Study on the Performance of Polymer-Modified Conductive Cement-Based Materials

Min Li, Jianjun Zhong, Guoqing Li, Qianyi Zhang, Feng Cen and Peiwei Gao

Abstract: In order to study the synergistic effect of polymer and conductive functional materials on the properties of cement-based materials, polymer conductive cement-based materials were prepared by mixing four polymer lotions of silicon–acrylate emulsion (SG), phenylacrylic emulsion (SR), waterborne epoxy resin emulsion (SH), and acrylic emulsion (SX) with carbon fiber (CF) and carbon black (CB), two conductive functional materials, in a certain proportion. The effects of the different polymer–cement ratios (P/C) of the four polymers on the physical, mechanical, and electrical properties of conductive cement-based materials were studied. The results illustrated that SH improved the fluidity of cement paste, and the four polymers all had a delaying effect, which led to the hardening of the specimens and the extension of the demoulding specimens to varying degrees. SH and SR can increase the ratio of flexural strength to compressive strength (F/C) in cement paste and improve the toughness of materials, and the maximum value is reached when the P/C is 0.15. Except for SX, the other three polymer lotions can reduce the resistivity of cement paste, which is beneficial to the improvement of conductivity. The improvement sequence is SH > SR > SG. Among them, both SH group and SR group achieved the lowest electrical resistivity at the P/C of 0.15. The four kinds of polymer lotion can significantly reduce the water absorption of the specimen and promote the waterproof performance. The improvement effect: SH > SR > SG > SX. Among them, both the SH group and SR group achieved the minimum water absorption at the P/C of 0.15.

Keywords: polymer; carbon fiber (CF); carbon black (CB); polymer–cement ratio (P/C); liquidity; flexural strength to compressive strength (F/C); resistivity

1. Introduction

Polymer cement-based materials are composite materials made by adding polymers as modifiers or reinforcing agents to conventional cement pastes [1]. The proportion of polymers in the matrix is expressed by the polymer–cement ratio (polymer/cement). Conductive polymer cement-based materials are made of cementitious materials such as cement and fly ash, and raw materials such as conductive fillers, polymers, and coarse and fine aggregates.

Common conductive components include carbon fiber [2–4], graphene [5], carbon nanotube [6–8], carbon black [9], graphite [10], steel fiber [11], etc. After single or compound doping and surface treatment in different forms, excellent conductive effect will be formed in the matrix and applied to the melting of ice and snow in roads and bridges [12,13] as well as building heating [14]. Due to the excellent flexibility and viscoelastic behavior of polymers, they are widely used in cement-based materials to improve the brittle-type structure of cement-based materials [15]. Polymers that can promote the performance of cement-based composite materials mainly include styrene–butadiene emulsion, polyurethane, epoxy resin, hydroxypropyl methyl cellulose ether, polyacrylamide, etc.
CF is a kind of high-performance carbon fiber material, which has the advantages of good conductivity, electrothermal property, high temperature resistance, corrosion resistance, and oxidation resistance. Cement products with conductive function can be prepared by adding CF into cement-based materials in a certain proportion. CF can be divided into two categories: one is PAN-based CF made from polyacrylonitrile, and the other is pitch-based CF made from pitch. Among them, the price of PAN-based CF is 5~10 times that of pitch-based CF [16]. The factors affecting the use effect of CF are the length, content, and dispersion. CF has different lengths, such as 3 mm, 6 mm, 9 mm, and carbon nano fibers. Shuhua Liu et al. [17] studied the workability, mechanical properties, electrical conductivity, and electrothermal effect of CF-modified conductive concrete (ECON). The results show that ECON, with a compressive strength of 30 MPa and a resistivity of 0.1 Ω·cm, can be prepared by using CF with volume content of 0.75% and length of 9 mm. Ilhwan You et al. [18] studied the effects of CF length, electrode spacing, and probe configuration on the conductivity of cement-based composites. The results show that when designing electrodes for cement composites containing CF, the CF length should be shorter than the electrode spacing. Ting Ding et al.’s [19] study found that CF content had a significant effect on resistivity, and that when the carbon fiber content was 0.65%, the penetration threshold was reached, and the resistivity of CF conductive concrete tended to be stable. CF content is reduced within a certain range, and the workability of carbon fiber conductive concrete is improved. Iftekar Gull et al. [20] observed that in surfactant-mixed water, a lower-speed mechanical stirring device successfully deagglomerates CF filaments without interfering with their individual morphology, resulting in a better distribution of fibers in concrete.

