

Structure Formation Mechanism and Properties of Polymer Cement Concrete Composites

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Abstract: This paper analyzes the structure formation mechanism and performance of polymer cement concrete composites. In order to ensure the effectiveness of the study, the method of experiment is selected for the study. In this process, curve research method, fiber spacing theory, research technology to characterize the microstructure of interface transition zone, ring constraint test, plate constraint shrinkage test and so on are introduced. In this paper, the structural properties of polymer cement concrete composites are analyzed with the support of various experiments, in which the probability of concrete deformation can be reduced by 21.4% with the support of polymers.

1. Introduction

Cement and concrete, as traditional building and basic materials, are the most important artificial materials in inorganic non-metallic materials, and are still the indispensable foundation of the whole construction project [1]. At the same time, this kind of material also belongs to brittle materials, and has the fatal weakness of low tensile strength. Due to the erosion of external corrosive materials, the concrete is accelerated and its service life is shortened [2].

Compared with ordinary cement-based materials, the microstructure of high-performance concrete materials has been greatly different, which greatly reduces the open pores and improves the elastic modulus and compressive strength. While the compressive strength and elastic modulus of high-performance cement-based materials are improved, their failure mechanism has changed to a certain extent [3]. How to improve the strength and durability of cement-based materials is an important part of research on the effectiveness of cement mixtures [4].

2. Literature review

In ancient times, the ancestors used natural fibers as reinforcements of some inorganic cementitious materials to reduce shrinkage cracks, maintain integrity and reduce brittleness. For example, the Shuanglin temple near the ancient city of Pingyao, Shanxi, China, has lasted more than 1000 years. The brick walls of more than 10 halls in the temple are made of lime clay mixed with hemp [5].

In modern times, especially from the 1960s to 1970s, great progress has been made in the development of new fiber-reinforced cement-based composites, especially the rapid development of glass fiber reinforced resin matrix composites has played a certain stimulating and promoting role. In 1963, Romualdi of the United States put forward the "fiber crack prevention theory", which promoted the development of fiber reinforced concrete [6].

3. Concrete

3.1 Classification of common fiber reinforced concrete

Polymer concrete is to try to mix polymer into concrete to form hybrid composites. Due to the addition of a small amount of polymer, the pores and micro cracks in the concrete are filled, which greatly improves the performance of the concrete [7].

Fiber-reinforced concrete usually refers to cement-based mortar, grout, or concrete-cement composites, with conventional short fibers or links adding long fibers for additional strength. The classification of fiber reinforced concrete can be carried out according to different criteria, different classification systems or classification basis [8]. Table 1 lists the classification of fibers used in common fiber reinforced concrete. Table 2 shows comparison of physical properties between polymer concrete and ordinary mixture.

Table 1 Classification of common fiber reinforced concrete

Classification basis	Category
Classification by material	<p>1. Metal fiber (such as carbon steel fiber, stainless steel fiber, metal glass fiber, etc.)</p> <p>2. Inorganic fiber</p> <p>Natural mineral fibers (such as chrysotile, acicular wollastonite, etc.) make mineral fibers (such as alkali resistant glass fibers, alkali resistant asbestos, etc.) carbon fibers</p> <p>3. Organic fiber</p> <p>Fiber forming (such as polypropylene fiber, nylon fiber, polyethylene fiber, high modulus polyvinyl alcohol fiber, modified polyacrylonitrile fiber, aryl polyamide fiber, etc.)</p> <p>Material fiber (such as sisal, sisal, jute, elephant grass, etc.)</p>
Classification by elastic modulus	<p>1. High modulus fibers (fibers with elastic modulus higher than that of cement matrix, such as steel fiber, asbestos, glass fiber, carbon fiber, high modulus polyvinyl alcohol fiber, aryl polyamide fiber, etc.)</p> <p>2. Fibers with low modulus whose elastic modulus is lower than that of cement matrix, such as polypropylene fiber, nylon fiber, polyethylene fiber and most plant fibers)</p>
Classification by fiber length	<p>1. Discontinuous short fibers (such as steel fiber, asbestos, chopped glass fiber Twistless roving, polypropylene monofilament fiber, polypropylene membrane crack fiber, nylon fiber, etc.)</p> <p>2. Continuous long fibers (such as continuous glass fiber untwisted roving, glass fiber mesh cloth, fiber polypropylene film, etc.)</p>

