Research Article

Study on the Effects of Powder-Liquid Ratio and Cement Ratio on Mechanical Properties and Microscopic Characteristics of Polymer-Cement Composite

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This paper is about a study on the mechanical properties of a new polymer-cement composite (PCC) in constant elongation, tension, and shear. The study explored the effects of powder-liquid ratio and cement ratio on the mechanical properties of PCC through detecting the strength, deformation, and energy consumption of specimens under different powder-liquid ratios and cement ratios. In addition, scanning electron microscope and mercury injection apparatus were used for an in-depth analysis on the micromorphology and pore structure features of PCC under different powder-liquid ratios and cement ratios to explore the influence of powder-liquid ratio and cement ratio of the micromechanical properties of PCC. The results showed that, with the increase of powder-liquid ratio and cement ratio, the constant elongation adhesion strength of PCC decreased, and, at a high powder-liquid ratio (0.55) or a high cement ratio (0.5), the constant elongation adhesion strength of PCC completely disappeared. Meanwhile, with the increase of powder-liquid ratio and cement ratio, the tensile shear strength of PCC increased, while the deformation capacity of PCC decreased. The optimal ranges of powder-liquid ratio and cement ratio for PCC were 0.35–0.4 and 0.3-0.4, respectively. Furthermore, the increased powder-liquid ratio and cement ratio made the total pore volume decreased and pore structure refined, which improved the compactness of PCC, thus influencing the performance of PCC macroscopically. An achievement for the study is a flexible composite material, which was formulated with the polymer film as continuous base phase, as well as the inorganic composition and cement hydrates as dispersion phase. The material can effectively improve the economy and practicability of cementation of fissures for airfield pavement.

1. Introduction

The defects in joints of airfield pavement are one of the important factors that affect the airport performance and threaten the air safety. In the design and building of airfield pavement, usually, there are a large number of joints set for expansion, contraction, and construction to avoid irregular cracks for temperature and humidity changes, which, at the same time, need to be sealed with fillers for preventing damage on soil foundation and pavement slabs. However, conventional fillers are susceptible to aging in engineering practice [1, 2]; that is, they will be shrunk, hardened, cracked, and peeled soon after perfusion. In some areas where there is a big temperature difference, the fillers may even break, lose adhesion, peel, or be squeezed out, thus losing their original effect for joint sealing and influencing the road maintenance and traffic security seriously. Therefore, the service performance and life of airfield pavement depend on the fillers, a critical link for the airfield pavement.

Polymer-cement composite (PCC) stands out as a new organic-inorganic composite material of high performance for its durability and high-cost effectiveness. Furthermore, it

is environmentally friendly and safe. By now, some scholars have made remarkable achievements for this. Ohama [3, 4] and Ma and Li [5] summarized the preparation methods, advantages and disadvantages, and the modification mechanism for kinds of polymer modified cement mortar and concrete. Song and Tan [6] prepared styrene-acrylic emulsion and styrene-butadiene emulsion modified cement mortar using polymer sand coating process and studied their changes in fluidity, frost resistance, and compressive strength. Al Zahrani et al. [7] carried out a comparative study on the durability of various common mortars and polymer emulsion modified mortars. Maranhao and John [8] studied the performance of polymer modified bonding mortar under different working conditions. Lho et al. [9] studied the influence of the content of polymer and slag on the performance of SBR emulsion modified concrete. Soufi et al. [10] investigated the influence of polymer content on the durability of PEASA modified repair mortar systematically from the perspective of water migration. Senff et al. [11] developed a high-performance polymer modified mortar with excellent shrinkage and crack resistance.

Obviously, the macroscopic mechanical properties and modification mechanism of PCC have been thoroughly studied in the past ten years. The performance and proportion of polymer and cement as two important components of PCC are critical to properties of PCC. For this, many scholars conducted many relevant studies. Schulze [12] studied the effects of water-cement ratio and cement content on mechanical properties of styrene-acrylic latex powder modified cement mortar. Liu et al. [13] studied the variation of working performance, compressive strength, and flexural strength of silicon-acrylic emulsion modified cement mortar with polymer-cement ratio. Ribeiro et al. [14] studied the effects of different polymer-cement ratio and curing time on the properties of SB emulsion modified cement mortar. Muhammad et al. [15] explored the influence of the polymer-cement ratio on the flexural property of epoxy modified mortar board. Zhang et al. [16] studied the effect of polymer emulsion content on the carbonation resistance of concrete.

The formation of PCC mainly includes the hydration and hardening process of the cement component, the dehydration and film formation process of the polymer component, and the reaction between the cement hydration product and the polymer component. Therefore, at the micro level, this type of material has the most significant characteristics. It is the formation of a three-dimensional hybrid structure composed of cement hydration products and polymer membrane structures intertwined. Different types of raw materials, different proportioning parameters, and different preparation processes result in the complex microscopic morphology and material composition of this mixed structure, which in turn makes the mechanical and durability properties of the composite material diversified at the macro level, making it have many technical performance advantages that pure cement-based materials or polymer-based materials do not have, and this is also the basic idea and principle of polymer-cement blending modification. Therefore, studying the morphology, structure, and composition of polymer-cement composites at the material component and micro level will help us understand and master the interaction mechanism between the two types of materials, polymer and cement, and then learn from fundamentally analyzing and explaining the different performance characteristics of different PCCs and provide the scientific basis for improving the utilization rate and use the effect of PCC, reducing the use cost and further optimizing the design of materials.

At the same time, the research on a new type of joint filling materials is still focused on oily organic polymer filling materials. On the one hand, this type of material is not environmentally friendly. It is easy to cause environmental pollution and damage the health of personnel during production and use, which does not meet the current advocacy. As regards the concept of green development, on the other hand, this type of joint filling material is affected by the performance defects of organic materials, and there are still certain deficiencies in durability, aging resistance, and bonding compatibility with cement substrates. In addition, the production cost of such synthetic polymer materials is usually high, which is not conducive to large-scale popularization and use. Therefore, it is necessary to research and develop a joint filling material that not only meets the requirements of the use conditions but also has the characteristics of high durability, low cost, and being pollution-free.

Considering that the fillers for airfield pavement in use mainly bear tensile load and shear load, this study, respectively, designed 6 powder-liquid ratios and 6 cement ratios through tensile test and shear test, so as to have a systematic study concerning the influence of powder-liquid ratio and cement ratio on mechanical properties of constant elongation, tension, and shear. Based on macroscopic tests, the study utilized scanning electron microscope and mercury injection apparatus to analyze the micromorphology and pore structure features of PCC under different powder-liquid ratios and cement ratios, thus further analyzing the microscopic mechanism for the influence of both ratios on mechanical properties of PCC and providing a scientific basis for the design of high-performance airfield pavement fillers.

2. Tests

2.1. The Test Materials. In this study, PCC is a kind of multicomponent composite mainly composed of liquid and powder. The liquid includes polymer emulsion and various liquid additives, and the powder includes cement and various inorganic fillers. The powder-liquid ratio refers to the mass ratio of powder to liquid, while the cement ratio is the mass ratio of cement to total powder. This paper mainly studies the influence of different powder-liquid ratios (the ratio of emulsion mass to total powder mass), cement ratio (the percentage of cement mass in total powder mass), and the number of additives. This is because, under the condition of a certain solid content of the emulsion, the powder-liquid ratio reflects the relative content between the organic component and the inorganic component, and the cement ratio reflects the relative content between the cement and the

filler inside the inorganic component, and the amount of each additive. Reflecting the respective contents of defoamer, dispersant, and film-forming aids, the above-mentioned proportioning parameters cover the changes in the contents of each main component of the joint filler, which is a key variable for the design of the joint filler ratio. The basic ratios of PCC are shown in Table 1.

2.2. Preparation of Test Specimens. With the basic ratios listed in Table 1 as the control group (i.e., DZ group), the influences of powder-liquid ratio and cement ratio on the mechanical properties of PCC were studied, respectively. Tables 2 and 3 list the corresponding mix ratios of groups of specimens. For each group, a total of 10 specimens were prepared: 3 used for constant elongation bonding test, 3 for tensile test, 3 for shear test, and 1 as spare specimen. The PCC specimens and their sizes are as shown in Figures 1 and 2, respectively.

In this study, the two sides of the specimen are cement mortar substrates, the middle is connected by wooden blocks, and the bottom is supported by glass. During the preparation of the test piece, first add SN-5040 dispersant, DN-12 coalescing agent, and half of SN-345 defoaming agent to the VAE emulsion; and use a mixer to stir evenly, and then add the well-mixed cement and quartz powder to the emulsion and continue to stir at high speed for 10 minutes, and then add the other half of the SN-345 defoaming agent and continue to stir at low speed. After the mixture is uniformly stirred, use a glass rod for manual stirring to reduce bubbles, and use a syringe to extract the mixture and pour it between cement-based materials. In order to ensure that the sample surface is flush with the upper surface of the base material and the cushion block after the specimen is cured and dried, the joint filler should be slightly higher than the base material and the cushion block during pouring. Then carry out the next phase of testing. After the test piece is formed, its shape and specific dimensions (size of the joint material, size of the test piece) are shown in the figure.