Although CF has good electrical conductivity, it is expensive and not suitable for a large number of applications. Single-phase conductive concrete is limited by the nature of the material, and there are more or less shortcomings in all aspects. The composite mixing of two or more conductive phase materials can simultaneously exert the characteristics of several materials, play a role of mutual compensation and mutual promotion, and make it easier to obtain conductive concrete with excellent performance, cost, and other aspects. The use of CB instead of CF can reduce costs and improve performance under the premise of ensuring the function of the material. Dehghanpour et al. [21] prepared 36 different kinds of concrete containing CF, recycled RNCB, waste wire erosion, and steel fiber. The test results show that RNCB has a significant effect on reducing resistance when used in combination with other fillers. Dong et al. [22] developed conductive rubber fiber-filled CB cement-based composites. The conductivity of 0.5% CB filled composites increased with the increase in rubber content. The composites with a CB content < 4.0% had better compressive strength. In this paper, based on the analysis of a large number of existing research findings, combined with the existing research results of the research group, the commonly used materials CF and CB were selected as conductive materials to prepare conductive cement-based composites, and polymer modification research was further carried out.

The addition of polymer can promote the durability of cement materials, such as impermeability, chemical-corrosion resistance, and adhesion between aggregate and cement materials. It can also reduce later shrinkage rate and improve mechanical properties [23]. Long et al. [24] found that the macromolecular structure formed by the reaction between acrylic emulsion and cement hydration product Ca(OH)\textsubscript{2}, and the combination of ionic bonds, improves the structural compactness and effectively enhances the impermeability of the material. Ohama et al. [23] proposed the following modification mechanism of polymer in cement matrix. After the polymer is added, the C-S-H gel is slowly formed with the hydration of the cement, and the polymer particles accumulate on the surface of the cement particles and the C-S-H gel. With the gradual completion of hydration and the hardening of the slurry, the polymer particles are limited in the capillary pores and flocculate. A layer of polymer film is formed on the surface of the particles, filling some large voids. Finally, with the evaporation of water and the completion of hydration, the polymer and cement
hydration products are bonded to each other, which improves the compactness and the microscopic pore structure of the material.

Schulze et al. [25] found that the macroscopic properties of styrene–butadiene-modified mortar are greatly affected by water–cement ratio and curing conditions. Wang Peiming et al. [26] found that the addition of styrene butadiene rubber emulsion can reduce water consumption, improve the mechanical characteristics of mortar, such as bending strength and binding strength, and improve the shrinkage deformation performance and durability of materials. Bureau et al. [27] carried out a three-point bending test on styrene–butadiene rubber emulsion-modified mortar. When the water–cement ratio was 0.45, the flexural strength of the mortar enlarged with the increase in styrene–butadiene rubber emulsion content. However, when the content was more than 10%, although the flexural strength continued to increase, the compressive strength decreased [28]. Yang et al. [29] explored the effect of waterborne epoxy and lignin epoxy on the mechanical properties of polymer-modified cement mortar based on the effective emulsification of waterborne epoxy with active emulsifier. It was found that the toughening effect of epoxy on mortar was obvious. With the increase in P/C, the flexural strength of the specimens increased and the compressive strength decreased. Aggarwal et al. [30] found that the waterproof performance of concrete was improved with the incorporation of acrylic polymer, which had the conditions for application in humid environment. With the continuous progress of research, polymer composite materials in different forms are widely used in concrete waterproof, anti-corrosion, and repair engineering field [14]. Based on its excellent performance, this paper intends to add polymers on the basis of conductive cement-based materials to study its modification mechanism.

