Article

Influence of a New Type of Graphene Oxide/Silane Composite Emulsion on the Permeability Resistance of Damaged Concrete

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Abstract: Through penetration depth tests, capillary water absorption tests under different abrasion depths, and capillary water absorption tests of a cement mortar test block with crack damage, a self-prepared, novel, graphene oxide/silane composite emulsion used for the effect of wear or cracking damage was studied. The waterproof performance of concrete and the protective mechanism of a composite emulsion was verified by scanning electron microscopy, X-ray diffraction, and thermogravimetric analysis. The test results showed that the penetration depth of the composite emulsion reached depths greater than 9 mm, which yielded a good waterproof effect; when the concrete was cracked or worn, the composite emulsion still had a stable waterproof performance. It was found that the composite emulsion could form a hydrophobic layer with a certain thickness inside the cement-based material, which explains why the composite emulsion had a good waterproof effect.

Keywords: graphene oxide/silane composite emulsion; cracking; abrasion; waterproofing; mechanism study

1. Introduction

Concrete is the most widely used building material in modern society. Research on the durability of concrete has attracted the attention of various researchers [1–3]. With the extension of the service time of the concrete, durability decreases, which leads to the destruction of the concrete structure [4,5]. Owing to the different environments in which concrete is used, there are many types of concrete damage, which can be roughly divided into the following: steel corrosion, freeze–thaw damage, chemical erosion, structural cracking [6,7], and abrasion damage (ground wear, erosion wear) [8–10]. Studies have shown that moisture has a direct or indirect effect on concrete damage. Concrete damage that is not directly related to moisture can also accelerate the transmission of moisture inside the concrete [11], such as with cracking damage and wear damage.

In view of the damage problems of concrete, such as cracking, spalling, and abrasion, and the waterproof performance of damaged concrete, researchers have studied all kinds of protective concrete coating [12–14], including traditional asphalt, such as epoxy resin, polyurethane, and acrylic resin. Practice in construction technology is mainly to besmear a certain thickness of materials on the concrete surface with brushes, filling the concrete pore, and preventing the effect of moisture intrusion; however, these sealing coatings affect the concrete’s breathability, also affecting the development of concrete hydration [15,16]. Engineering practice has proved that permeable waterproof material can achieve an excellent waterproofing effect [17–24]. A waterproof material can be coated on the surface of the concrete, penetrating into the material, and connecting with the concrete to form a water-repellent layer or reacting with cement-based materials to generate substances that block the pores of the concrete to achieve a waterproof effect. However, coating on the surface of early concrete will affect the hydration of the cement to a certain extent, thereby reducing the hardness of the concrete surface [25].
As an emerging material, graphene oxide has attracted the attention of researchers due to its special applications and properties. Some studies have found that graphene oxide can compound with cement-based materials to improve their compactness, thereby improving mechanical properties [26,27]. However, a direct incorporation of graphene oxide will lead to a sharp decline in the workability of cement-based materials, and graphene oxide can easily agglomerate and is difficult to uniformly disperse in cement-based materials [28].

In the previous research of this group, a new type of composite waterproof material was synthesized by combining the good hydrophobic effect of silane materials and the effect of graphene oxide to improve the microstructure of concrete surface, and its hydrophobic effect has been verified [29]. This article continues the previous research to test the waterproof effect of self-developed silane emulsions and composite waterproofing materials on damaged cement-based materials and provides experimental data support for subsequent repairs of actual engineering concrete after damage.

2. Experimental

2.1. Preparation of Cement-Based Materials

Tables 1–3 present the mixing ratios of cement-based materials used in the test.

Table 1. Formulation ratios of concrete unit: kg/m³.

| Materials          | Volume of Use |
|--------------------|---------------|
|                    | W/C = 0.4     |
| Cement             | 380           |
| Sandstone          | 627           |
| Aggregate          | 1269          |
| Water              | 152           |
| Additive           | 1.46          |

Table 2. Formulation ratios of mortar unit: kg/m³.

| Materials | Volume of Use (kg·m⁻³) |
|-----------|------------------------|
|           | W/C = 0.6              |
| Cement    | 450                    |
| Sandstone | 1350                   |
| Water     | 270                    |

Table 3. Formulation ratios of cement paste unit: kg/m³.

| Materials | Volume of Use (kg·m⁻³) |
|-----------|------------------------|
|           | W/C = 0.4              |
| Cement    | 1500                   |
| Water     | 600                    |

This experiment used ordinary Portland cement (PO 42.5), with the chemical composition shown in Table 4. The concrete used river sand with a fineness of 2.9, the cement mortar used Chinese ISO standard sand, and the concrete aggregate used basalt with a particle size of 5–20 mm. Polycarboxylic acid was used as a water-reducing agent with a water reducing effect of 30%.

