium silicate, enhancing the mechanical performance of the binder material [30,52].

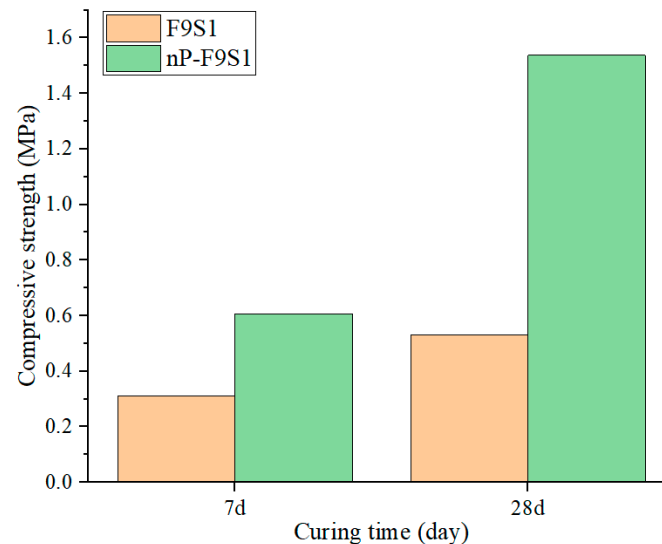


Figure 6. UCS control of 10% slag parameters at different ages.

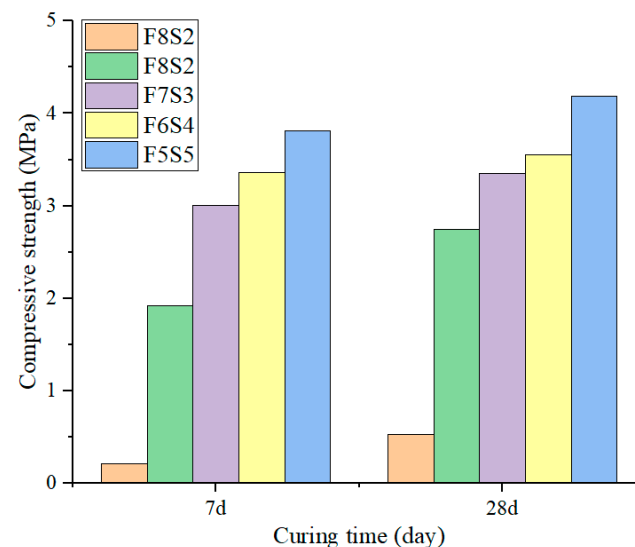


Figure 7. UCS of HSBF at different curing times.

Backfill materials for goaf support must have a particular strength to support the overlying strata. Generally, it is required that the minimum UCS of backfill material samples after 28 d of curing should be between 0.7 and 2 MPa [53]. The UCS of the hydrophobic samples is above 2.7 MPa, satisfying the strength requirements.

3.4. Water Contact Angle

To validate the hydrophobic performance of the HSBF material, water contact angle tests were conducted on samples cured for 28 d, and the results are shown in Figure 8. The material's hydrophilic or hydrophobic properties are defined based on the range of the contact angle. If the contact angle formed by a water droplet on a solid surface is greater than 90° , indicating that the water droplet cannot adhere well to the solid surface (forming a bead), and there is a smaller contact area, it suggests that the solid surface is hydrophobic. If the formed contact angle is less than 90° , the water droplet will spread

on the solid surface, indicating that the solid surface is hydrophilic [54]. According to the measurement results, F8S2 possessed the highest water contact angle at 134.9° . As the slag content increased, the contact angles of F7S3, F6S4, and F5S5 gradually decreased. This is because the C-S(A)-H gel formed in the early reaction of slag is not conducive to the adhesion of PDMS [55]. However, C-S(A)-H gel can effectively improve the strength of HSBF. Therefore, for HSBF with 20% to 50% slag content, hydrophobicity is inversely proportional to UCS.

