Study on the influence of organic polymers on the physical and mechanical properties of cement-based materials

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Abstract: Four kinds of organic polymer emulsions of silicone acrylic, styrene-acrylic, waterborne epoxy and acrylic acid were selected and mixed into cement paste according to different poly-ash ratio, and experimental studies on their physical properties (fluidity and water-absorption rate) and mechanical properties (compressive strength, bending strength and bend-press ratio) were carried out. The results show that in terms of physical properties, only the waterborne epoxy emulsion improves the fluidity of the material, the four organic polymer emulsions reduce the water-absorption rate of the material, and the water-absorption rate of waterborne epoxy emulsion and styrene-acrylic emulsion decreases respectively by 61.8% and 51.5% at a poly-ash ratio of 0.15. In terms of mechanical properties, the four organic polymer emulsions fail to improve the compressive strength of the material, but the toughness of the material is improved. The waterborne epoxy emulsion has a 16.7% improvement in the bending strength at a poly-ash ratio of 0.2, and the styrene-acrylic emulsion has a 9.7% improvement in the bending strength at a poly-ash ratio of 0.15.

1. Introduction

As a kind of civil engineering material, cement-based materials are not only widely used, but also used in a large amount[1]. However, ordinary cement-based materials have disadvantages such as low strength and poor durability[2-3], while polymers have excellent performance in impermeability and alkali resistance[4]. A large number of scientific experimental studies[5-6] show that the incorporation of polymers improves the flexibility, impermeability and durability of cement-based materials[7]. Polymer modified cement-based materials can be used as pavement materials, self waterproof materials or waterproof films, adhesives, decorative coatings, repair materials for cultural relics and historic sites[8].

At present, there are many research on polymer modified cement-based materials at home and abroad. Ukrainczyk N[9] modified styrene butadiene latex modified calcium aluminite cement mortar as the research object. The research showed that with the incorporation of polymer emulsion, the compressive strength and the bending strength of cement-based materials increased. Kong[10] developed a polymer emulsion controlled by magnetic field and applied it to modified concrete. The results showed that a dense protective layer was formed in the cement matrix driven by magnetic force, which improved the impermeability and bending strength of the material. Etsuo Saka[11] took the vinyl acetate copolymer modified cement as the research object, and the research showed that the toughness and bending strength of the material were improved after adding the vinyl acetate copolymer. Lu Z[12-14] had studied the properties of styrene acrylic emulsion cement mortar. The
research showed that styrene acrylic emulsion played an important role in improving the fluidity of cement mortar. Lu Pengfei [15] studied the toughening effect of epoxy resin emulsion on cement based materials. The results showed that the toughness of cement-based materials increased with the increase of epoxy resin emulsion content, and when the emulsion was added to 20%, the toughness increased by 3.76 times. Zuo Yanmei [16] studied the microstructure of styrene acrylic emulsion modified cement based materials. The research showed that the good film forming property and stability of styrene acrylic emulsion made it better penetrate into the pores of cement based materials and improved the compactness of cement-based materials.

Most of the research at home and abroad only focus on the single performance of a single polymer on cement-based materials, while few researches focus on the influence of a variety of polymers on a variety of properties of cement-based materials. Different polymers have different effects on the different properties of cement-based materials [17]. Therefore, four organic polymer emulsions, including silicone acrylic (G), styrene-acrylic (R), waterborne epoxy (H) and acrylic acid (X), were selected to study the physical and mechanical properties of cement-based materials incorporating polymers.

2. Material and Methods

2.1. Test material
Ordinary portland cement P·O 42.5 (a cement manufacturer in Nanjing); micro silica fume and polycarboxylate superplasticizer (a manufacturer of materials in Nanjing); phosphoric acid butyl ester TBP (defoamer, eliminating excess bubbles in the slurry, a manufacturer of materials in Qingdao); organic modified silicone acrylic emulsion (solid content 48%, a material manufacturer in Henan); organic modified styrene-acrylic emulsion (solid content 45%, a material manufacturer in Henan); waterborne epoxy emulsion (solid content 50%, a material manufacturer in Qingdao); organic modified acrylic acid emulsion (solid content 43%, a manufacturer of materials in Henan).