Table 2 Comparison of physical properties between polymer concrete and ordinary mixture

Nature	Ordinary concrete	Polymer impregnated concrete	Polymer bonded concrete	Polymer cement concrete
Compressive strength (MPa)	28-35	100-150	40-150	28-56
Tensile strength (MPa)	2.1-2.5	8-11.5	7-14	4-6.5
Breaking strength (MPa)			8.5-21	10-12.5
Modulus of elasticity (10^4 MPa)	2-2.5	3.5-4	0.7-3.5	1-1.5

3.2 Composite mechanics theory

There are mainly two theories about the reinforcement mechanism of fiber to concrete. One is the theory of composite mechanics, and the other is the theory of fiber spacing based on fracture mechanics [9]. Today's research is further deepened to the interface mesostructure and the resulting interface effect, and the relationship between the microscopic and macroscopic behavior of fiber reinforced concrete [10].

The theory of composite mechanics regards composite materials as a multiphase system, and simplifies fiber reinforced concrete as a two-phase composite with fiber as one phase and concrete as the other phase [11]. The properties of the composites are the sum of the phases. According to the above basic assumptions, the calculation formula of the average stress and elastic modulus of the composite material is shown in formula (1):

$$P_c = P_f + P_m(1)$$

Where $P_c/P_f/P_m$ are the loads of composite material, fiber and matrix respectively. When the strain of fiber and matrix is the same, that is, as shown in formula (2):

$$\varepsilon_c = \varepsilon_f = \varepsilon_m(2)$$

Convert the load into stress to obtain formula (3) and formula (4):

$$\sigma_c = \sigma_f V_f + \sigma_m V_m(3)$$

$$E_c = E_f V_f + E_m V_m(4)$$

The order in the formula is: composite material, fiber and matrix stress; Elastic modulus of composites, fibers and matrix; Volume fraction of dimension and matrix. As shown in formula (5):

$$V_f + V_m = 1(5)$$

According to the distribution of fibers in the cement matrix and the length of fibers, the composite mechanics theory can be subdivided into. Therefore, the theory of composite mechanics is only applicable to the situation before the initial crack of fiber reinforced concrete. Once the matrix cracks, this theory is not applicable.

Although the fiber direction effective coefficient, fiber length effective coefficient and interface bonding coefficient are used in this theory, this empirical formula is difficult to reflect the real stress situation of cement-based composites. Therefore, the theory of composite mechanics does not fully reflect the anti cracking effect of fiber on cement matrix.

3.3 Polymers

There are many kinds of polymer additives for cement concrete improvement, but basically there are three types: latex, liquid resin and water-soluble polymer, among which latex is the most used. Natural rubber liquid was first used in the 1930s, followed by polyvinyl acetate lotion. After the 1960s, polymers such as styrene butadiene latex, chloroprene latex and vinylidene chloride lotion, acrylic copolymer lotion, etc. were widely used. The polymer morphology used for cement concrete modification is shown in figure 1.

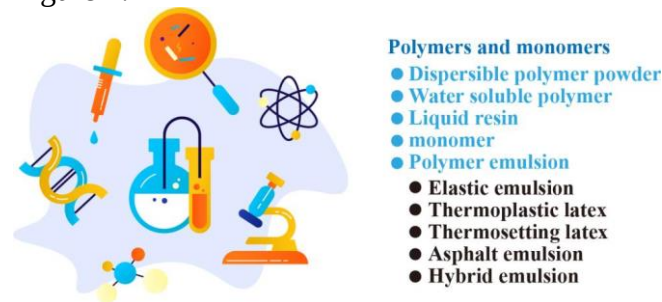


Figure 1 Polymer morphology of cement concrete modification

The first stage: when the polymer lotion is mixed into the concrete during the mixing process of cement concrete, the polymer particles in the lotion are evenly distributed in the cement paste to form polymer cement paste [12]. In this system, with the hydration of cement, cement gel gradually formed, and reached saturation in the liquid phase.