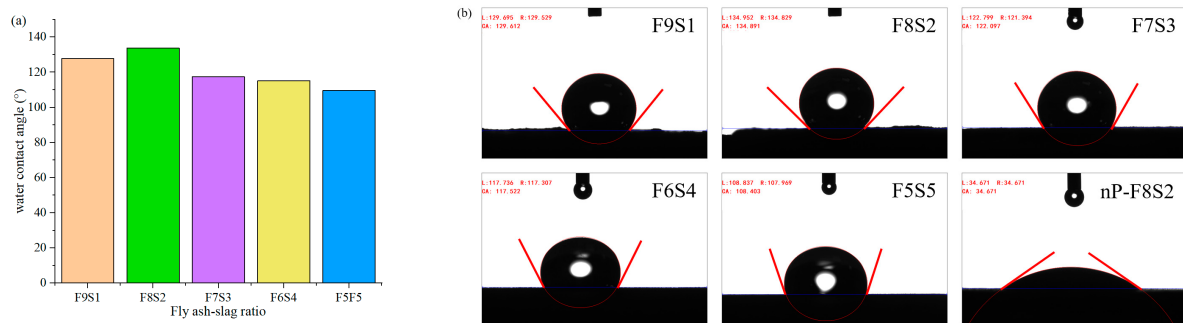


Figure 8. The measurement results of the water contact angle of HSBF (a) Water contact angle test results (b) Comparison of HSBF and base case test results.

Notably, the smallest water contact angle was 108.4° in the F5S5 sample. It was still greater than 90° , indicating hydrophobicity. To confirm that the hydrophobic property of the material is not determined by the inherent properties of slag and fly ash, the contact angle of nP-F8S2 was tested as a control case. The water contact angle of nP-F8S2 is 34.7° , indicating hydrophilicity. The control test of the reference group indicates that PDMS mainly confers the hydrophobic performance and is not related to the inherent properties of slag and fly ash.

It can be seen from Figure 9 that when the slag content increased from 20% to 50%, the change in the water contact angle of the hydrophobic backfill body was negatively correlated to that of UCS. In terms of hydrophobicity, the five groups of backfill materials with different fly ash–slag ratios have good hydrophobic responses. When considering the mechanical properties of HSBF, the 28 d UCS strength of HSBF with 10% slag content does not meet the requirements. HSBF with a fly ash content between 20% and 50% has good hydrophobic properties and mechanical properties, which can be flexibly selected in practical applications.

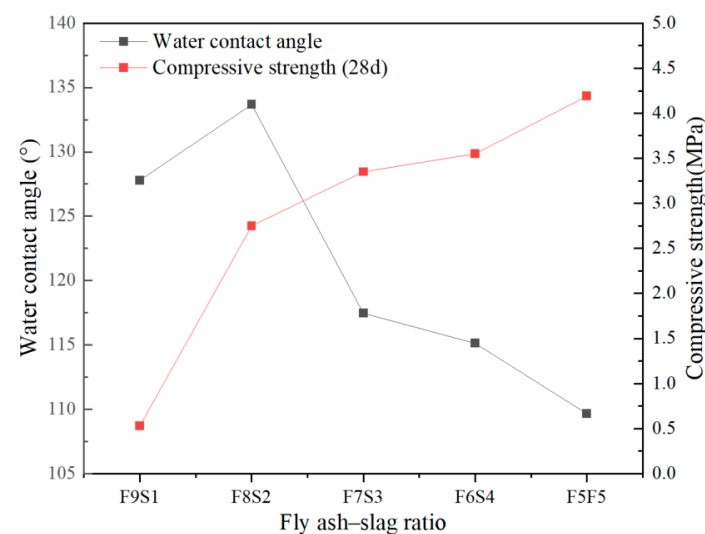


Figure 9. The relationship between UCS and water contact angle of HSBF.

3.5. Microstructure and Hydration Products

Figure 10 shows the SEM images and EDS element analysis results of F8S2 and nP-F8S2 at 28 d.