2.2. Test scheme and method
Four kinds of organic polymer emulsions were blended into cement paste, and the physical and mechanical properties were tested. The different poly-ash ratio of different organic polymer emulsions are shown in Table 1. Among them, the water to binder ratio is 0.55, the silica fume is 10%, and the water reducing agent is 1.2%.

| Group number | A | G1 | G2 | G3 | G4 | R1 | R2 | R3 | R4 |
|--------------|---|----|----|----|----|----|----|----|----|
| Poly-ash ratio | 0 | 0.05 | 0.10 | 0.15 | 0.20 | 0.05 | 0.10 | 0.15 | 0.20 |

| Group number | A | H1 | H2 | H3 | H4 | X1 | X2 | X3 | X4 |
|--------------|---|----|----|----|----|----|----|----|----|
| Poly-ash ratio | 0 | 0.05 | 0.10 | 0.15 | 0.20 | 0.05 | 0.10 | 0.15 | 0.20 |

2.2.1. Physical property test
The truncated cone test mold is placed horizontally on a glass plate, and moisturized to ensure no water stains. The freshly mixed slurry is poured into a mold, scraped flat, and the truncated cone test mold is lifted vertically, so that the slurry can freely expand on the surface of the glass plate for 30s, and the maximum diameter in both vertical directions is measured, the average value is taken, and this value is used as the fluidity.

Select a 40mm × 40mm × 160mm test piece, place it in an oven at (80 ± 2) °C, dry it for 48 hours, and then take it out to cool to room temperature. Record the weight of the test piece $G_{io}$, and immerse the test piece in water at (20 ± 2) °C. Take it out after 2d, wipe it dry, and record the weight of the test piece $G_1$. The water-absorption rate $W_A$ (%) of the test piece is calculated according to Equation (1).
In the Equation (1): $W_A = \frac{(G_1 - G_0)}{G_0} \times 100\%$

2.2.2. Mechanical property test
40mm × 40mm × 160mm specimens are selected for bending strength test, and loaded at a speed of 50N / s ± 10N / s. There are 3 specimens in each group and the average value is taken. The bending strength $f_b$ (MPa) is calculated according to Equation (2).

$$f_b = \frac{1.5PL}{b^3}$$

In the Equation (2): $P$—Breaking load (N); $L$—Distance between two fulcrum points (mm); $b$—Side length of specimen cross section (mm).

The compressive strength test uses the test piece of the bending strength test. The compression area is 40mm × 40mm, and it is loaded at a speed of 2400N / s ± 200N / s. There are 3 specimens in each group and the average value is taken. The compressive strength $f_c$ (MPa) is calculated according to Equation (3).

$$f_c = \frac{P}{S}$$

In the Equation (3): $P$—Breaking load (N); $S$—Compressed area (mm²).

The bend-press ratio $\gamma$ is calculated according to Equation (4).

$$\gamma = \frac{f_b}{f_c}$$

2.2.3. SEM scanning analysis
A 10 mm × 10 mm × 5 mm test piece is cut out, soaked in anhydrous ethanol for 3 days and taken out, placed in an oven at 60 °C and dried for 48h. Before testing, spray metal powder on the observation surface, and use JSM-6510 high-resolution scanning electron microscope for image scanning analysis.

3. Results and Discussion

3.1. Results and discussion of physical property tests
The fluidity results of each group according to the fluidity test are shown in Figure 1.