So far, there are many studies on the properties of polymer-modified cementitious materials, and a large number of research results have been produced [31]. However, there are a few pieces of research on polymer-modified conductive cement-based materials. In this paper, from the perspective of improving the toughness, electrothermal performance, and durability of cement-based materials, four polymers of SG, SR, SH, SX, and two conductive functional materials of CF and CB were selected to carry out the preparation and performance research of polymer conductive cement-based materials, so as to select the best polymer to be applied to conductive cement-based materials and improve their physical, mechanical, and electrothermal properties.

2. Materials and Methods

2.1. Raw Materials

The cement was P.O 42.5 grade cement produced by a factory in Nanjing, Jiangsu Province, and the silica fume was micro silica fume produced by a factory in Nanjing, Jiangsu Province. Admixtures included polycarboxylate superplasticizer. The water reduction rate was about 30–40%. The methyl cellulose dispersant was a white granular powder. Tributyl phosphate was used as a defoaming agent, and magnesia expansive agent was mainly composed of MgO and CaO.

Polymer emulsion: SH, solid content (50 ± 1)%. SR, solid content (45 ± 1)%. SG, solid content (48 ± 1)%. SX, solid content (43 ± 1)%. Some performance parameters are shown in Tables 1 and 2.

Table 1. Performance parameters of SH.

<table>
<thead>
<tr>
<th>Epoxy Resin EP-20 (%)</th>
<th>Polyethylene Glycol (%)</th>
<th>Epoxy Value</th>
<th>Proportion</th>
<th>Viscosity (mPa·s/25 °C)</th>
<th>Solid Content (%)</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>25</td>
<td>0.20</td>
<td>1.10</td>
<td>≤2000</td>
<td>50 ± 1</td>
<td>7</td>
</tr>
</tbody>
</table>
Table 2. Performance parameters of SR.

<table>
<thead>
<tr>
<th>Styrene (%)</th>
<th>Butyl Acrylate (%)</th>
<th>Methyl Methacrylate (%)</th>
<th>Methacrylate (%)</th>
<th>Viscosity (mPa·s/25 °C)</th>
<th>Solid Content (%)</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.9</td>
<td>23.8</td>
<td>1.96</td>
<td>0.96</td>
<td>≤1800</td>
<td>45 ± 1</td>
<td>8</td>
</tr>
</tbody>
</table>

Functional filler: chopped CF, performance parameters are shown in Table 3. Conductive CB, performance parameters are shown in Table 4.

Table 3. Performance parameters of CF.

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Carbon Content (%)</th>
<th>Rate of Elongation (%)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Electrical Resistivity (Ω·cm)</th>
<th>Density (10^3 kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤8</td>
<td>97</td>
<td>2.1</td>
<td>230</td>
<td>4000</td>
<td>1.3</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table 4. Performance parameters of CB.

<table>
<thead>
<tr>
<th>Product Feature</th>
<th>Specific Surface Area (m²/g)</th>
<th>Electrical Resistivity (Ω·cm)</th>
<th>Particle Size (nm)</th>
<th>Density (kg/m³)</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black solid powder</td>
<td>230</td>
<td>101</td>
<td>15</td>
<td>144</td>
<td>8</td>
</tr>
</tbody>
</table>

2.2. Mix Proportion and Specimen Making

The existing research results of the research group show that the percolation threshold of 5 mm chopped CF is about 1.0% [32], and the percolation threshold of CB is about 2.0%. Therefore, in this paper, the CF blending ratio was 1.0%, and the CF was replaced at a 50% substitution rate, which ensured that the cost was reduced and the working performance was improved under the condition of constant conductivity. The content of the silica fume was 10%, which allowed for CF and CB to be more evenly dispersed in the cement matrix. Four kinds of polymers, SG, SR, SH, and SX, were selected to prepare polymer-modified cement paste. The P/C were 0% (S0 control group), 5%, 10%, 15%, and 20%, respectively. The water cement ratio was 0.55, the dispersant was 0.4%, the defoamer was 0.15%, the water reducing agent was 0.4%, and the expansion agent was 5%. The test mix ratio is shown in Table 5.