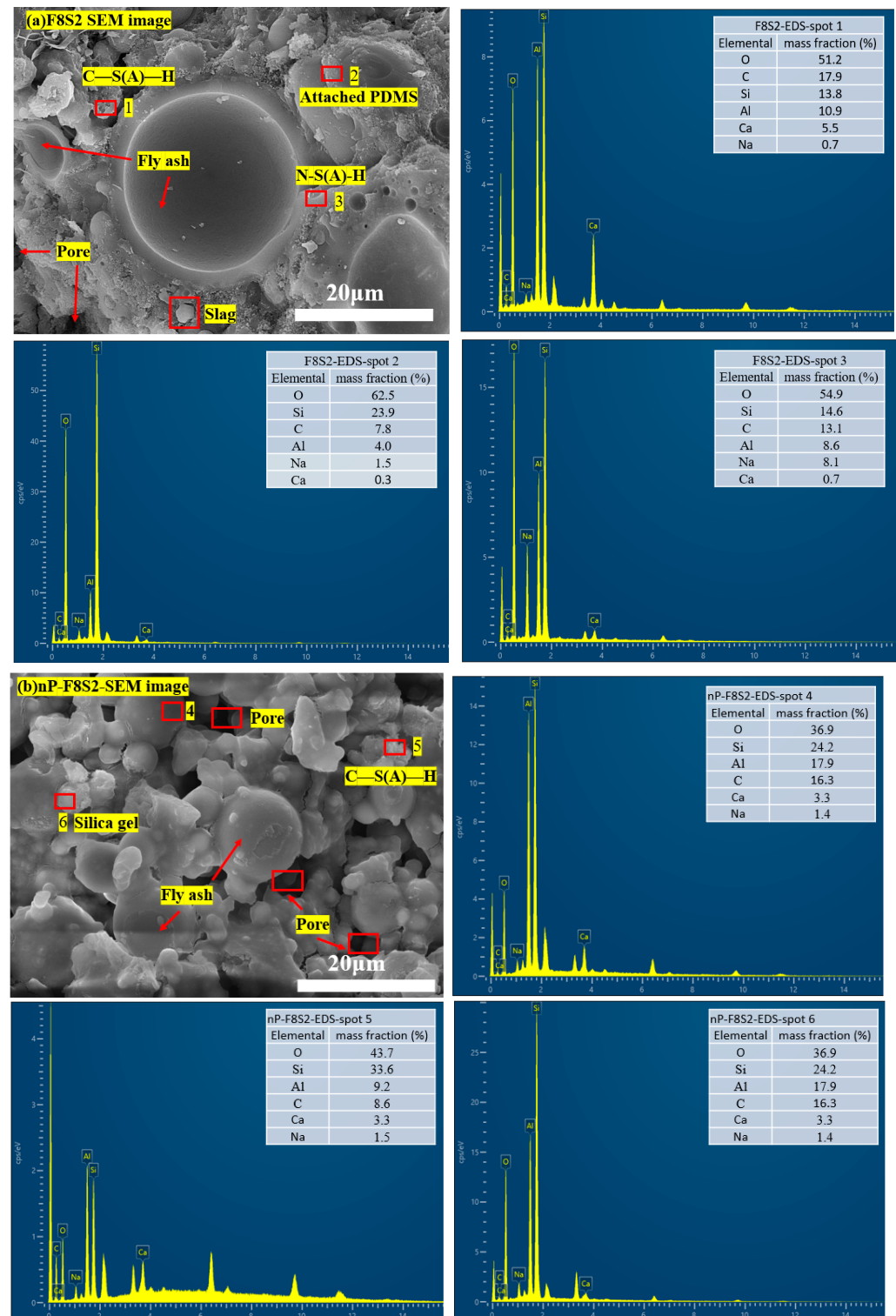
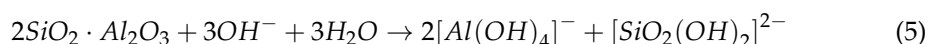
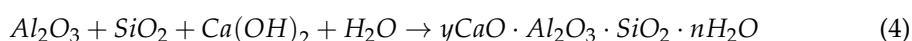


Figure 10. SEM of 20 μm images and representative energy spectrum of F8S2 and nP-F8S2.

The results indicated that the hydration products of slag and fly ash are mainly gel-like substances. At measurement point 1, a large amount of Si, Al, O, and Ca can be observed. Combined with the morphological analysis, it is identified that the C-S(A)-H gel