![Figure 1. Fluidity of cement paste mixed with polymer emulsion.](image)

Compared with the control group of inorganic cement paste, the fluidity of waterborne epoxy emulsion cement paste increases, while the fluidity of silicone cement emulsion cement paste, styrene-acrylic emulsion cement paste and acrylic acid emulsion cement paste decreases to varying degrees. From the standpoint of each group, the fluidity of the waterborne epoxy emulsion cement paste has an upward trend with the increase of the poly-ash ratio, while the fluidity of silicone cement emulsion cement paste, styrene-acrylic emulsion cement paste and acrylic acid emulsion cement paste decreases slowly with the increase of the poly-ash ratio. Therefore, from the aspect of fluidity, the
performance of waterborne epoxy emulsion is the best, followed by styrene-acrylic emulsion.

The water-absorption rate of each group according to the water-absorption rate test is shown in Figure 2.

![Figure 2. Water-absorption rate of cement paste mixed with polymer emulsion.](image)

It can be seen from Figure 2 that the water-absorption rate of cement slurry mixed with each polymer emulsion decreases, and decreases with the increase of the poly-ash ratio, and then gradually stabilizes. This is because polymer emulsion emulsified particles can produce flocculation products, which can encrust cement hydration products, fill the cement void, and enhance the compactness of the matrix. After the emulsion particles are solidified into film, a compact waterproof cementation layer is formed inside the slurry, and the water-absorption rate is reduced. Among them, the water-absorption rate of waterborne epoxy emulsion cement paste is the lowest when the poly-ash ratio is 0.15, and its lowest value is 61.8% lower than that of the inorganic cement paste group. The water-absorption rate of styrene-acrylic emulsion cement paste is the lowest when the poly-ash ratio is 0.15, and its lowest value is 51.5% lower than that of the inorganic cement paste group. The silicone acrylic emulsion cement paste and the acrylic acid emulsion cement paste are the next. However, when the poly-ash ratio is further increased, the air content of the modified cement paste will gradually increase, and the water-absorption rate will slightly increase again. So, the optimal water-absorption rate should be maintained at about 0.15. Therefore, from the aspect of water-absorption rate, the performance of waterborne epoxy emulsion is the best, followed by styrene-acrylic emulsion.

### 3.2. Results and discussion of mechanical property tests

The compressive strength and bending strength test results are shown in Figure 3 and Figure 4.

![Figure 3. Compressive strength of cement paste mixed with polymer emulsion.](image)

![Figure 4. Bending strength of cement paste mixed with polymer emulsion.](image)

From the perspective of compressive strength, the four types of polymer emulsion cement pastes have been reduced compared to the inorganic cement paste control group, but the loss of compressive
strength of the waterborne epoxy emulsion cement paste is the smallest, followed by the styrene-acrylic emulsion cement paste and the silicone acrylic emulsion cement paste, acrylic acid emulsion cement paste has the largest loss of compressive strength. The peak strength loss rates of the four polymer emulsion cement pastes are 19.0% of waterborne epoxy emulsion cement paste, 26.0% of styrene-acrylic emulsion cement paste, 30.3% of silicone acrylic emulsion cement paste, and 41.5% of acrylic acid emulsion cement paste. Therefore, from the aspect of compressive strength, the performance of waterborne epoxy emulsion is the best, followed by styrene-acrylic emulsion.

From the perspective of bending strength, both the waterborne epoxy emulsion cement paste and the styrene-acrylic emulsion cement paste increase compared to the starting point. The bending strength of waterborne epoxy emulsion cement pastes increases with the increase of poly-ash ratio, and tends to be stable. It reaches a maximum when the poly-ash ratio is 0.20. The 28-day bending strength of waterborne epoxy emulsion cement paste increases by 16.7% compared with the inorganic cement paste control group. The bending strength of styrene-acrylic emulsion cement paste first increases and then decreases slightly with the increase of poly-ash ratio, and reaches the maximum when the poly-ash ratio is 0.15. The 28-day bending strength of styrene-acrylic emulsion cement paste increases by 9.7% compared with the inorganic cement paste control group. However, the bending strength of the silicone acrylic emulsion cement paste decreases slightly, and the bending strength of the acrylic acid emulsion cement paste shows poor performance. Therefore, from the aspect of bending strength, the performance of waterborne epoxy emulsion is the best, followed by styrene-acrylic emulsion.