2.3. Test Methods

(1) Constant elongation test: Constant elongation test is mainly used to test the performance of specimens under long time tension, and its failure modes include cohesion failure and adhesion loss failure. Cohesion failure refers to the rupture of a specimen under tensile load due to its weak deformability. The adhesion loss failure is debonding caused by insufficient bonding strength between the specimen and the substrate. During the experiment, first, a grip as shown in Figure 3 was used to slowly stretch the specimen to a predetermined width (the tensile width in this study was 60% of the initial width of specimen), and a location block of corresponding size was placed. Then the specimen was removed and placed in a room to maintain a constant extension

state for 24 h, so as to observe the damage on the specimen. If the specimen has no obvious cohesion failure or adhesion loss failure, the location block may be removed and the specimen is placed horizontally on a smooth glass sheet for 24 h. The widths of the specimen after elastic recovery at both ends were measured, respectively, and R_e, the corresponding elastic recovery rate, was calculated with equation (1). Each test was repeated 3 times, and the results were averaged.

$$R_e = \frac{W_1 - W_2}{W_1 - W_0} \times 100\%, \tag{1}$$

where W_0, W_1, and W_2 are the initial width, constant elongation width, and width after elastic recovery of the specimen, respectively.

(2) Tensile test: The HS-3001B electronic tensile tester of Shanghai Hesheng Instrument Co., Ltd. was adopted for the test, as shown in Figure 4(a). During the test, the specimen was first loaded into the grip as shown in Figure 4(b) and then stretched at a tensile rate of 5 mm/min until it was destroyed. Corresponding load and displacement curves were plotted. All of the tensile tests were carried out in a room. For each group, the test was repeated for 3 times, and the measured values were averaged.

(3) Shear test: The HS-3001B electronic tensile tester of Shanghai Hesheng Instrument Co., Ltd. was adopted for the test. During the test, the specimen was first loaded into a grip as shown in Figure 4(c), ensuring that the cement mortar substrate was fixed and clamped, and then the right ascending end was lifted upward at a rate of 5 mm/min until the specimen was damaged. Corresponding load displacement curve was plotted. All of the shear tests were carried out in a room. For each group, the test was repeated 3 times, and the measured values were averaged.

(4) Microscopic test: The microtopography observation was conducted with the EM-30 scanning electron microscope (SEM) of COXEM, South Korea, as shown in Figure 5(a). In order to improve the conductivity of the surface of specimen, before the test, the ETD-800 automatic ion sputtering instrument of Beijing Washede Technology Co., Ltd. was used for 90 s of metallization, as shown in Figure 5(b), and then the specimen was observed under different magnifications, respectively. The pore structure was determined with the Pore-Master33 mercury injection apparatus of Quantachrome Instruments, USA, as shown in Figure 5(c). Before the test, the mass of specimen was weighed by a precision electronic balance, and then the specimen was placed in a low-pressure station and a high pressure, respectively, for mercury injection test.

Table 1: Basic ratios of PCC.

Proportioning parameters	Powder-liquid ratio	Cement ratio	Defoaming agent content	Coalescing agent content	Dispersant content
	0.45	0.35	0.5% for total mass of emulsion and powder	6% for mass of emulsion	0.7% for total mass of emulsion and powder
Raw material	Emulsion	Cement	Filler	Defoaming agent	Coalescing agent	Dispersant
	Celvolit 1350 VAE emulsion	Class 42.5 ordinary Portland cement	Quartz powder	SN-345 defoaming agent of silicone	DN-12 coalescing agent	SN-5040 dispersant

Table 2: Ratios with powder-liquid ratio as the variable.

| No. | Ratio | | Ratio of raw material | | | | | |
	Powder-liquid ratio	Cement ratio	VAE emulsion	Quartz powder	P.O 42.5 cement	SN-5040 dispersant	SN-345 defoaming agent	DN-12 coalescing agent
Y1	**0.30**	0.35	100	19.5	10.5	0.91	0.65	6
Y2	**0.35**	0.35	100	22.8	12.2	0.95	0.68	6
Y3	**0.40**	0.35	100	26.0	14.0	0.98	0.70	6
Y4 (DZ)	**0.45**	0.35	100	29.2	15.8	1.02	0.73	6
Y5	**0.50**	0.35	100	32.5	17.5	1.05	0.75	6
Y6	**0.55**	0.35	100	35.8	19.2	1.09	0.78	6

Table 3: Ratios with cement ratio as the variable.

| No. | Ratio | | Ratio of raw material | | | | | |
	Powder-liquid ratio	Cement ratio	VAE emulsion	Quartz powder	P.O 42.5 cement	SN-5040 dispersant	SN-345 defoaming agent	DN-12 coalescing agent
CR1	0.45	**0.25**	100	33.8	11.2	1.02	0.73	6
CR2	0.45	**0.30**	100	31.5	13.5	1.02	0.73	6
CR3 (DZ)	0.45	**0.35**	100	29.2	15.8	1.02	0.73	6
CR4	0.45	**0.40**	100	27.0	18.0	1.02	0.73	6
CR5	0.45	**0.45**	100	24.8	20.2	1.02	0.73	6
CR6	0.45	**0.50**	100	22.5	22.5	1.02	0.73	6

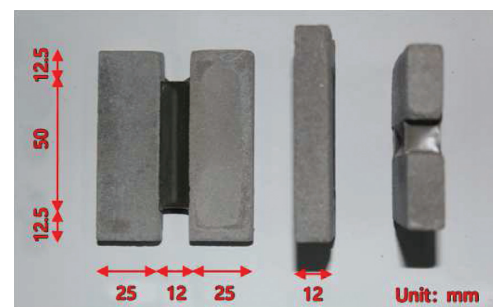Figure 1: Some prepared PCC specimens.

Figure 2: Sizes of specimens.

3. Test Results and Analysis

3.1. Constant Elongation Bonding Property. Figure 6 shows typical constant elongation failure modes of groups of specimens. According to the figure, for groups of specimens, the bonding property is generally good, and only a few specimens showed slight cohesion failure or adhesion loss failure. Among them, the CR1 group had a slight adhesion loss failure for small cement ratio and low bond strength, and the CR6 group had a slight cohesive failure on the specimen surface for high powder proportion and poor flexibility (see Figure 6).

The influence of powder-liquid ratio and cement ratio on the elastic recovery rate of PCC is shown in Figure 7. Obviously, with the increase of powder-liquid ratio, the
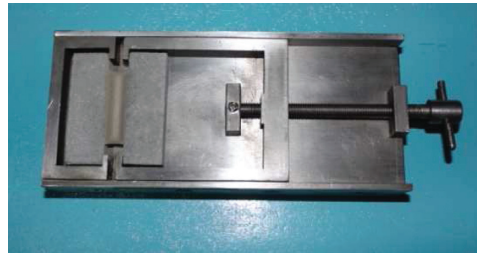
FIGURE 3: Grip for constant elongation bonding test.

(a)   (b)   (c)

FIGURE 4: Tensile and shear testers: (a) electronic tensile tester; (b) grip for tensile test; (c) grip for shear test.

(a)   (b)   (c)

FIGURE 5: Microscopic test instruments: (a) scanning electron microscope; (b) ion sputtering apparatus; (c) automatic mercury injection apparatus.
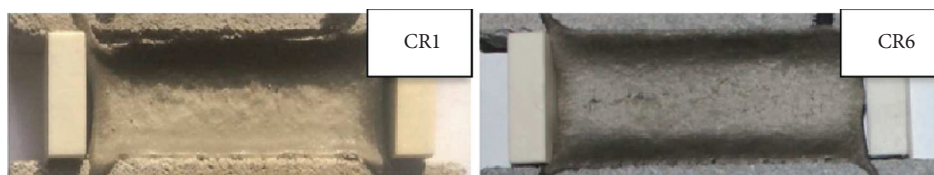

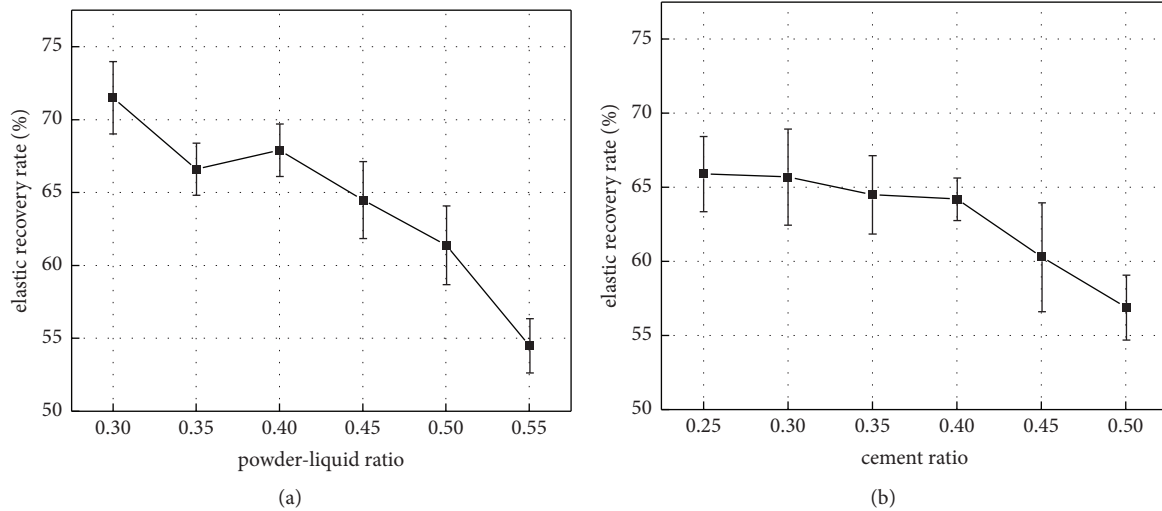FIGURE 6: Typical constant elongation failure modes of groups of specimens.