rapidly formed in the early hydration reaction of slag [56]. The reaction of CaO in the slag produces $\text{Ca}(\text{OH})_2$, which combines with sufficient Al_2O_3 to form C-S(A)-H, as shown in Equations (3) and (4). Similarly, due to a large amount of Si, Al, and Ca, the gel substance at measurement point 5 is also identified as C-S(A)-H gel. Since F8S2 has a lower slag content, a large amount of fly ash failed to participate in the development of C-S(A)-H gel; thus, more unreacted fly ash can be seen in Figure 10a. Comparing the elemental content of Si, Al, Ca, and Na, it can be determined that measurement point 6 is silica gel [57]. Measurement points 2 and 4 are both fly ash surfaces. Both points have relatively low Ca and Na elemental contents, which plausibly resulted from the attachment of C-S(A)-H and N-S(A)-H. The fly ash at measurement point 4 is smooth, while the Si content at measurement point 2 is much higher than the Al content. PDMS (molecular formula: $(\text{CH}_3)_3\text{Si}-\text{O}-[\text{Si}(\text{CH}_3)_2-\text{O}]_n-\text{Si}(\text{CH}_3)_3$) is a polymer composed of Si, O, and methyl (CH_3) groups, containing a large amount of C, Si, and O elements. This matches the EDS element characteristics of measurement point 2. Therefore, measurement point 2 is identified as PDMS attached to the surface of fly ash. The main elements at measurement point 3 are O, Si, Al, and Na. The substance is in a gel state, and the Ca content is relatively low, identifying it as N-S(A)-H gel formed by the hydration of fly ash [58]. When fly ash reacted with sodium hydroxide solution, the alkaline environment led to the reaction of silicon oxide in the slag with sodium hydroxide, forming sodium silicate gel, as shown in Equation (5).



By comparing the EDS information of F8S2 and nP-F8S2, it can be observed that the addition of PDMS does not significantly alter the products of the hydration reaction, and the main generated substances are still C-S(A)-H and N-S(A)-H gels.

To investigate the influence of different fly ash–slag ratios on the HSBF, the morphological characteristics of HSBF under four other slag ratios were compared. The results are shown in Figure 11.

When the fly ash–slag ratio is F9S1, a large number of free fly ash particles can be observed, leaving many voids between them, with only a tiny amount aggregating into clusters under the action of the gel. The loose particle structure gave F9S1 higher fluidity but led to a decrease in strength. As the slag content increased, there was almost no smooth fly ash surface in F7S3 compared to F8S2, but the fly ash was still relatively dispersed. With the continued increase in slag content, more blocky colloids can be observed. When the slag–fly ash ratio was 5:5, the C-S(A)-H gel generated by the slag wraps the fly ash, and almost no noticeable fly ash particles are observed.

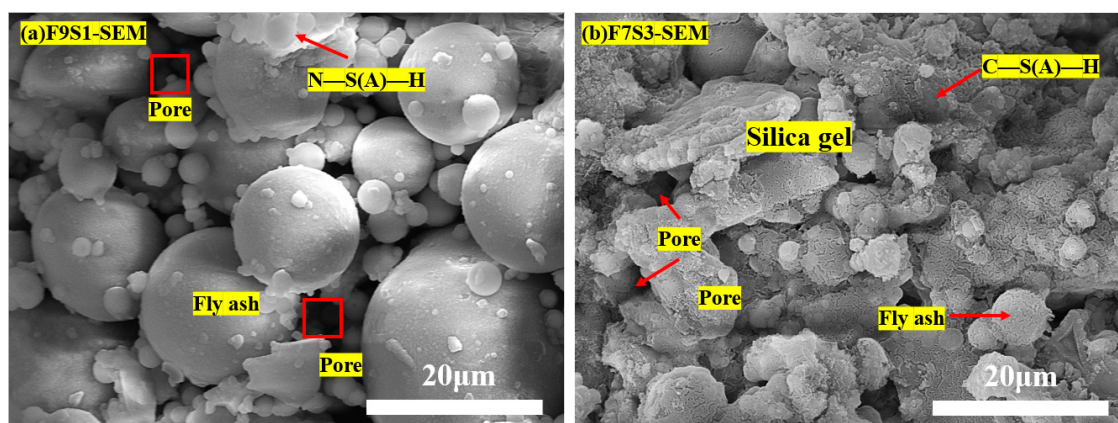


Figure 11. Cont.