The second stage: with the decrease of water volume, the cement gel structure is developing, and the polymer is gradually limited in the capillary pores. The surface of hydrated gel (including unhydrated cement particles) forms a polymer sealing layer, which also binds the surface of aggregate particles and the surface of the mixture of cement hydrated gel and cement particles. Since the size of pores in cement paste ranges from a few tenths of a meter to hundreds of nm, and the size of polymer particles generally ranges from 50nm to 500nm, this theory that polymer particles are mainly filled in the pores of cement paste is acceptable. See figure 2 for details.

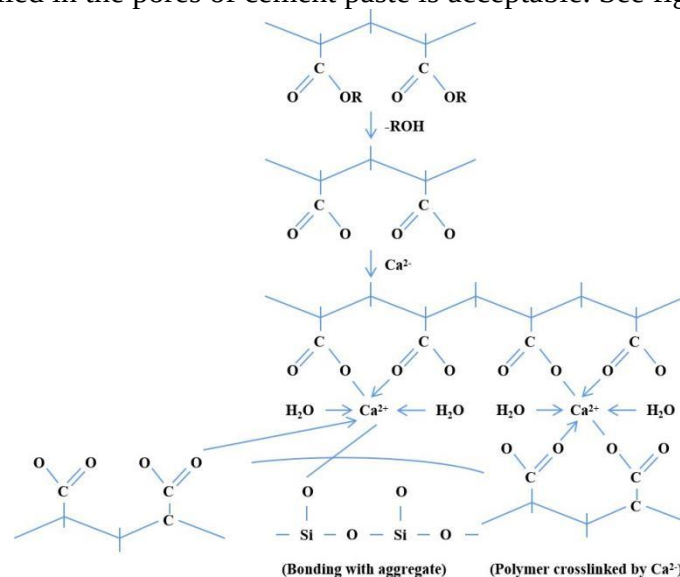


Figure 2 Reaction diagram

The specific strength of polymer matrix composites reinforced with organic fibers such as carbon fiber and boron fiber is 3 to 5 times that of titanium alloy, and the specific modulus is 4 times that of

steel. This parameter will be different depending on the fiber reinforced. Vibration experiments were performed on beams of the same shape and size, and it took 9 seconds for light alloy beams to stop vibrating, while carbon fiber composites only needed 2.5 seconds to stop the same amount of vibration [13].

4. Method

In the experiment, we assume that 3.564g polyvinyl alcohol is dissolved in warm water, and then 10.236g metal Fe powder is sprinkled into it. After stirring evenly, two kinds of coatings (3.5mm and 2.5mm) are made on the glass sheet. It can be left at room temperature for several hours or placed in some other equipment to speed up its solidification process. The V-I curve results of polyvinyl alcohol polymer were measured after solidification.

4.1 V-I curve of thick Fe/ polyvinyl alcohol polymer

1) The specific data of Fe/ polyvinyl alcohol polymer (width: 2.6cm, length: 1.5cm, thickness: 3.5mm) are shown in figure 3.

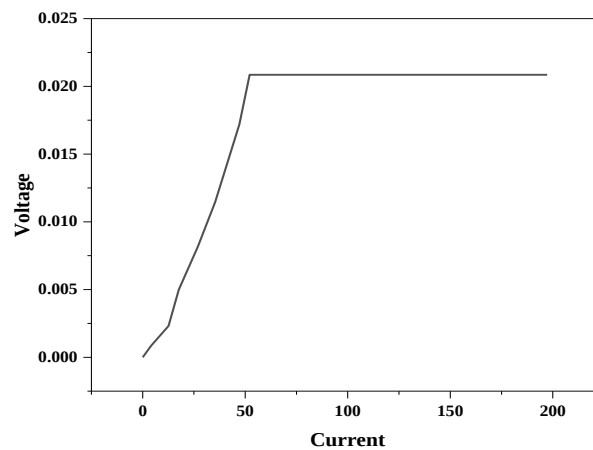


Figure 3 Data

2) The specific data of Fe/ polyvinyl alcohol polymer (width: 2.6cm, length: 2.0cm, thickness: 3.5mm) are shown in figure 4; the critical voltage is 79V.