FIGURE 7: Changes of elastic recovery rate of PCC with powder-liquid ratio and cement ratio: (a) powder-liquid ratio; (b) cement ratio.

elastic recovery rate of PCC decreased, and when the powder-liquid ratio increased to 0.55, the elastic recovery rate of specimen was lower than 60% and failed to meet the requirements for use [17]. Generally, with the increase of cement ratio, the elastic recovery rate of specimen decreased, and when the cement ratio increased to 0.50, the elastic recovery rate of specimen was also lower than 60%. Therefore, the powder-liquid ratio and cement ratio of PCC should not be excessively high.

3.2. Mechanical Properties of Tension

3.2.1. Analysis on the Strength Index. The strength of PCC under tensile load was mainly analyzed by tensile strength and tensile modulus. The influence of powder-liquid ratio and cement ratio on the tensile strength and tensile modulus of PCC is shown in Figure 8. Obviously, the tensile strength and tensile modulus of PCC increased continuously with powder-liquid ratio and cement ratio, while the influence of powder-liquid ratio is more significant. When the powder-liquid ratio was higher than 0.4, the tensile strength and tensile modulus of PCC increased dramatically. When powder-liquid ratio was 0.55, the tensile strength and tensile modulus of PCC were maximum, that is, 0.339 MPa and 0.338 MPa, respectively. When the cement ratio was 0.35–0.4, the tensile strength and tensile modulus of PCC increased rapidly with cement ratio. When the cement ratio was higher than 0.4, the tensile strength and tensile modulus of PCC increased slowly. Obviously, increasing the powder-liquid ratio and cement ratio can improve the tensile strength of PCC.

After analysis, the main reasons for the significant increase in tensile strength and tensile modulus are as follows: First, as the powder-liquid ratio increases, the polymer component can combine with the cement hydrate inside the PCC. They form an interwoven network structure; at the same time, as the cement ratio in the material increases, the cement involved in the hydration reaction in the PCC increases, and the hydration products increase correspondingly. The increase in the hydration products makes the internal structure of the material. The gelation effect is enhanced. Under the combined action of cement hydration products and polymer molecular chains, the pores existing in the internal structure of PCC materials are filled and refined, and the overall material tends to be dense; and the increased hydration products harden, making the PCC material more rigid, and thus the tensile strength and tensile modulus are significantly improved.

3.2.2. Analysis on Deformation Index. The deformation performance of PCC under tensile load was mainly analyzed through ε_T, R_b and $\Delta\varepsilon_{PT}$, that is, peak strain, elongation at break, and plateau tensile strain.

For plateau tensile strain, $\Delta\varepsilon_{PT} = \varepsilon_{0.95b} - \varepsilon_{0.95a}$, where $\varepsilon_{0.95a}$ and $\varepsilon_{0.95b}$ are strain values corresponding to the ascending and descending sections of the tensile stress-strain curve, respectively, when the stress value was equal to 0.95 F_T (see Figure 9). This index was mainly used to represent the approximate plateau section of the PCC stress-strain curve, aiming to describe the yield deformation characteristics during tension of PCC. The larger the plateau tensile strain, the greater the displacement near the tensile strength that PCC can bear, and the better the tensile deformation performance.

The influence of powder-liquid ratio and cement ratio on the tensile deformation indexes of PCC is shown in Figures 10 and 11. According to the figures, with the increase of powder-liquid ratio, the elongation at break, peak strain, and plateau tensile strain of PCC decreased continuously. When the powder-liquid ratio was between 0.40 and 0.45, the elongation at break and the plateau tensile strain decreased dramatically, with decrease rates of 11.2% and 26.2%, respectively. When the powder-liquid ratio was between 0.35 and 0.50, the peak strain plummeted approximately. When the powder-liquid ratio was between 0.50 and 0.55, the downtrend of peak strain slowed down.
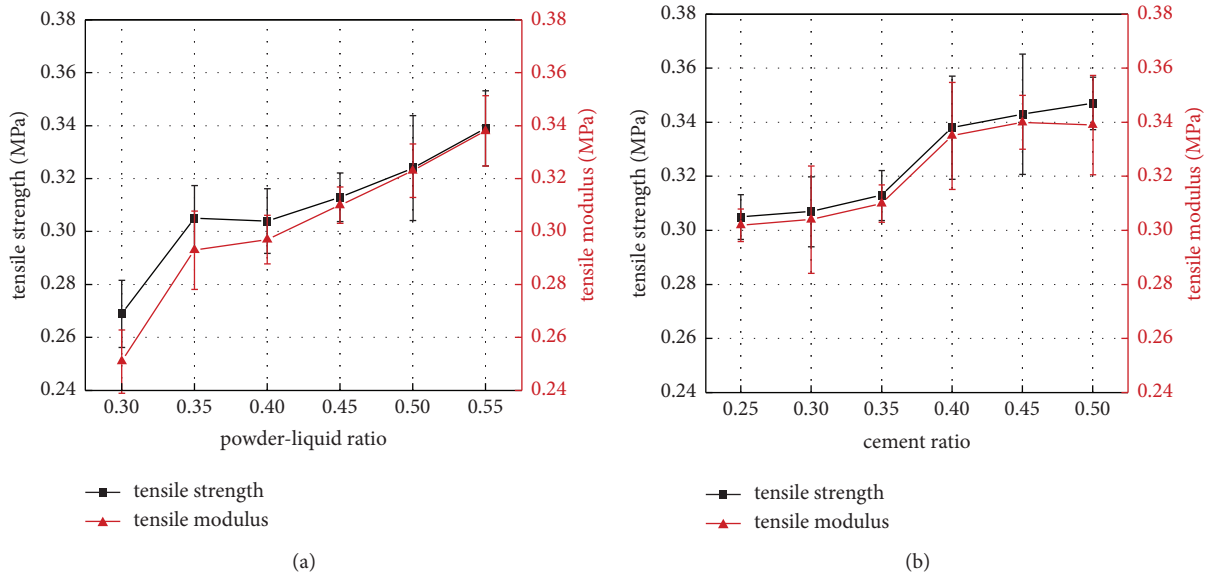
FIGURE 8: Changes of PCC tensile strength with powder-liquid ratio and cement ratio: (a) powder-liquid ratio; (b) cement ratio.
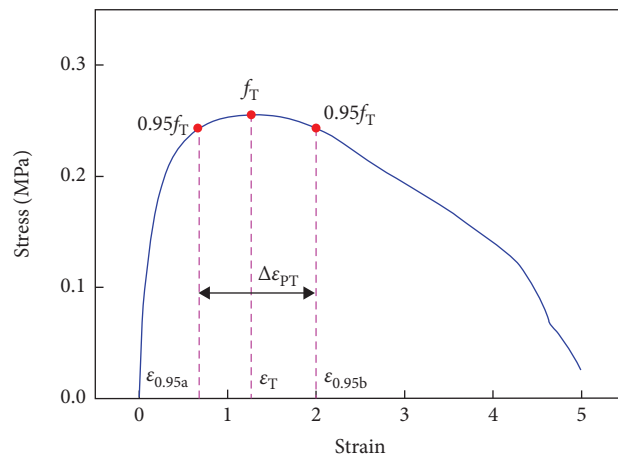

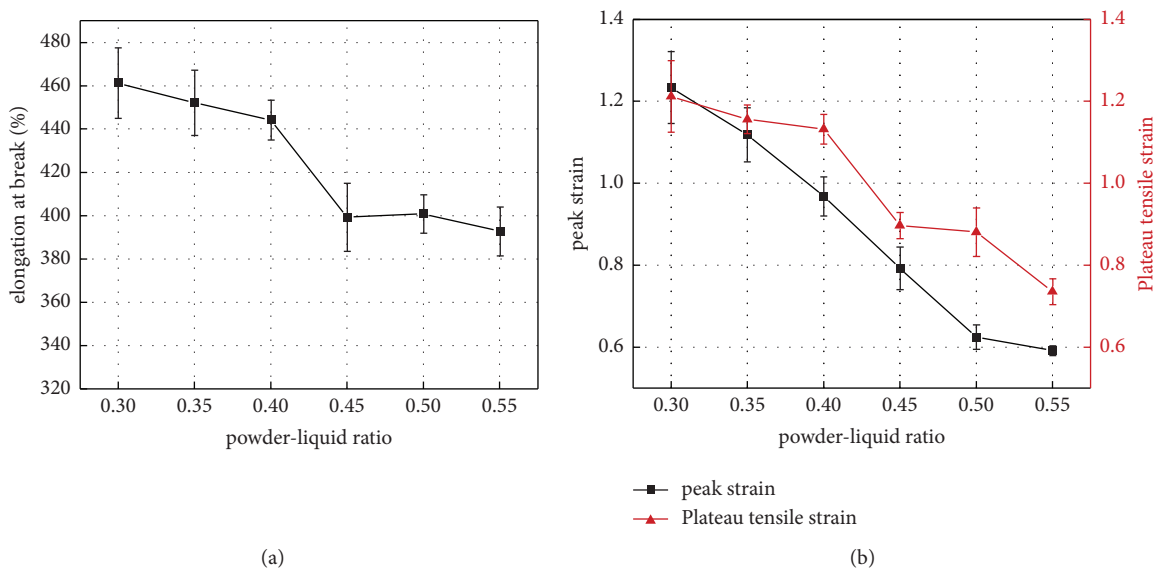FIGURE 9: Definition and calculation of plateau tensile strain.