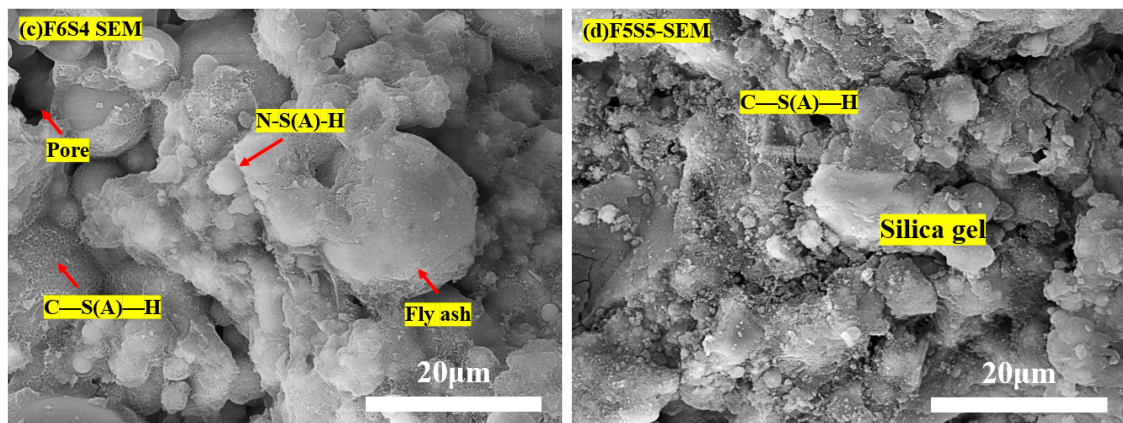


Figure 11. SEM results of HSBF with different fly ash-slag ratios at 20 μm , (a) F9S1 SEM test results (b) F7S3 SEM test results (c) F6S4 SEM test results (d) F5S5 SEM test results.

To explore the mechanism of PDMS, SEM tests with resolutions of 5 μm and 1 μm were conducted on F8S2 and nP-F8S2, and the results are shown in Figure 12.