Table 5. Test mix ratio.

<table>
<thead>
<tr>
<th>Group Number</th>
<th>CF (%)</th>
<th>CF (g)</th>
<th>CB (%)</th>
<th>CB (g)</th>
<th>P/C (%)</th>
<th>Polymer Emulsion (g)</th>
<th>Cement (g)</th>
<th>Water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>1300</td>
<td>770</td>
</tr>
<tr>
<td>SG1</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>5</td>
<td>135</td>
<td>1300</td>
<td>716</td>
</tr>
<tr>
<td>SG2</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>10</td>
<td>271</td>
<td>1300</td>
<td>646</td>
</tr>
<tr>
<td>SG3</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>15</td>
<td>406</td>
<td>1300</td>
<td>575</td>
</tr>
<tr>
<td>SG4</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>20</td>
<td>542</td>
<td>1300</td>
<td>505</td>
</tr>
<tr>
<td>SR1</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>5</td>
<td>144</td>
<td>1300</td>
<td>707</td>
</tr>
<tr>
<td>SR2</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>10</td>
<td>289</td>
<td>1300</td>
<td>628</td>
</tr>
<tr>
<td>SR3</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>15</td>
<td>433</td>
<td>1300</td>
<td>548</td>
</tr>
<tr>
<td>SR4</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>20</td>
<td>578</td>
<td>1300</td>
<td>469</td>
</tr>
<tr>
<td>SH1</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>5</td>
<td>130</td>
<td>1300</td>
<td>722</td>
</tr>
<tr>
<td>SH2</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>10</td>
<td>260</td>
<td>1300</td>
<td>657</td>
</tr>
<tr>
<td>SH3</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>15</td>
<td>390</td>
<td>1300</td>
<td>592</td>
</tr>
<tr>
<td>SH4</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>20</td>
<td>520</td>
<td>1300</td>
<td>527</td>
</tr>
<tr>
<td>SX1</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>5</td>
<td>151</td>
<td>1300</td>
<td>700</td>
</tr>
<tr>
<td>SX2</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>10</td>
<td>302</td>
<td>1300</td>
<td>614</td>
</tr>
<tr>
<td>SX3</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>15</td>
<td>453</td>
<td>1300</td>
<td>528</td>
</tr>
<tr>
<td>SX4</td>
<td>0.5</td>
<td>6.5</td>
<td>1</td>
<td>13</td>
<td>20</td>
<td>605</td>
<td>1300</td>
<td>442</td>
</tr>
</tbody>
</table>
In this experiment, the ultrasonic dispersion method was used to improve the stirring process to prepare CF dispersion, and quantitative water was added to the constant temperature water bath to 60 °C. The 0.4% dispersant methyl cellulose was slowly added to water and stirred at a constant speed to fully dissolve it. Then, a calculated amount of conductive CF was added and fully stirred. During the stirring process, 0.15% defoamer was added to eliminate excess bubbles. Then, the prepared conductive CF dispersion was transferred to an ultrasonic cleaner and ultrasonically dispersed for 1 h to obtain a well-dispersed conductive CF dispersion. Then, according to DL/T 5126-2021 [33], cement, sand, CB, silica fume, expansion agent, etc., were dry-mixed in a cement paste mixer for 1 min; following this, the abovementioned CF dispersion was mixed with water reducing agent and water into the dry material, and then the polymer emulsion was added to the slurry. Mixing, stirring slowly for 120 s, pausing for 15 s, and then stirring quickly for 120 s to was performed to obtain a freshly mixed composite slurry. The specimens were formed at 40 mm × 40 mm × 160 mm dimensions, with copper mesh electrodes of 30 mm × 50 mm being embedded at 10 mm from both ends of the specimen and 40 mm from the center. All electrodes are inserted directly into the bottom of the specimen. The specimens were cured by dry–wet cycle method. After curing in the wet curing box for 24 h (+24 h), the specimens were demoulded. After 2 days of curing in the wet curing box, the specimens were placed in water at 20 ± 3 °C for 5 d, and then cured in the dry curing box for 21 d. The specimen making process is shown in Figure 1.