FIGURE 10: Changes of PCC tensile deformation indexes with powder-liquid ratio: (a) elongation at break; (b) peak strain.
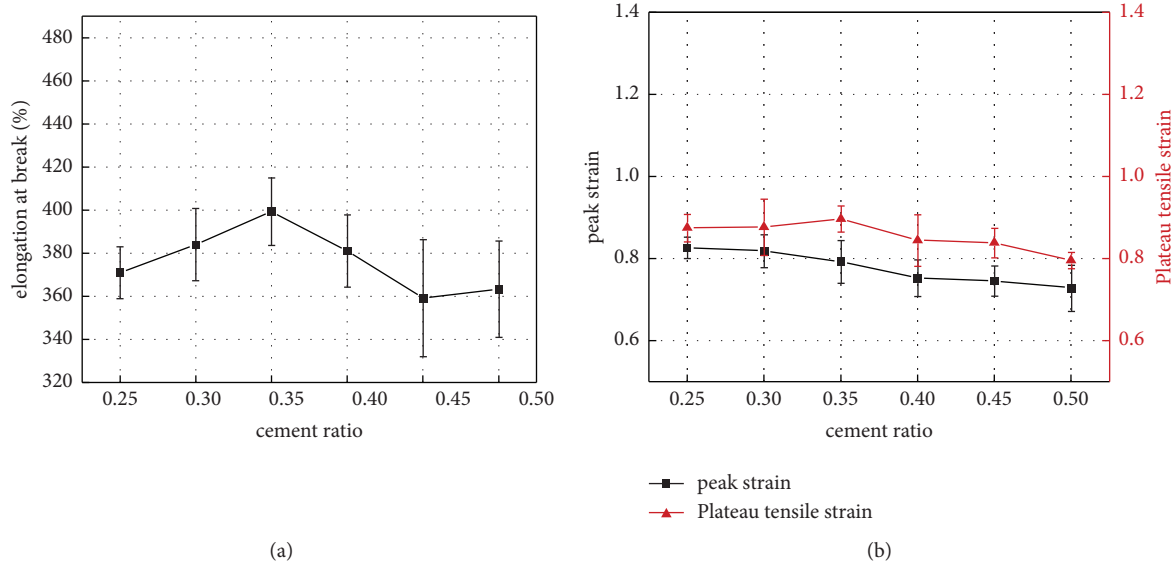
FIGURE 11: Changes of PCC tensile deformation indexes with cement ratio: (a) elongation at break; (b) peak strain.

Generally, with the increase of cement ratio, the elongation at break and the plateau tensile strain of PCC increased first and then decreased, and the peak strain decreased continuously. When the cement ratio was 0.35, the elongation at break and plateau tensile strain of PCC were maximum, that is, 399.3% and 0.897, respectively, and when the cement ratio was 0.45, the elongation at break was minimum, that is, 359.2%. When the cement ratio was 0.25, the peak strain of PCC was maximum, that is, 0.827, and when the cement ratio was 0.50, the peak strain was minimum, that is, 0.729, with a decrease rate of 11.9%. Obviously, PCC had a good tensile deformation performance when the powder-liquid ratio was in the range of 0.3-0.4, and when the cement ratio was 0.35, the tensile deformation performance of PCC was optimal.

After analysis, the main reasons for the influence of the powder-liquid ratio and cement ratio on the tensile deformation properties of PCC materials are in the following aspects: as the powder-liquid ratio increases, there are hydration products in the PCC which have not reacted with the emulsion and unhydrated cement particles are randomly interspersed in the PCC structure or randomly attached to the surface, so that the free pores inside the PCC that are used for the displacement and deformation of the polymer molecular chain to undergo stretching and shearing are filled, which hinders the polymer structure. Free deformation and displacement have weakened the deformability of PCC materials to a certain extent; in addition, with the increase of cement ratio, the gelation in the internal structure of PCC materials will increase, and the filling of pores in the internal structure of the material will be refined. Therefore, the material is denser and the hydration product is harder, which increases the tensile strength. When the material fractures, its peak stress increases, but its toughness decreases and its deformability also decreases. Therefore, macroscopically, the tensile deformation performance of PCC is generally reduced.

3.2.3. Analysis on Energy Consumption Indexes.

The energy consumption indexes of PCC under tensile load were mainly analyzed with tensile toughness and prepeak tensile toughness. Tensile toughness (T_t) is the area under the PCC tensile stress-strain curve, which represents the energy absorbed by the specimen in the whole process of tensile load, and the prepeak tensile toughness (T_{tq}) is the area under the rising section of the PCC tensile stress-strain curve, which represents the energy consumption index of specimen before reaching the tensile strength.

The influence of powder-liquid ratio and cement ratio on the tensile energy consumption indexes of PCC is shown in Figure 12 (the number in the brackets is the percentage of prepeak tensile toughness in the total tensile toughness). The figure shows that, with the increase of powder-liquid ratio, the tensile toughness and prepeak tensile toughness of PCC decreased continuously, and the percentage of prepeak tensile toughness in the total tensile toughness also decreased continuously, indicating that the energy dissipation mainly occurred after the material reached the peak stress. When the powder-liquid ratio was 0.55, the tensile toughness and prepeak tensile toughness of PCC were minimum, that is, 0.799 J•cm^{-3} and 0.152 J•cm^{-3}, respectively, and decreased by 11.1% and 46.1%, respectively, as compared with those when the powder-liquid ratio was 0.3.

With the increase of cement ratio, the tensile toughness and prepeak tensile toughness of PCC increased, and the percentage of prepeak tensile toughness in tensile toughness showed an overall upward trend. When the cement ratio was 0.5, the tensile toughness and prepeak tensile toughness of PCC were maximum, that is, 0.877 J•cm^{-3} and 0.221 J•cm^{-3}, respectively, and increased by 19.5% and 24.2%, respectively, as compared with those when the cement ratio was 0.25. Therefore, increasing the powder-liquid ratio can significantly reduce the tensile energy consumption of PCC, while increasing the cement ratio can increase the tensile energy consumption of PCC.
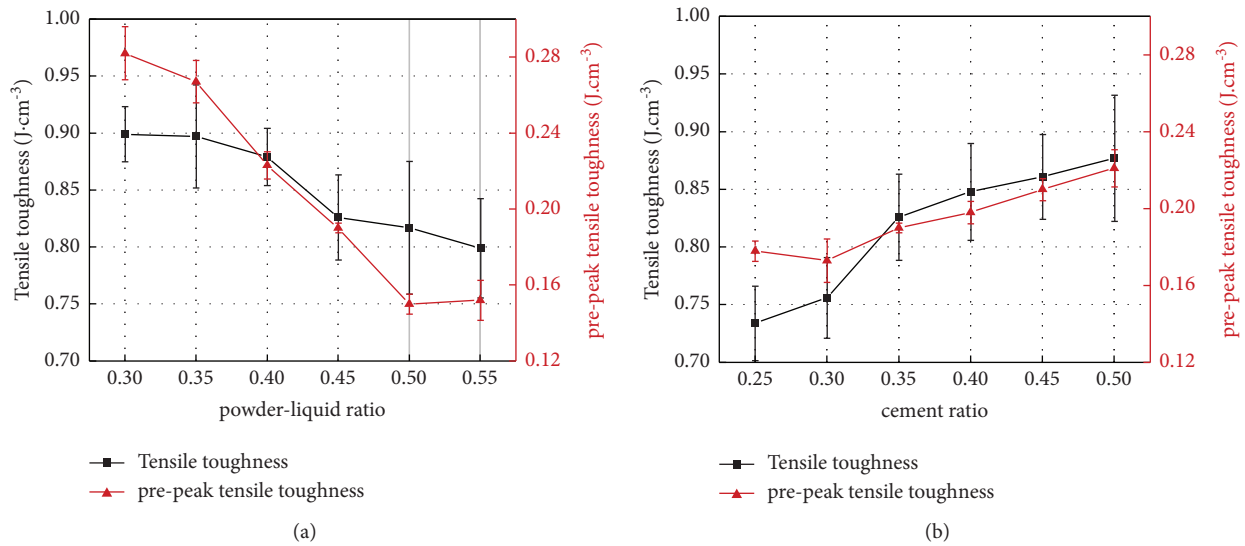
FIGURE 12: Changes of PCC tensile energy consumption indexes with powder-liquid ratio and cement ratio: (a) powder-liquid ratio; (b) cement ratio.

When the cement ratio is larger, the PCC internal hydration products will increase after hardening, so not only will the free volume in the PCC decrease but also more cement hydration products will participate in the reaction with the polymer molecular chain, resulting in more multipolymer molecular chains being cross-linked with each other, which further hinders the movement and stretching under the action of external force. Therefore, as a whole, the strength and deformation properties of joint fillers increase and decrease with the increase of cement ratio, so the peak tensile strain keeps increasing, but the peak strain keeps decreasing. The tensile toughness and the prepeak tensile toughness depend on the changes in tensile stress and strain. It may also happen that when the peak strain of PCC decreases more than the increase of peak strain, the tensile toughness before the peak decreases.