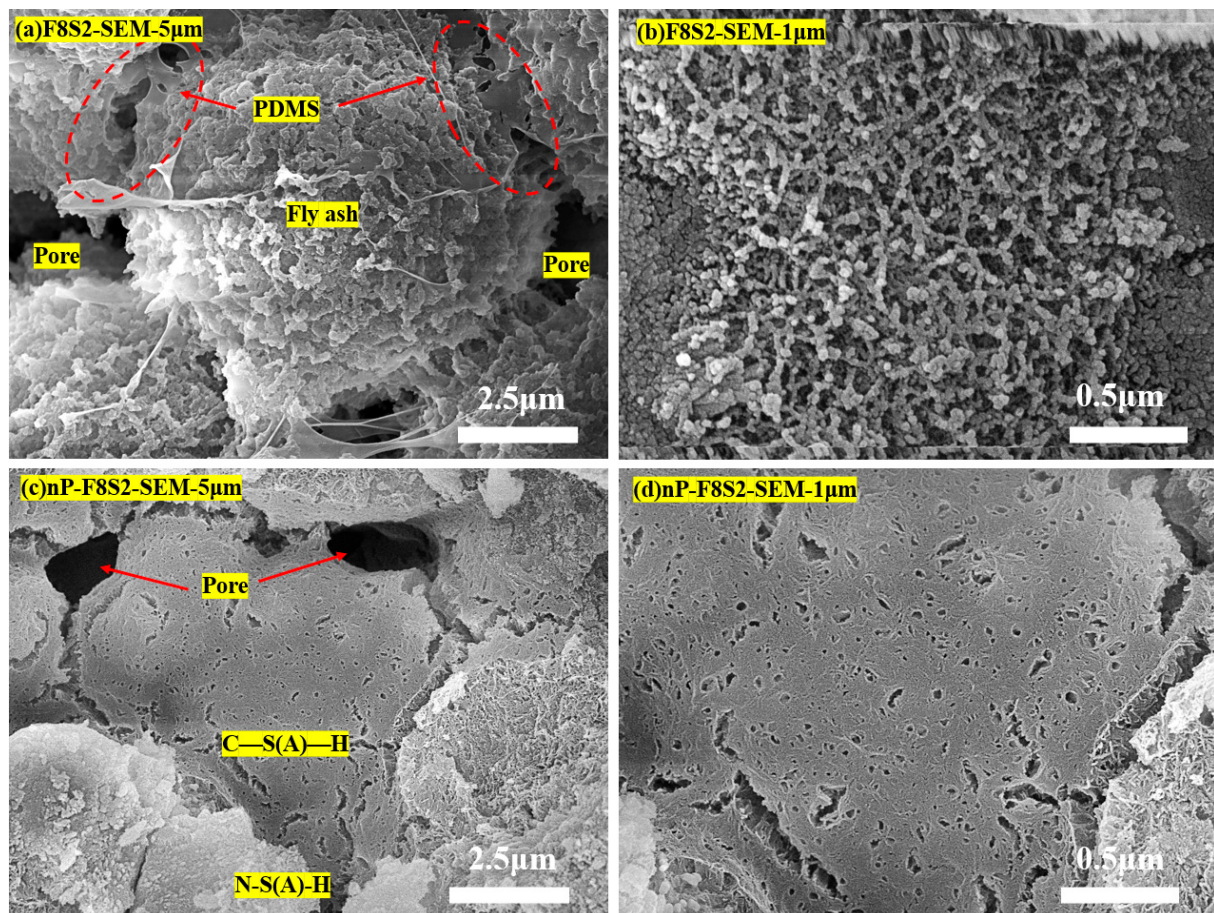


Figure 12. SEM results of F8S2 and nP-F8S2 at 5 μm and 1 μm , (a) 5 μm SEM test of F8S2, (b) 1 μm SEM test of F8S2, (c) 5 μm SEM test of nP-F8S2, (d) 1 μm SEM test of nP-F8S2.

It can be seen from the results that a PDMS connection can be seen between the fly ash particles in the F8S2 (Figure 11a). PDMS is connected to inorganic substances such as fly ash and slag through the bridging effect of the SCA coupling agent.

The silane functional groups in the silane coupling agent reacted with the active sites (such as OH^- groups) on the PDMS surface to form a silicon-oxygen-silicon bond [59].

The formation of this covalent bond made the silane coupling agent firmly adhere to the PDMS surface. At the same time, the organic groups of the silane coupling agent can also react with the active sites on the surface of the slag and fly ash to form Si-O-inorganic surface bonds [44]. In this way, the originally inert PDMS is attached to the surface of inorganic molecules such as fly ash and slag through the bridging effect of the coupling agent to form a uniform and dense capillary structure (Figure 11b), which makes the backfill body hydrophobic. The addition of PDMS inhibited the activation reaction and reduced gel formation and fly ash molecule aggregation. The increase in slag content then generated a large number of dense and compact gel structures, which improve the strength characteristics. The test results match the rheological and strength properties of the slurry.

3.6. Hydration and Carbonation Products in the HSBF Sample

The results of XRD analysis of the HSBF samples after 28 d of curing are shown in Figure 13.