The index of bend-press ratio is used to examine the effect of improving the flexibility of cement paste by each polymer emulsion. The bend-press ratio of cement paste of each polymer emulsion is shown in Figure 5.

From Figure 5 (a), it can be seen that the bend-press ratio of the four types of polymer emulsion cement slurry increases significantly with the increase of the poly-ash ratio, and then all tend to be stable. The styrene-acrylic emulsion cement paste reaches a peak at a poly-ash ratio of 0.15, the waterborne epoxy emulsion cement paste reaches a peak at a poly-ash ratio of 0.15, the waterborne epoxy emulsion cement paste reaches a peak at a poly-ash ratio of 0.20, the silicone acrylic emulsion cement paste reaches a peak at a poly-ash ratio of 0.10, and the acrylic acid emulsion cement paste reaches a peak at a poly-ash ratio of 0.20. Among them, the bend-press ratio of styrene-acrylic emulsion cement paste and waterborne epoxy emulsion cement paste is more prominent. The bend-press ratio of styrene-acrylic emulsion cement paste is 48.5% higher than that of the inorganic cement paste control group at a poly-ash ratio of 0.15, and the bend-press ratio of waterborne epoxy emulsion cement paste is 40.8% higher than that of the inorganic cement paste control group at a poly-ash ratio of 0.20. From Figure 5 (b), it can be seen that the bend-press ratio of the four polymer
emulsion cement pastes and inorganic cement pastes at the poly-ash ratio of 0.15 decrease with age, but the bend-press ratio of the four polymer emulsion cement pastes in all ages is much higher than that of inorganic cement pastes. It can be seen that the four polymer emulsions have a significant effect on improving the flexibility of the cement pulp. Therefore, from the aspect of the bend-press ratio, the performance of styrene-acrylic emulsion and waterborne epoxy emulsion are the best.

3.3. SEM microstructure analysis
The SEM micrographs of inorganic cement paste and polymer emulsion cement paste test specimens are shown in Figure 6.

As shown in Figure 6 (a), in the SEM electron micrograph of the inorganic cement slurry test specimen, it can be clearly seen that there are a large number of pores and capillary channels in the interior. The unhydrated cement clinker particles are larger and the pores are larger. The cement slurry is not dense.

As shown in Figure 6 (b), in the SEM electron microscopy of the polymer emulsion cement slurry test specimen, it can be clearly seen that the number of internal pores and capillary channels is reduced, and the pores are smaller, mainly because of the cement slurry The size of the pores is between tens of nanometers and tens of micrometers, and the size of the polymer particles is between several micrometers and tens of micrometers. Therefore, the polymer particles fill the pores and form a continuous polymer film on the surface of the hydrate, forming a dense matrix structure, improving its bending strength and waterproof performance.

4. Conclusions
(1) Different organic polymer emulsions can affect the physical properties of cement paste. Waterborne epoxy emulsions can improve the fluidity of cement pastes. Styrene-acrylic emulsions, silicone acrylic emulsions, and acrylic acid emulsions can't improve the fluidity of cement pastes. All four polymer emulsions reduce the water-absorption rate of cement paste and improve the waterproof performance.

(2) Different organic polymer emulsions can affect the mechanical properties of cement paste. All four polymer emulsions fail to improve the compressive strength of cement paste. Waterborne epoxy emulsions and styrene-acrylic emulsions increase the bending strength of cement pastes, while silicone acrylic emulsions and acrylic acid emulsions do the opposite. All four polymer emulsions improve the toughness of cement paste.

(3) From the microstructure point of view, the matrix of the polymer emulsion cement paste has a denser microscopic appearance, and the dense effect of the polymer on the cement matrix can effectively improve the performance of the material.
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