3.3. Mechanical Properties of Shear

3.3.1. Analysis on Relevant Strength Indexes. Relevant strength performance of PCC under shear load was mainly analyzed by two indexes: shear strength and shear modulus. For comparison with the tensile strength of PCC, the shear strength (f_S) is defined as the peak stress of specimen in the shear process, and the shear modulus (E_S) is similarly defined, that is, the elastic modulus when the shear displacement of specimen reaches its original width, that is, 60%.

The influence of powder-liquid ratio and cement ratio on the shear strength and shear modulus of PCC is shown in Figure 13. According to the figure, with the increase of powder-liquid ratio and cement ratio, the shear strength and shear modulus of PCC generally showed an upward trend, and when the powder-liquid ratio was 0.3-0.4, the shear strength increased rapidly. When the powder-liquid ratio was 0.4-0.5, the shear strength changed slightly, while the shear modulus showed an

approximate linear growth generally. When the powder-liquid ratio was 0.55, the shear strength and shear modulus were maximum, that is, 0.324 MPa and 0.174 MPa, respectively, and increased by 9.09% and 42.6%, respectively, as compared with those when the powder-liquid ratio was 0.3.

Generally, the shear strength and shear modulus of PCC increased with the cement ratio. When the cement ratio was 0.25–0.35, the shear strength and shear modulus of PCC increased rapidly, while when the cement ratio was 0.35–0.45, the shear strength and shear modulus increased slowly. When the cement ratio was 0.5, the shear strength and shear modulus were maximum, that is, 0.338 MPa and 0.163 MPa, respectively, and increased by 19.0% and 19.0%, respectively, as compared with those when the cement ratio was 0.25. Therefore, increasing the powder-liquid ratio or cement ratio can significantly increase the shear strength of PCC.

3.3.2. Analysis on Deformation Indexes. The peak shear strain, shear elongation at break, and plateau shear strain were defined with the definitions of corresponding tensile deformation indexes as references for analyzing the shear deformation performance of PCC.

The influence of powder-liquid ratio and cement ratio on the shear deformation index of PCC is shown in Figures 14 and 15. So, with the increase of powder-liquid ratio, the shear elongation at break, the peak shear strain, and the plateau shear strain of PCC showed a downward trend generally, and when the powder-liquid ratio was 0.40–0.55, the three indexes decreased dramatically.

With the increase of cement ratio, the shear elongation at break, peak shear strain, and plateau shear strain of PCC increased first and then decreased and reached the maximum when the cement ratio was 0.35, 526.6%, 2.667, and 1.305, respectively. When the cement ratio was 0.50, the shear elongation at break and the plateau shear strain of PCC were
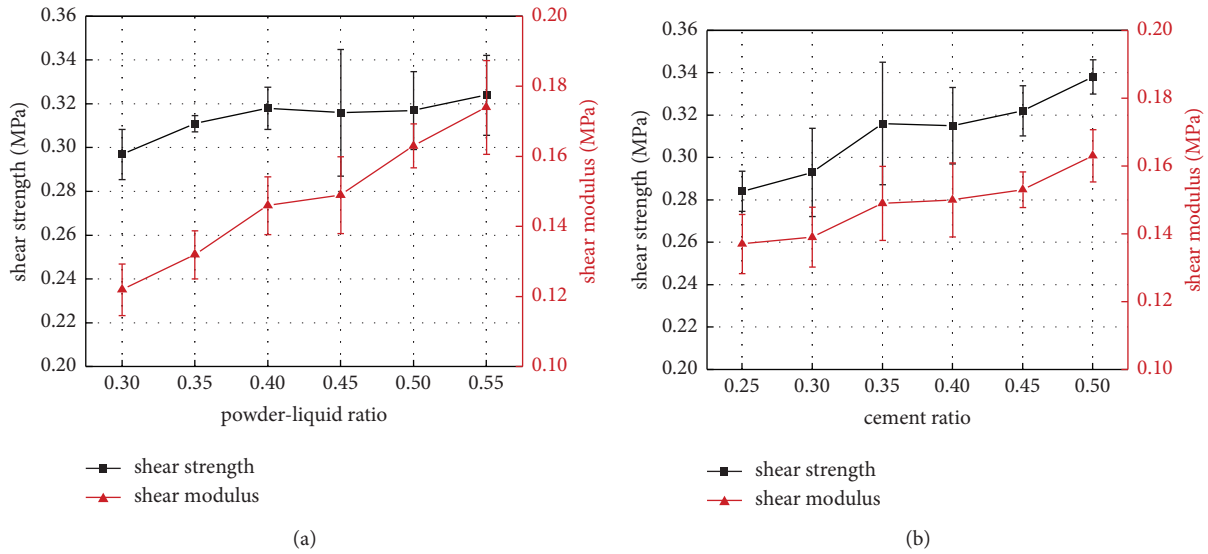
FIGURE 13: Changes of PCC shear strength indexes with powder-liquid ratio and cement ratio: (a) powder-liquid ratio; (b) cement ratio.
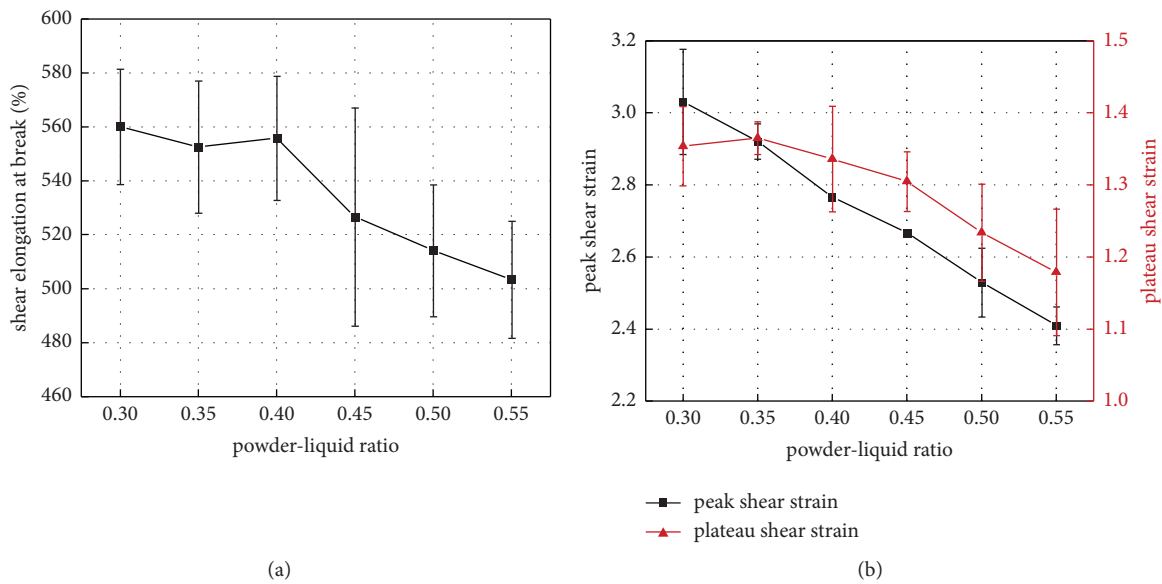

FIGURE 14: Changes of PCC shear deformation indexes with powder-liquid ratio: (a) shear elongation at break; (b) peak shear strain and plateau shear strain.

minimum, that is, 474.2% and 1.212, respectively, and the peak shear strain was 2.53, which was close to the peak shear strain when the cement ratio was 0.30. Therefore, when the powder-liquid ratio was 0.3-0.4 and the cement ratio was 0.35, the shear deformation performance of PCC was optimal.

When the polymer content and the proportion of inorganic components are appropriate, the polymer components can combine with the cement hydrates inside the PCC to form an interwoven network structure with each other, which enhances the internal bonding force of the PCC and enhances the viscosity of the PCC. Therefore, when the powder-liquid ratio increases from 0.35 to 0.4, the shear elongation may increase with the increase of the powder-liquid ratio. At the same time, the toughness increases at the peak strain, and the greater the

displacement and deformation that can be sustained near the peak strain, the greater the shear platform strain.

3.3.3. Analysis on Energy Consumption Indexes. The energy consumption indexes of PCC under shear load were mainly analyzed by shear toughness and prepeak shear toughness, which were defined similarly to tensile energy consumption indexes.