2.3. Test Method

The fluidity test was carried out according to GB/T 8077-2012 [34]. The water absorption test was carried out with reference to DL/T 5126-2021 [33]. The calculation formula of water absorption is shown in Equation (1).

\[ W_A = \frac{G_1 - G_0}{G_0} \times 100\% \]  

where \( W_A \) is water absorption (%), \( G_1 \) is the mass of the specimen after water absorption (g), and \( G_0 \) is the drying quality of the specimen (g).
The flexural strength and compressive strength test refer to DL/T 5126-2021 [33]. The resistivity was tested by the four-electrode method, and the schematic diagram is shown in Figure 2. The relationship between resistance value $R$, voltage value $U$, and current value $I$ is shown in Equation (2). The calculation formula of the volume resistivity value ($\Omega \cdot m$) of the specimen is shown in Equation (3).

$$ R = \frac{U}{I} $$

$$ \rho = \frac{RS}{L} $$

where $\rho$ represents the resistivity ($\Omega \cdot m$), $R$ represents the resistance value ($\Omega$), $S$ represents the cross-sectional area of the specimen ($m^2$), and $L$ represents the length between the outer electrodes in the direction of the specimen ($m$).

3. Results and Discussion

3.1. Effect of Polymer on Physical Properties

The cement paste of the S0 control group without polymer was plastic, easy to pour, good in construction workability, and shows 24 h of stripping. Compared with the S0 group, the construction workability of the four cement pastes with polymer emulsion was the best in the SH group, followed by the SR group, and the membrane was removed after 48 h with high integrity. The construction workability of cement paste mixed with SX was the worst, which was dry and hard and could not meet the requirements of the specification. The low dispersibility of CF and the low hydrophilicity of CB, as well as the resulting huge polar interaction, led to the extreme aggregation of particles, which was the main reason for the poor fluidity and workability of the cement paste. However, the addition of SH and SR could significantly improve the delaying effect of conductive cement-based materials and maintain good construction workability due to good toughness, bonding strength, and water retention.

The effect of polymer on the fluidity of cement paste is shown in Figure 3. The fluidity of cement paste in the SH group showed an upward trend and was higher than that in the control group. The fluidity of cement paste in the SG, SR, and SX groups showed a downward trend and was lower than that in the control group. When the P/C is 15%, the fluidity of cement paste in the SH group and SR groups was 183 mm and 169 mm, respectively, which is 1.1% and 6.6% higher than that of the control group, indicating that SH and SR had little effect on the fluidity of cement paste. This is because the addition of polymer emulsion can introduce a large amount of gas, so that the material has better thixotropy and shear thinning properties, thereby improving the fluidity of cement paste. The addition of SH and SR can improve the negative effects caused by CF and CB, so that the conductive cement-based materials maintain good fluidity. Therefore, based on the influence of polymer on physical properties such as fluidity, setting time and workability, SH and SR are preferred.
3.2. Effect of Polymer on Mechanical Properties

The flexural strength to compressive strength (F/C) was selected to investigate the toughness of the specimen, so as to explore the influence of polymer on the toughening performance of cement paste. The effect of polymer on the F/C is shown in Figure 4.