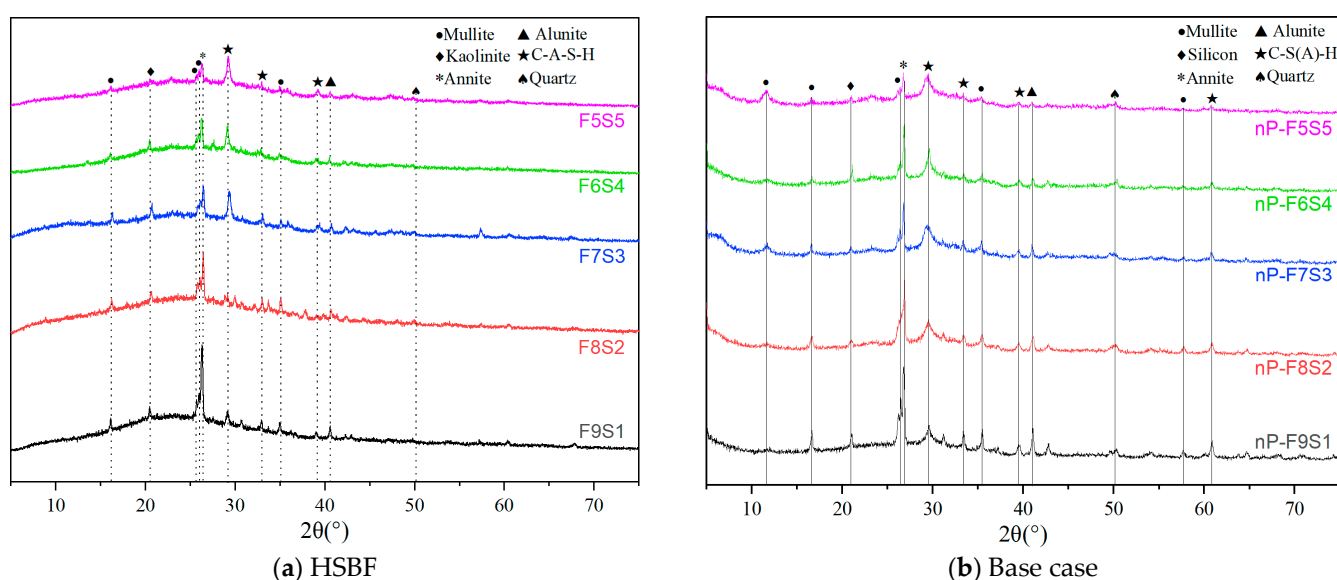


Figure 13. XRD spectra of backfill samples, (a) HSBF, (b) Base case.

The graph shows that the XRD spectra of samples with added PDMS are similar in peak shape to those without PDMS, mainly containing diffraction peaks of mullite, SiO_2 , annite, and C-S(A)-H, which is consistent with previous studies [29,30]. Several shorter peaks can be observed in the XRD spectrum without PDMS, indicating that adding PDMS may have some adverse effects on XRD testing [49]. The observed annite peak gradually decreases with the addition of slag, and the corresponding C-S(A)-H peak gradually increases. Annite is generated from Al_2O_3 and SiO_2 in fly ash in an alkaline environment. With the addition of slag, the CaO in the slag reacts to form C-S(A)-H gel, which adheres to the surface of fly ash, inhibiting the subsequent hydration of fly ash [47].

Overall, the XRD test results of the material after adding PDMS show no significant difference, indicating that no new substances are generated after adding PDMS, and PDMS does not participate in the hydration reaction.

3.7. Infrared Spectroscopy Analysis

The results of the FTIR analysis are shown in Figure 14. The characteristic peaks at 1035 cm^{-1} and 990 cm^{-1} observed in the spectrum belong to the stretching vibration absorption peaks of Si-O. The peak at a low wavenumber of 460 cm^{-1} corresponds to the deformation vibration of Si-O. The intensity and position of the principal peak depend on the length and angle of the chemical bond [60]. The characteristic peak at 990 cm^{-1} was more considerable, indicating that more Si-O bonds were generated in the reference

group [61] and the hydration reaction was sufficient, which confirmed that the addition of PDMS inhibited the hydration reaction to a certain extent. OH stretching vibration generates peaks at 3470 cm^{-1} and 3440 cm^{-1} [62]. Compared with the hydrophobic sample with PDMS, the OH stretching vibration peak of the reference group was more prominent and produced an additional OH stretching vibration peak at 1680 cm^{-1} . Since the sample was dried before the test, this result indicated that the reference group contained more bound water. This is because the hydration reaction of the reference group is sufficient, and more hydration products are generated. The test results are consistent with the microstructure and mechanical properties tests.