The influence of powder-liquid ratio and cement ratio on the shear energy consumption indexes of PCC is shown in Figure 16 (the number in brackets represents the percentage of the prepeak shear toughness in the total shear toughness). According to the figure, with the increase of powder-liquid
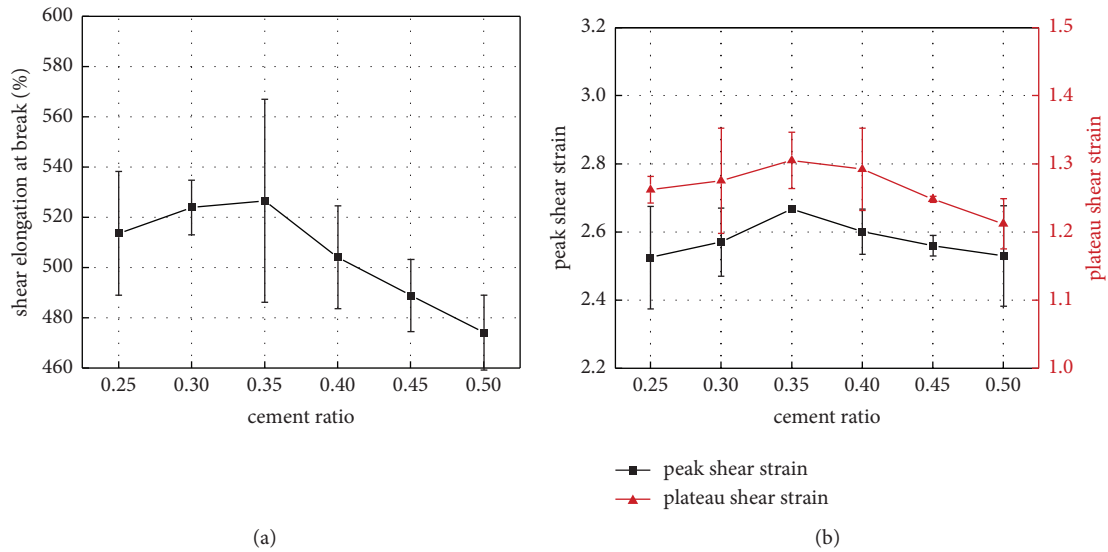
(a)

(b)

FIGURE 15: Changes of PCC shear deformation indexes with cement ratio: (a) shear elongation at break; (b) peak shear strain and plateau shear strain.
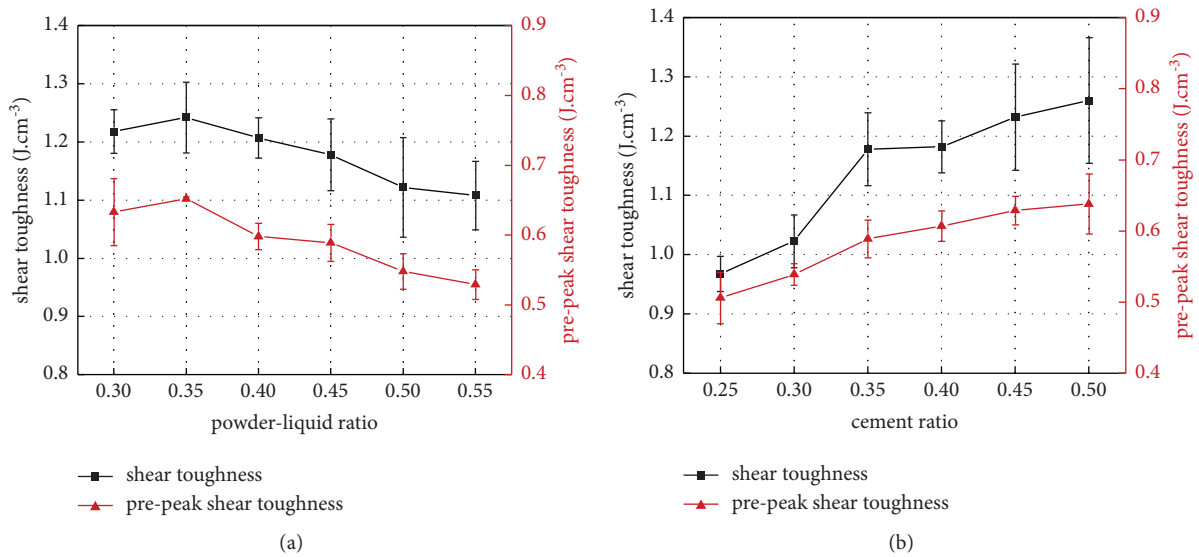

(a)

(b)

FIGURE 16: Change of shear energy consumption indexes of PCC with powder-liquid ratio and cement ratio: (a) powder-liquid ratio; (b) cement ratio.

ratio, the shear toughness and the prepeak shear toughness of PCC both increased first and then decreased. When the powder-liquid ratio was 0.35, both reached the maximum. The percentage of the prepeak shear toughness in the shear toughness of PCC showed a fluctuating downward trend, and the overall amplitude of variation was small.

The shear toughness and preshear toughness of PCC increased with cement ratio, the percentage of the prepeak shear toughness in the shear toughness of PCC showed a fluctuating downward trend, and the overall amplitude of variation was small. When the cement ratio was 0.3–0.35, the shear toughness and prepeak shear toughness of PCC increased rapidly, and the increase rates were 15.2% and 9.3%, respectively. When the cement ratio was greater than 0.35,

the shear toughness and preshear toughness of PCC increased slowly. Obviously, when both powder-liquid ratio and cement ratio were 0.35, the shear energy consumption performance of PCC was optimal.

4. Microscopic Analysis

4.1. Analysis on Microscopic Morphology Indexes. In recent years, scholars all over the world have been deepening studies on the microtopography of PCC. Su et al. [18] found that the polymer component had two main effects on the cement component: First, the cement hydration reaction was delayed by the formation of membrane structure between polymer particles. Second, the microstructure of hydrates
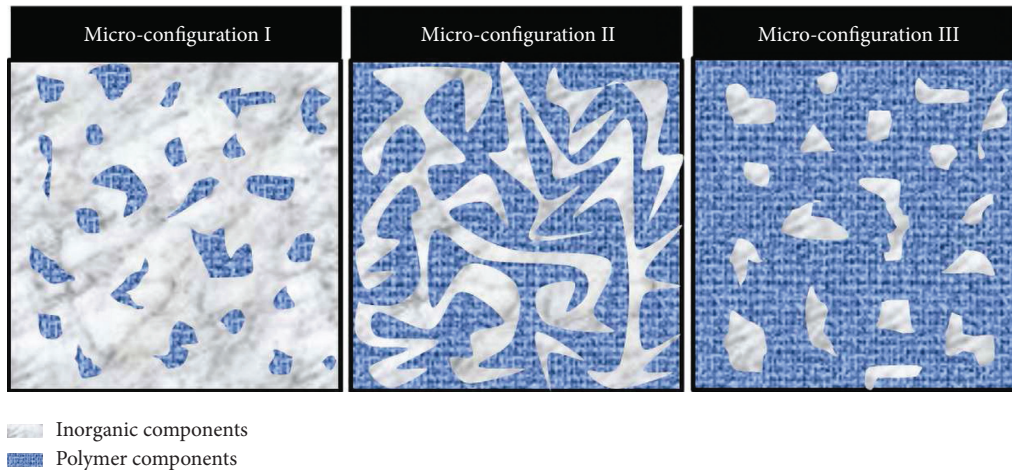
Inorganic components
Polymer components

FIGURE 17: Three microscopic PCC configurations.

was changed by some polymer particles that failed to form membrane structure and filled the pores. Relevant studies [19, 20] have shown that polymers can improve the compactness of the internal structure of the composite material, so as to improve the properties of composites. For this, the polymer-cement ratio is an important factor. Based on studies concerning internal component binding form and microstructure of PCC [21, 22], some scholars proposed corresponding evolution models for describing the microstructure formation process for PCC, among which the three-stage model proposed by Ohama [23] and the four-stage model by Konietzko [24] were relatively mature. Gtetz and Plank [25] developed and expanded the models.

When one or several substances are granular or discontinuously dispersed in a continuous substance, the entire system is called a dispersed system, the dispersed substance is called the dispersed phase, and the continuous substance is called the continuous phase. In the polymer-cement composite material dispersion system, when the polymer component content is low and the cement inorganic filler and gelling component occupy the main body, the polymer component is dispersed into discontinuous particles and filled in the continuous inorganic filler. The polymer component is now the dispersed phase. When the content of the polymer component is sufficient, a continuous polymer film structure can be formed inside the material instead of being dispersed into discontinuous particles. At this time, the polymer component is a continuous phase.

Typically, the basic PCC microstructures are divided into three categories according to the difference in the relative content of organic polymer composition and inorganic composition, as shown in Figure 17. (1) The polymer composition content is low. When the inorganic fillers and the gel components are dominant, the polymer composition cannot form a continuous phase but can only be locally aggregated or scattered in the base phase composed of cement hydrates and fillers in a form of disperse phase. At this point, the material is still rigid macroscopically, and the polymer is mainly for modification and optimization through plasticizing,

toughening, shrinking, and pore reducing. (2) When the polymer composition is equivalent to inorganic composition in content, a continuous structure of polymer film adhesive may be formed, and, at the same time, the rigid grid structure composed of cement hydrates and fillers is not complete and is interspersed and wrapped by polymer film, and thus the two compositions are continuous phases of each other overall, forming a complex network structure, in which the two run through and interweave each other for jointly resisting external forces, and, for this, the stiffness of the material is greatly reduced. (3) When the polymer composition is dominant, the content of inorganic fillers and gel components content is relatively low, the continuous and amorphous polymer film structure constitutes the base phase of the composite, while the inorganic composition merely forms an incomplete gel network structure in a local area, and, on the whole, it is still embedded in the polymer base phase as a dispersed phase. At this point, the material with dominant polymer composition may present a good flexible deformation capacity, while the inorganic composition is mainly for strengthening and filling.