It can be seen from Figure 4a,b that the F/C of the four polymer test groups increased significantly with the increase in the P/C and then decreased slowly. Among them, the SR group was the best, followed by the SH group. When the P/C was 0.15, the peak value was reached. The folding pressure of the SR group was 48.5% higher than that of the control group, and the pressure of the SH group was 40.8% higher than that of the control.
group. The improvement in the mechanical strength of cement paste is due to the excellent flexibility and viscoelasticity of polymer chains, which can improve the brittle structure of cement-based materials. The polymer emulsion can increase the contact angle of the cement paste surface, effectively improve the flexural strength and tensile strength of the material, enhance the toughness, and improve the cracking phenomenon of the material.

It can be seen from Figure 4c that the F/C of the four polymer test groups decreased with the increase in age. The reason is that cement slurry dehydrated slowly after adding polymer. In the early stage of cement hydration, more dispersed polymer particles were adsorbed around the cement particles, significantly hindering the hydration of cement. Therefore, in the early stage of curing, the slurry exhibited slow setting, high flexibility, and a high F/C. With continuous hydration, the degree of hardening of the slurry increased, the flexibility decreased, and the F/C decreased. This is also the reason why polymer mortar needs to be brought into the curing box with a mold and needs special curing processes such as partial age water curing. It can be seen that the F/C of the four polymer test groups in the whole age are much higher than those of the control group, which fully shows the toughening advantages of the polymer on the cement-based materials, especially the SR group and the SH group. Therefore, based on the influence of polymer on F/C and toughness, SR and SH are preferred.

3.3. Effect of Polymer on the Conductivity

The effect of polymers on the conductivity of cement paste is shown in Figure 5. It can be seen from Figure 5a that the resistivity of cement paste in the SG, SR and SH groups decreased with the increase in P/C and gradually stabilized, indicating that the incorporation of polymer can improve the conductivity of cement paste. Among them, the SH group had the best conductivity, and the resistivity decreased by 43.0% compared with the control group at the P/C of 0.20, followed by the SR group, and the resistivity decreased by 20.3% compared with the control group at the P/C of 0.20. The reason is that after the polymer was added to the slurry, the matrix was denser, the cohesion between the cement hydration components was enhanced, the pores were reduced, the conductive network was more closely lapped, and the resistivity was reduced. In addition, the resistivity of the SX group increased slightly after reaching the lowest value at the P/C of 0.15, the resistivity of the SG group did not decrease, and the conductivity of the two groups was poor. It can be seen from Figure 5b that, except the resistivity of the SX group, which exceeds that of the control group, the resistivity of the other three groups decreases; the resistivity of the SH group decreases greatly, which obtained the optimal conductivity, followed by the SR group.

![Graph: Change in resistivity with P/C](image1)

(a) Change in resistivity with P/C

![Graph: 28 days electrical resistivity at 0.15 P/C](image2)

(b) 28 days electrical resistivity at 0.15 P/C

Figure 5. Resistivity of polymer cement paste.

The change in the resistivity of the specimen with age is shown in Figure 6. The resistivity of each polymer group and the control group increased with the increase in
age and then gradually stabilized. The reason is that due to the high water content of
the specimen in the initial stage of cement hydration, the material was in a liquid phase
and solid phase blending environment, the conductivity was strong, and the resistivity
was low. With the continuous hydration and hardening, the water content decreased, and
the conductive network was completely constructed by solid phase conductive filler and
cement hydration products. The resistivity rose and tended to be stable. Therefore, based
on the influence of polymer on the conductivity, SH and SR are preferred.

Figure 6. Change of resistivity with age at 0.15 P/C.