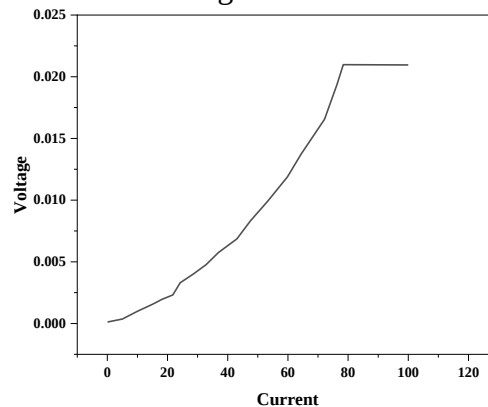


Figure 4 Curve

3) The specific data of Fe/ polyvinyl alcohol polymer (width: 2.6cm, length: 3.0cm, thickness:

3.5mm) are shown in figure 5; the critical voltage is 93V.

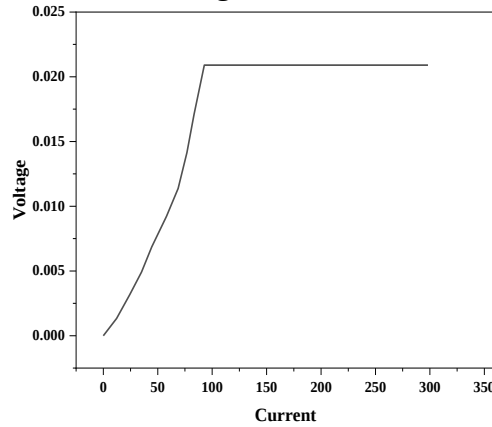


Figure 5 Curve

4) The specific data of Fe/ polyvinyl alcohol polymer (width: 2.6cm, length: 3.5cm, thickness: 3.5mm) are shown in figure 6; the critical voltage is 141V.

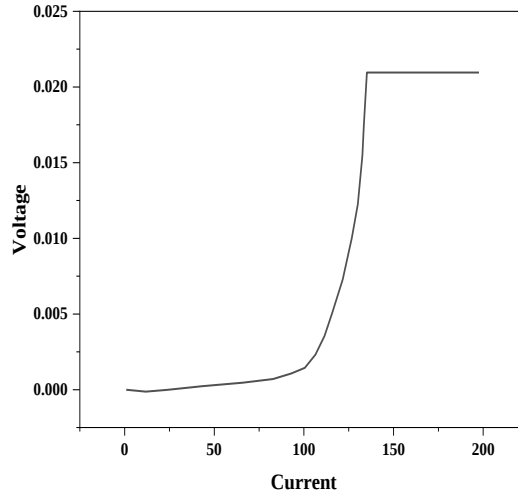


Figure 6 Data chart

It can be observed from the curve that when the voltage increases to a certain value, the resistance of the composite tends to infinity, and the change of the material resistance is a nonlinear change, and the change rate of the resistance also increases with the change of temperature, especially at the critical point, the resistance tends to infinity, and the circuit is in an open circuit state. At room temperature, the iron powder in the composite contacts with each other to form a conductive network with a certain density. With the increase of voltage and temperature, the specific volume of the polymer increases exponentially, while the specific volume of iron powder is basically unchanged, resulting in the thermal mismatch of two-phase materials at the same temperature T , increasing the distance between conductive particles or aggregates composed of particles, destroying the conductive network, reducing the conductive channel in unit volume, and rapidly increasing the resistivity. When the voltage reaches the critical point, the conductive network is completely destroyed, so the resistance tends to infinity, as the experimental data show [14].

4.2 Fiber spacing theory of fiber reinforced cement-based composites

The fiber spacing theory was proposed in 1963. Based on the on-line elastic fracture mechanics,

this theory believes that there are micro cracks, pores and defects with different scales in the concrete. When an external force is applied, large stress concentration will occur in the holes, joints and other parts, causing the expansion of cracks and ultimately the destruction of the structure.