Figure 18 shows typical microscopic morphology of PCC specimens with different ratios at different magnifications. According to the figure, on the whole, the prepared PCC specimens are Class III microscopic configuration mentioned above, that is, with the polymer film adhesive as the continuous base phase, kinds of inorganic components are embedded and dispersed in it. At the same time, the composite network structure formed through interweaving of polymer film, inorganic fillers, and cement hydrates can also be observed at local sites where inorganic components are relatively enriched, similarly to the Class II microscopic configuration mentioned above. There are many different sizes of pores randomly distributed in PCC, which are mainly shrunk holes formed after evaporation of water and bubbles introduced in the process of dispersion and mixing. Inorganic powder is not dispersed in PCC so evenly, and "agglomeration" phenomenon exists to some extent.
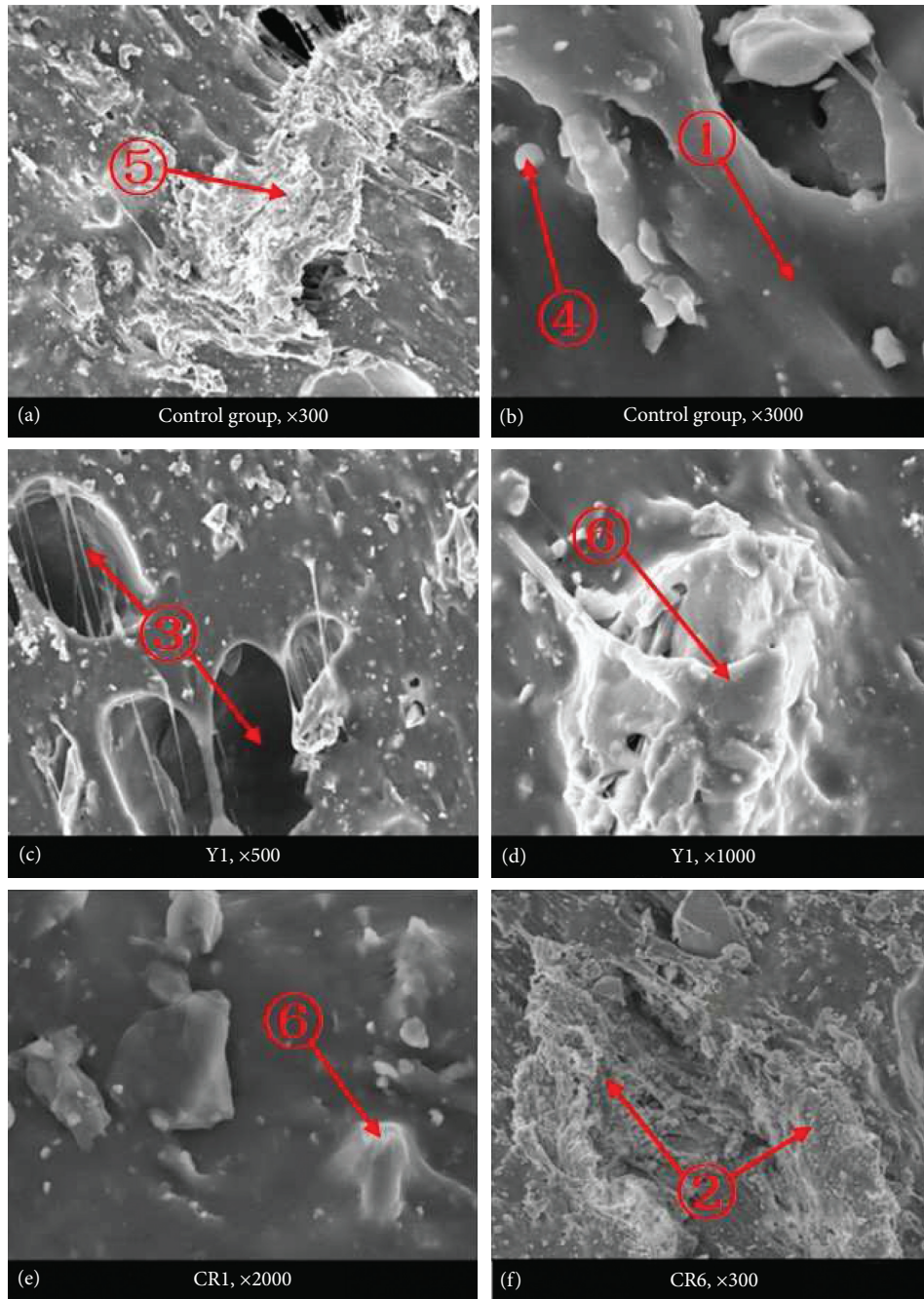
FIGURE 18: Typical microscopic morphology of PCC. ① Polymer film structure; ② the composite network structure; ③ pores; ④ unhydrated cement particles; ⑤ aggregates formed by fillers and cement hydration products; ⑥ agglomeration phenomenon. (a) Control group, ×300, (b) Control group, ×3000, (c) Y1, ×500, (d) Y1, ×1000, (e) CR1, ×2000, and (f) CR6, ×300.

There are unhydrated cement particles in PCC, which are mainly in the form of filler. When the ambient temperature and humidity conditions are met, these cement particles may undergo a secondary hydration reaction, thus improving the compactness of PCC. The changes of powder-liquid ratio and cement ratio will not change the basic microscopic configuration and feature of PCC. However, the change of powder-liquid ratio may significantly alter the microporous structure of PCC. According to Figure 19, compared with the control group

(DZ), the pores of PCC increase with the decrease of powder-liquid ratio (e.g., Y1); on the contrary, with the increase of powder-liquid ratio (e.g., Y6), the pores shrink and become sparse.

4.2. Analysis on Pore Structure Features.

The size distribution for the PCC pore structure is closely related to its macroscopic mechanical performance, impermeability, and corrosion resistance. Therefore, based on the mercury injection
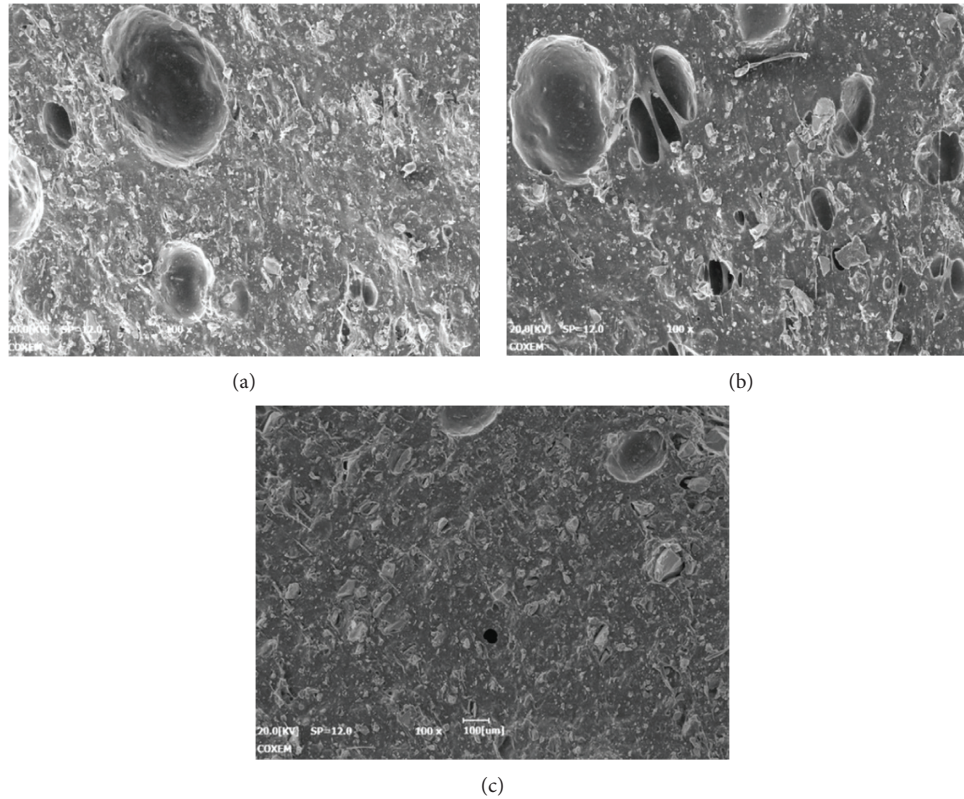
(a)

(b)

(c)

FIGURE 19: Observation results of microscopic pores. (a) Control group, ×100, (b) Y1, ×100, (c) Y1, ×100.

TABLE 4: Pore structure parameters.

Specimen no.	Average pore size (nm)	Most probable pore size (nm)	Median pore size (nm)	Total pore volume (mL/g)	Pore percentage (%)				Pore fractal dimension D_P
					Less than 10 nm	10–100 nm	100–1000 nm	More than 1000 nm	
DZ	63.16	7857	2654	0.1111	6.12	15.48	14.31	64.09	2.7801
Y1	72.86	9261	5092	0.1685	5.46	12.82	9.91	71.81	2.7280
Y6	61.87	7.16	2082	0.1001	6.10	16.88	15.68	61.34	2.7821
CR1	72.35	8648	4905	0.1228	4.89	14.41	11.48	69.22	2.7616
CR6	58.38	7.16	2601	0.1099	6.51	17.27	13.56	62.66	2.7811

test results, the basic pore structure features of PCC were studied through analyzing pore structure parameters, including the differential curve of pore size distribution and average pore size (the ratio of the total pore volume to average pore surface area), most probable pore size (the pore size corresponding to the peak on the differential curve of pore size distribution), median pore size (accumulated into mercury reaching the 50% corresponding pore size), and total pore volume.