3.4. Effect of Polymer on Waterproof Performance

The effect of polymers on the waterproof performance of cement paste is shown in
Figure 7. The water absorption rate of the four polymer groups decreased with the increase
in the P/C, and the water absorption rate was SH < SR < SG < SX. The SH group and the
SR group reached the lowest value when the P/C was 0.15, and the water absorption rate
was reduced by 61.8% and 51.5%, respectively, compared with the control group. After that,
the water absorption rate increased slightly with the increase in the P/C, indicating that
the P/C of 0.15 was the best blending amount and that the optimal water absorption rate
could be obtained. The reason is that the flocculation product generated by the emulsion
particles of the polymer emulsion encapsulated the cement hydration product and filled
the gap among the particles, which greatly improved the compactness of the cement slurry.
When the emulsion particles were solidified into a film, a dense waterproof cementing
layer was formed inside the slurry, so that the water absorption rate was reduced. When
the P/C was 0.15, the water absorption rate reached the lowest value. However, with the
further increase in the P/C, the water absorption rate increased. The reason is that the air
content of the modified cement paste increased, so that the moisture absorption rate
increased slightly. Therefore, based on the influence of polymer on water absorption, SH
and SR are preferred.

Figure 7. Water absorption of cement paste with different P/C.
3.5. Microscopic Analysis

The influence of polymer lotion on the microstructure of the conductive cement-based composite matrix is very critical. The SEM scanning microscopic morphology of the SH specimen is shown in Figure 8. Figure 8a shows the cement sample mixed with 5% SH and Figure 8b shows the cement sample mixed with 15% SH. It can be seen that the matrix of 15% polymer cement sample was denser, and there was more distinct membrane substance adhesion between cement hydration products, which made the matrix integrity stronger. The morphology of the 5% polymer sample was relatively dispersed, while the relatively dense matrix of the 15% polymer lotion sample made the material more waterproof, and also provided a good complete conductive matrix for electronic transition.

![Figure 8. SEM scanning diagram of SH specimen.](attachment:image.png)

4. Conclusions

In this study, four polymer emulsions of SG, SR, SH, and SX and two conductive functional materials of CF and CB were used to prepare polymer conductive cement-based materials according to a certain proportion. The effects of different polymer–cement ratios of four polymers on the physical, mechanical, and conductive properties of conductive cement-based materials were studied experimentally. An SEM analysis of the specimens was carried out to explore the mechanism of polymer-modified conductive cement-based materials, and the modification effects of the four polymer emulsions were compared. According to the test results, the following conclusions are drawn.

1. The fluidity of cement paste was improved by SH and increased with the increase in P/C. SG, SR, and SX all reduced the fluidity of the cement paste, and the reduced rate of SR was the smallest. All four polymers have a delaying effect, resulting in the hardening and peeling time of the specimens extending to 48 h.

2. With the increase in flexural strength and the loss of compressive strength, the F/C of waterborne epoxy and SR-modified cement paste was increased to varying degrees, and the toughness of the material was improved. Both of them reached their maximum value when the P/C was 0.15. The improvement effect of SR was greater than that of SH.

3. Except for SX, which can lead to cement paste resistivity increasing, the rest of the three kinds of polymer emulsion can reduce the resistivity of cement paste, which is beneficial to improving its electrical conductivity, with the improved effect of SH > SR > SG. Among them, the SH group and the SR group obtained the lowest resistivity at the P/C of 0.15.

4. Four kinds of polymer emulsions can significantly reduce the water absorption of the specimens and improve the waterproof performance. The improvement effect is SH > SR > SG > SX. Among them, both the SH group and the SG group obtained the minimum water absorption at the P/C of 0.15.
(5) Microscopic morphology shows that a polymer-modified cement-based sample with a P/C of 0.15 can obtain a denser matrix, making the material more waterproof and providing a good and complete conductive network for electronic transitions.

(6) SH and SR selected in this experiment can be used to improve the toughness and waterproof performance of conductive cement-based materials, which is conducive to the preparation of cement mortar with high waterproof-performance requirements and low strength requirements. One can effectively use the electrothermal performance of conductive cement-based materials for electrothermal dehumidification, while improving the durability and corrosion resistance of materials. On this basis, our research group plans to further study the electrothermal dehumidification performance and corrosion resistance of polymer-modified conductive cement-based materials.

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