When calculating the fiber spacing S , it is assumed that the fibers are distributed in a square chessboard shape in the plane [15]. The average fiber spacing S obtained from theoretical and experimental research is shown in formula (6):

$$S = 13.8d \sqrt{\frac{1}{p}} \quad (6)$$

Where: d - fiber diameter; p is the percentage of fiber volume fraction.

$$P = V_f \times 100 \quad (7)$$

In formula (7), the concept of effective spacing coefficient is not only to statistically describe the spacing of fiber centers, but also to explain the interaction and failure mode of fiber matrix. Its expression should include the factors affecting the fiber shape of spacing. The expression of effective fiber spacing given by them is shown in formula (8):

$$S = 25.0 \sqrt{\frac{d}{pl}} \quad (8)$$

This concept is applied to the uniformly distributed random short fiber reinforced concrete. The results show that the initial crack stress of fiber reinforced concrete is inversely proportional to the square root of fiber spacing. The research work further improved and developed the fiber spacing theory. He regarded steel fiber reinforced concrete as a particle composite, and the tensile strength of the composite is inversely proportional to the square root of the average particle spacing. The tensile strength formula of steel fiber reinforced concrete is shown in formula (9):

$$f_{cu} = K \left(\frac{1}{\sqrt{s}} - \frac{1}{\sqrt{s_c}} \right) + f_{mm} \quad (9)$$

Where: k is the constant determined by the bond strength; s - average fiber spacing; s_c - the upper limit of fiber spacing when steel fiber can play a reinforcing role;

Based on linear elastic fracture mechanics, fiber spacing theory emphasizes the inhibition of fiber reinforced concrete on crack initiation and propagation in the process of structure formation and stress, which is closely related to fiber spacing.

4.3 Research techniques for characterizing the microstructure of interface transition zone

X-ray diffraction method usually splits the slurry from the aggregate surface before testing, and then uses X-ray diffraction technology to analyze the change of orientation of calcium hydroxide with the distance from the aggregate surface layer by layer. The orientation of calcium hydroxide crystal in the interface transition zone between aggregate and cement paste was studied by this method for the first time. Later, some scholars studied the change of the normal average size of the crystal plane with the distance from the aggregate surface.

4.4 Ring restraint test

Ring test is one of the most widely used restrained shrinkage cracking tests of concrete in recent years. When pouring concrete outside the rigid restraint ring, the shrinkage of the concrete ring is limited by the internal steel ring, resulting in circumferential stress and cracking. The stress of concrete ring is analyzed by using the theory of elasticity. The experimental data of annular

constraint are shown in figure 7.

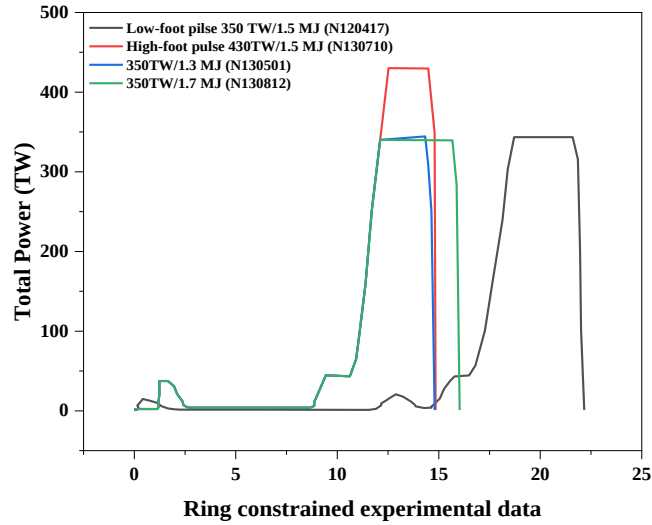


Figure 7 Experimental data of circular constraint

4.5 Plate restraint shrinkage test

Circumferential and axial constraints are essentially unidirectional constraints. In the research on the resistance of concrete to plastic shrinkage and drying shrinkage cracking, the research team of Michigan State University in the United States adopted a flat plate test device restrained by bent steel plates; The characteristics of these two different concrete shrinkage measuring devices are shown in Table 3. The relationship between mortar shrinkage strain and time is shown in figure 8.