Table 4 shows the pore structure parameters for groups of specimens, and the corresponding differential curve of pore size distribution is shown in Figure 20. In addition, the pore structures measured by mercury injection test are generally divided into four categories-based pore sizes [26], that is, macropores (>1000 nm), capillary pores (100–1000 nm), transition pores (10–100 nm), and gel pores (<10 nm). Based on this, the pore percentages of the four

categories of pores for groups of specimens are shown in Figure 21.

According to Figure 21, with the increase of powder-liquid ratio $(Y1 \longrightarrow DZ(Y4) \longrightarrow Y6)$, the total pore volume and characteristic pore sizes of PCC decrease continuously, the percentage of macropores decreases, the proportion of pores with pore size less than 1000 nm increases, and the pore structure is refined as a whole. The reason for this is as follows: at a high powder-liquid ratio, the volume of solid content in PCC is large and the compactness of material is high, with a high resistance to drying and shrinkage deformation, and so the number of pores formed after water evaporation, as well as the pore size, is small. The influence of cement ratio on the pore structure of PCC is the same as that of powder-liquid ratio. With the increase of cement ratio $(CR1 \longrightarrow DZ(CR3) \longrightarrow CR6)$, the total pore volume and
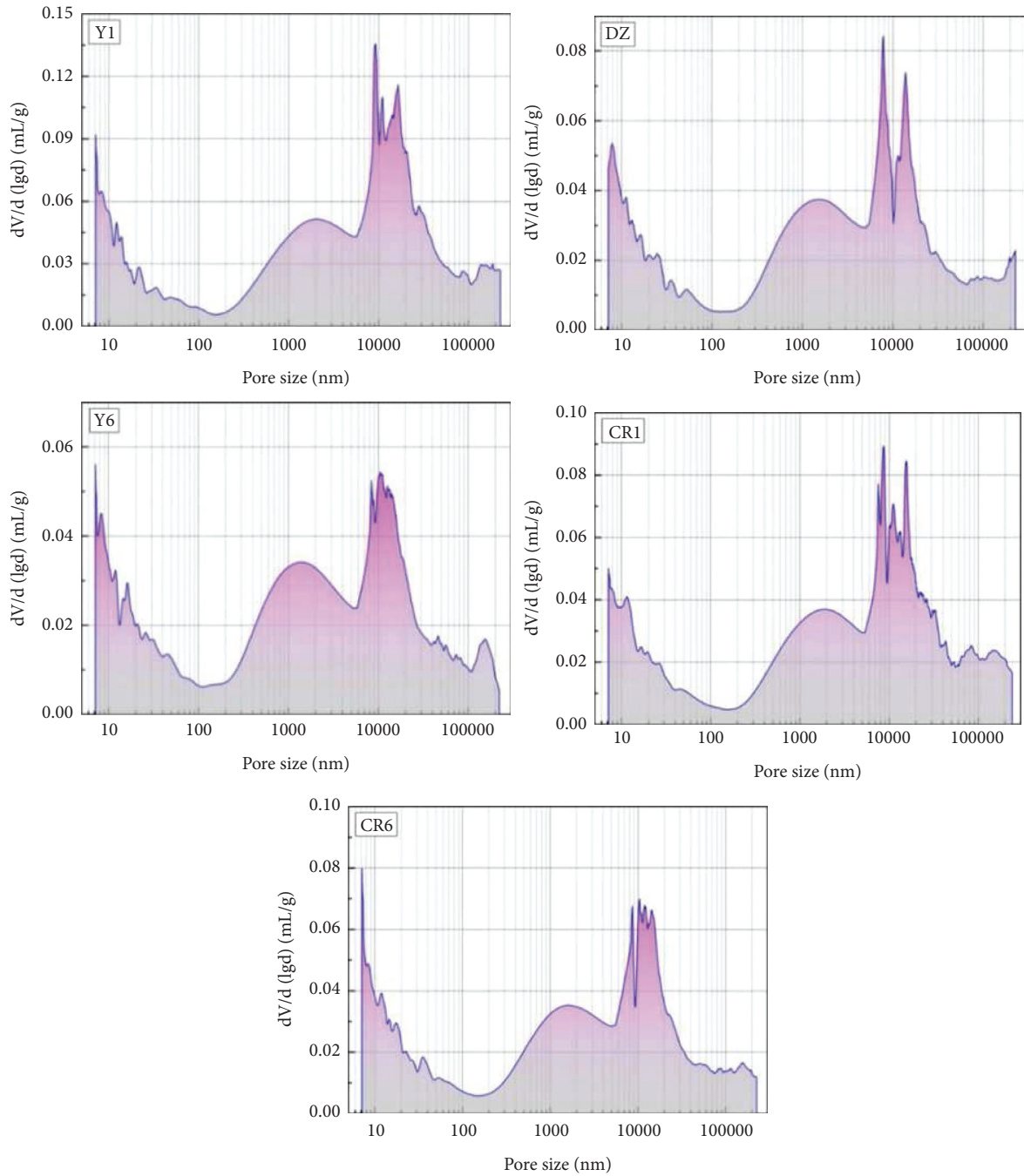
FIGURE 20: Differential curve of pore size distribution.

characteristic pore sizes of PCC decrease continuously, the numbers of gel pores and transition pores increase significantly, and the pore sizes tend to become small, indicating that the increase of cement ratio decreases the internal pore volume and pore size of PCC and increases the compactness of PCC. This is because the high the cement content, the more obvious the cement hydration, for which, on the one hand, the evaporation of water and the resulting number of shrunk holes may be reduced, and, on the other hand, cement hydrates may be increased continuously, and the filling and blocking effects of these hydrates make the internal pores of PCC reduced and refined.
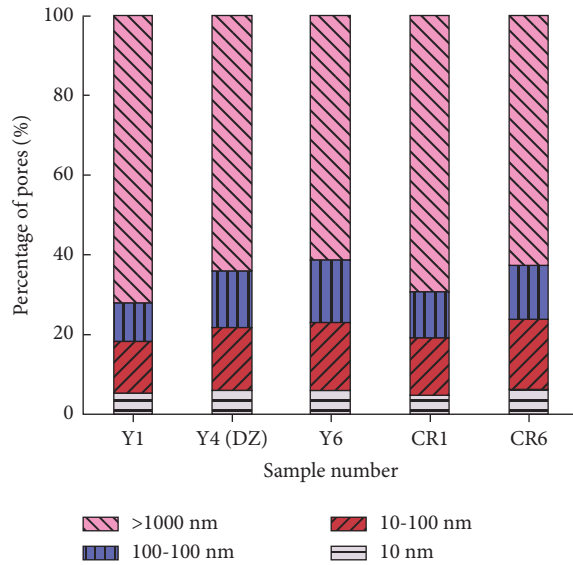
FIGURE 21: Pore percentage distribution.

5. Conclusion

In this study, the influence of powder-liquid ratio and cement ratio on the mechanical performance indexes of PCC was systematically studied through constant elongation and tensile and shear tests; and, at the same time, basic microscopic PCC configurations and pore structure features observed by SEM and mercury injection tests were combined for an in-depth analysis on the effects of powder-liquid ratio and cement ratio on the PCC microtopography and pore structure, as well as the mechanism of influence on the macroscopic mechanical performance of PCC. The main conclusions of this study are as follows:

(1) With the increase of powder-liquid ratio, the constant elongation bonding property of PCC decreased. When the powder-liquid ratio increased to 0.55, the elastic recovery rate of specimens did not meet the requirements for use. With the increase of cement ratio, the elastic recovery rate of specimens decreased generally. When the cement ratio increased to 0.5, the elastic recovery rate of specimens also failed to meet the requirements for use. Therefore, the powder-liquid ratio and cement ratio should not be excessively high.

(2) With the increase of powder-liquid ratio and cement ratio, the tensile shear strength of PCC increased generally, while the deformation performance and the overall energy consumption performance decreased in a fluctuation mode, and the energy consumption performance increased continuously before the peak stress was reached in the tensile and shear process. Therefore, the reasonable range for powder-liquid ratio was 0.35–0.4, while that for cement ratio was 0.3-0.4.

(3) In PCC, there formed a basic microscopic configuration, with polymer film adhesive as the continuous base phase, and inorganic components and cement hydrates embedded and wrapped in it as a dispersed phase. At the same time, there was also a network structure formed through interweaving of polymer film adhesive, inorganic fillers, and cement hydrates locally.

(4) The internal pore structure of PCC was dominated by large pores with pore size greater than 1000 nm (generally more than 60% of the total pore volume), while the volume of gel pores with pore size less than 10 nm was relatively small (less than 10% of the total pore volume). Therefore, increasing the powder-liquid ratio and cement ratio can reduce the total pore volume and refine the pore structure of PCC, thus advancing its compactness.

Data Availability

Some data used to support the findings of this study are included within the article, and other data used to support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Huang and Leng were responsible for the experiments and essay writing, and Professor Xu guided the thesis work. Ren, Chang, Xia, and Wang helped in completing the experiments. All authors have reviewed the manuscript and agreed to publish it.

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