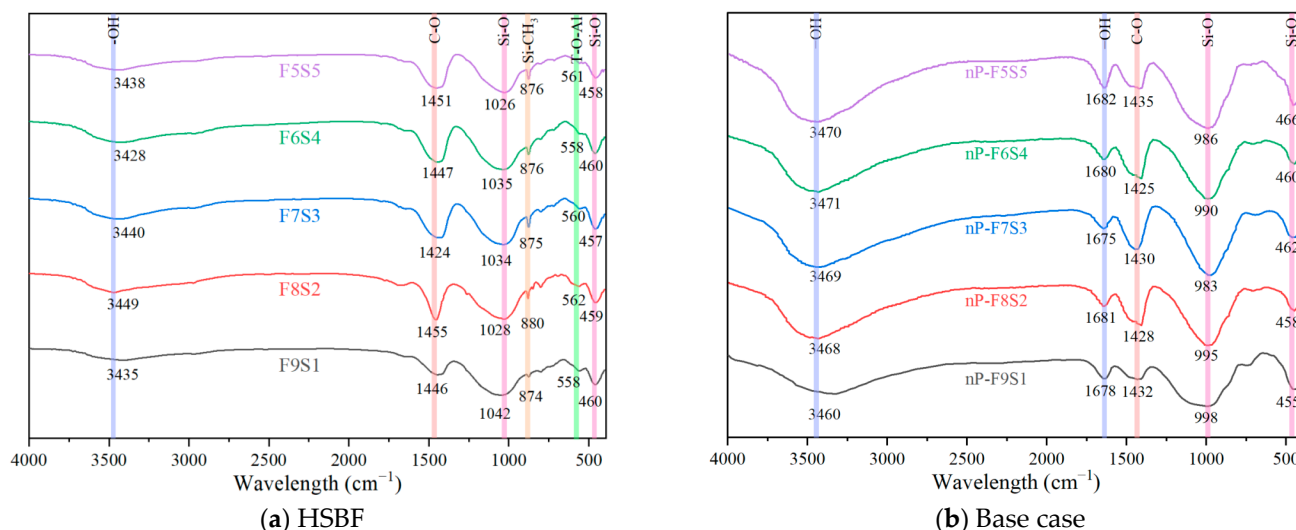


Figure 14. FTIR spectra of backfill samples, (a) HSBF, (b) Base case.

The signal peak from 1400 cm^{-1} to 1450 cm^{-1} was produced by C-O bond vibration, which may be produced by sodium carbonate and calcium carbonate [63,64]. After adding PDMS, compared with the reference group, new characteristic absorption peaks appeared at 875 cm^{-1} and 562 cm^{-1} : the narrow peak at 875 cm^{-1} was generated by the stretching vibration of the Si-CH₃ bond of PDMS [65]. Because less PDMS was added, the peak value formed was smaller. Si-O-T (T represents the active group on the surface of inorganic molecules) formed by the interaction between the coupling agent and inorganic substances such as fly ash and slag at 562 cm^{-1} [66,67]. The formation of Si-O-T indicates that PDMS was attached to the surface of inorganic molecules such as fly ash and slag by a coupling agent. The more Si-O-T bonds are formed, the better the adhesion effect of PDMS, resulting in better hydrophobic performance. The test results are consistent with the water contact angle test results.

3.8. Strengths and Applications

In the design of the novel HSBF, the use of cement is ultimately eliminated. So, the backfill cost is significantly reduced, the comprehensive utilization rate of solid waste is improved, and the construction of green mines is actively promoted. The hydrophobic backfill material shows superior hydrophobic properties, which not only effectively reduce groundwater seepage but also ensure the stability of groundwater around the mining area. It also helps the filling body resist the corrosion-weakening effect of mine water. In addition, the advantages of high early strength and short setting time of the hydrophobic filling body also help to improve the filling efficiency.

4. Conclusions

Utilizing fly ash and slag as the primary raw materials, a novel hydrophobic solid backfill (HSBF) material has been developed by employing PDMS and SCA as hydrophobic

modification agents. Experimental studies were conducted to evaluate its feasibility from rheological and mechanical perspectives. Additionally, morphological analyses (XRD, SEM, FTIR) were carried out to discover the underlying mechanisms of PDMS in HSBF. The following conclusions can be drawn:

- (1) The HSBF paste conforms to the Modified Bingham model and exhibits shear-thinning behavior. The thixotropy of the HSBF paste was consistent with the yield stress.
- (2) After PDMS hydrophobic modification, the water contact angle of the backfill material increased up to 134.9° , exhibiting excellent hydrophobic properties. SEM, XRD, and FTIR tests showed that the PDMS adhered to the surface of inorganic molecules such as fly ash and slag through the bridging action of the coupling agent to form a dense capillary structure, which gave the backfill a hydrophobic effect.
- (3) The overall strength of HSBF increased up to 98% by increasing the slag content from 20 to 50% through the fly ash–slag ratio optimization. The strength enhancement was obtained by the greater development in C-S(A)-H gel, which was achieved in the case of high slag content.
- (4) This research demonstrates that HSBF with various slag ratios (F8S2, F7S3, F6S4, F5F5) exhibits excellent mechanical performance and hydrophobic characteristics. The novel developed HSBF materials are feasible to implement in underground construction with active water interaction.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author due to privacy and ethical restrictions to ensure lawful use of the data.

Conflicts of Interest: The authors declare no conflict of interest.

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