Table 3 Comparison of test methods

Index	Research methods used	Research method
Size	560\365\114	610\914\19
Constraint	Wavy constraint	L-shaped constraint
Maintenance system	The temperature is controlled at 37 °C, and the humidity is controlled at %40	Rapid dehydration
Scope of application	Study shrinkage drying	Study the problem of mortar screening

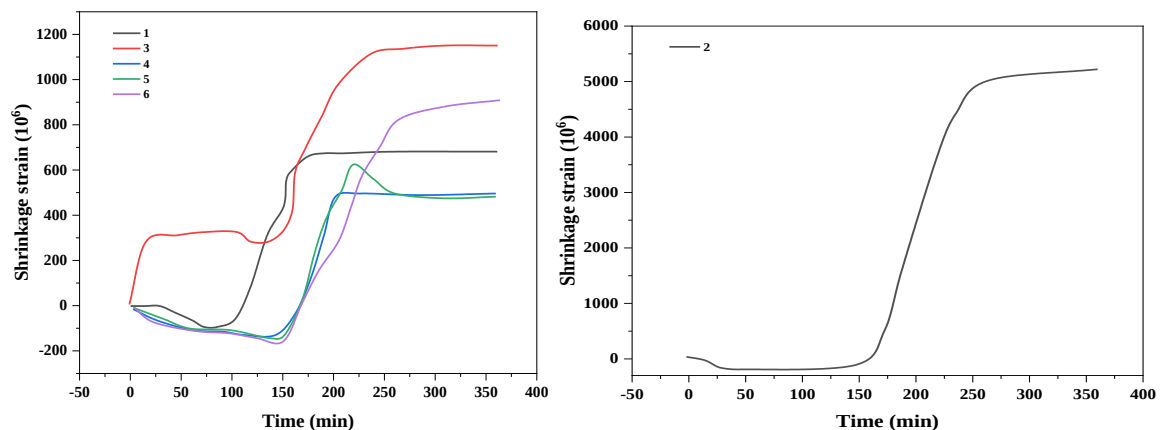


Figure 8 Relationship between early shrinkage strain of mortar and time

4.6 Results

First, with the beginning of cement hydration process, the solid particles in polymer lotion are adsorbed on the surface of cement particles, reducing the contact area between cement particles and water. The influence of polymer lotion added according to the quality of cement on the hydration heat release rate of cement paste is shown in figure 9.

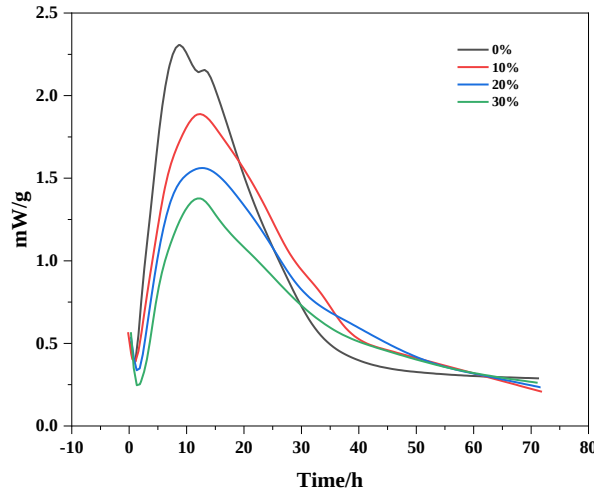


Figure 9 Hydration heat release rate of cement paste

The long-term shrinkage deformation test results of polymer mortar with different dosage are shown in figure 10.

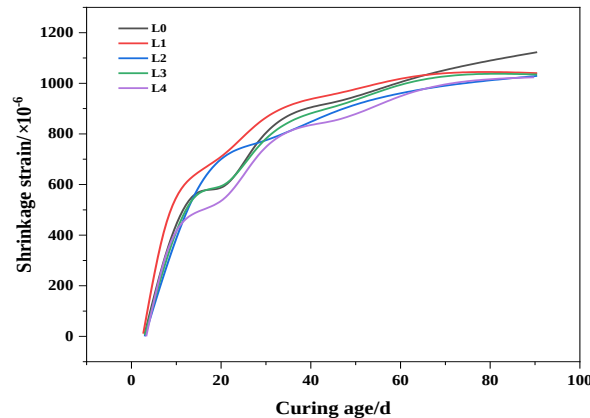


Figure 10 Effect of polymer on long-term shrinkage performance of mortar

The addition of polymer lotion makes the shrinkage strain of mortar at 90d age decrease slightly. For example, when the polymer content is 6%, the long-term shrinkage deformation of mortar decreases the most, up to 9.4%; For 21d mortar, when adding 12% polymer lotion, the shrinkage deformation decreases to 21.4%.

5. Conclusion

While measuring a large number of experimental data, we also encountered some regrettable things. For example, when dissolving polymer, due to the lack of instrument, the water temperature is not enough, resulting in the insufficient dissolution of polyvinyl alcohol, which has a certain impact on the experimental results. When preparing thin films, due to the limited sensitivity of manual operation, the surface distribution of smears is not uniform, which also affects the

experimental results.

References

- [1] Jo, Y. K. (2020). Adhesion in tension of polymer cement mortar by curing conditions using polymer dispersions as cement modifier. *Construction and Building Materials*, 242(48-50), 118134.
- [2] Szelg, M. (2020). Evaluation of cracking patterns in cement composites—from basics to advances: a review. *Materials*, 13(11).
- [3] Kujawa, W., Olewnik-Kruszkowska, E., & Nowaczyk, J. (2021). Concrete strengthening by introducing polymer-based additives into the cement matrix—a mini review. *Materials*, 14(20), 6071.
- [4] Wang, Z., Wei, Y., Li, N., Zhao, K., & Ding, M. (2020). Flexural behavior of bamboo–concrete composite beams with perforated steel plate connections. *Journal of Wood Science*, 66(1).
- [5] Domagaa, L., & Podolska, A. (2022). Effect of lightweight aggregate impregnation on selected concrete properties. *Materials*, 15(1), 198-.
- [6] Manalo, A., Maranan, G., Benmokrane, B., Cousin, P., & Gangarao, H (2020). Comparative durability of gfrp composite reinforcing bars in concrete and in simulated concrete environments. *Cement and Concrete Composites*, 109(5), 103564.
- [7] Aswini, G., & Kalpana. (2020). Conventional concrete over polymer impregnated concrete using silica fumes. *IOP Conference Series: Materials Science and Engineering*, 923(1), 012046 (5pp).
- [8] Suleimanov, A (2020). Method for predicting the durability of polymer-composite reinforcement in cement concrete. *IOP Conference Series: Materials Science and Engineering*, 890(1), 012100 (12pp).
- [9] Nodehi, M., & Nodehi, S. E (2022). Ultrahighperformance concrete (uhpc): reactive powder concrete, slurry infiltrated fiber concrete and superabsorbent polymer concrete. *Innovative Infrastructure Solutions*, 7(1).
- [10] Zhang, D., Jaworska, B., Zhu, H., Dahlquist, K., & Li, V. C (2020). Engineered cementitious composites (ecc) with limestone calcined clay cement (lc3). *Cement and Concrete Composites*, 114(6), 103766.
- [11] Qiao, G., Hou, D., Wang, P., & Lu, Z (2021). Insights on failure modes of calcium-silicate-hydrate interface strengthened by polyacrylamides: structure, dynamic and mechanical properties. *Construction and Building Materials*, 278(47), 122406.
- [12] Zhao, C., Zhao, C., Yi, Z., Yi, Z., Wu, W., & Wu, W., et al. (2021). Experimental study on the mechanical properties and durability of high-content hybrid fiber–polymer concrete. *Materials*, 14(21), 6234.
- [13] Sharma, A., & Kumar, R (2016). Performance comparison and detailed study of AODV, DSDV, DSR, TORA and OLSR routing protocols in ad hoc networks. *2016 Fourth International Conference on Parallel, Distributed and Grid Computing (PDGC). IEEE*.
- [14] Zhao, X. L., Liu, X., Liu, J., Chen, J., Fu, S., & Zhong, F (2019). The effect of ionization energy and hydrogen weight fraction on the non-thermal plasma vocs removal efficiency. *Journal of Physics D Applied Physics*.
- [15] R. Huang, X. Yang, "The application of TiO₂ and noble metal nanomaterials in tele materials," *Journal of Ceramic Processing Research*, vol. 23, no. 2, pp. 213–220, 2022.