Table 4. Composition of Portland (PO) 42.5 cement unit: %.

| Item | Chemical Composition |
|------|----------------------|
|      | SiO₂  Fe₂O₃ AL₂O₃ CaO MgO SO₃ K₂O Na₂O TiO₂ Other |
| Content (%) | 22.9  3.10  7.35  57.46  4.07  1.52  0.47  0.99  0.35  1.79 |
According to the mixing ratio shown in Tables 1–3, the raw materials, such as aggregate and sand, were weighed. Then, the required cement-based materials were prepared. The preparation of concrete was based on the “Standard for Test Methods of Mechanical Properties of Ordinary Concrete” [30], the laboratory temperature was 20 ± 5 °C, and the humidity was more than 50%. The preparation was cured under standard conditions (temperature 20 ± 2 °C and the humidity was more than 95%) for 28 days. A sample size of 100 mm × 100 mm × 100 mm was used for the capillary water absorption test of concrete after abrasion. The preparation of the cement mortar test block was based on “Mortar, Concrete Waterproofing Agent” [31], cured under water conditions (temperature was 20 ± 2 °C). The laboratory temperature was 20 ± 2 °C and the humidity was more than 50%. Its size was 25 mm × 40 mm × 160 mm, and a Φ8 (8 mm in diameter) smooth steel bar was installed inside the mortar test block for capillary water absorption tests of cement mortar with a crack. The cement paste test block was prepared in accordance with “Mortar, Concrete Waterproofing Agent” [31], cured under water conditions (temperature was 20 ± 2 °C). The laboratory temperature was 20 ± 2 °C and the humidity was more than 50%, with a size of 40 mm × 40 mm × 160 mm, which was used for observation of the micro morphology of cement paste (SEM), and X-ray diffraction (XRD) and comprehensive thermal analysis (TGA) tests.

2.2. Preparation and Coating of Waterproof Material

2.2.1. Preparation of a New Type Graphene Oxide/Silane Compound Emulsion

The preparation methods and related raw materials of graphene oxide (GO)/silane composite waterproof materials have been studied by our group. The main preparation steps are as follows: certain amounts of GO powder and distilled water were weighed and the mixture was put into an ultrasonic bath for vibration to prepare GO dispersion with certain proportions. GO dispersion was utilized to replace distilled water and prepare the GO/silane composite emulsion according to the preparation method for silane emulsion [29].

2.2.2. Coating Amount of Waterproof Material

The coating amount of silane emulsion and graphene oxide/silane composite emulsion is shown in Table 5. The most cost-effective coating had been identified in the previous research by our group [32].

| Item                        | Uncoated Silane Emulsion | GO/Silane Composite Emulsion |
|-----------------------------|--------------------------|------------------------------|
| Coated amount/(g·m⁻²)       | -                        | 600                          |
| Absorption time/d           | -                        | 7                            |

2.3. Penetration Depth Test

The penetration depth test was based on “Mortar, Concrete Waterproofing Agent” [31]. A 28-day-cured concrete test block was placed in a blast drying oven to a constant weight, and the block was transferred to a laboratory at temperature 20 ± 3 °C and the humidity was above 80%. Then the spraying method was used to waterproof the molding surface. The amount of waterproof material used is shown in Table 5, with all of the material completely penetrating into the concrete. Afterward, the test block was split along the coated surface, and then the fracture surface was sprayed with water. The white-light depth of the fracture surface was the penetration depth of the waterproof material. Several points were taken to measure the penetration depth, and finally the average value was taken [33].

2.4. Capillary Water Absorption Test under Different Wear Depth

The capillary water absorption test was based on “Mortar, Concrete Waterproofing Agent” [31]. A 28-day-cured concrete test block was placed in a blast drying oven to bake
to a constant weight, leaving a molding surface and its opposite surface; the other four surfaces were sealed with epoxy resin. The spraying method was used to waterproof the molding surface. The amount of waterproof material used is shown in Table 5. After the waterproof material completely penetrated into the concrete, the capillary water absorption test was conducted: the laboratory temperature was 20 ± 3 °C and the humidity was more than 80%; the capillary water absorption of the concrete was measured at 0, 1, 2, 4, 6, 8, 12, 24, 36 and 48 h. Then, the test block was taken out and placed in a blast drying box for drying. A mill was used to grind off the coated surface by 3 mm, epoxy resin was used to repair the damaged parts around, and then capillary water absorption on the worn concrete was again tested at different time points. The above steps were repeated to measure the capillary water absorption of the concrete at different time points after a 5 mm abrasion. Finally, the capillary water absorption coefficient of the different groups test block was calculated to Equation (1), and the 48 h water absorption ratio of the different groups test block was calculated to Equation (2):

$$\Delta W = A \sqrt{t}$$  \hspace{1cm} (1)

where $A$ is the capillary water absorption coefficient (g·m$^{-2}$·h$^{-1/2}$); $\Delta W$ is the water absorption of the test block within $t$ (g·m$^{-2}$); and $t$ is the capillary water absorption time (h).

$$R = \frac{W_{tm}}{W_{rm}} \times 100\%$$  \hspace{1cm} (2)

where $R$ is the water absorption ratio between tested mortar and reference mortar (%); $W_{tm}$ is the water absorption of mortar under test (g); and $W_{rm}$ is the water absorption of mortar under reference (g).

2.5. Capillary Water Absorption Test of Cement Mortar Test Block with Crack Damage

This test mainly simulates the waterproof condition of the concrete after the cracks appear in the concrete after the waterproof material treatment in the actual project.

The capillary water absorption test was based on "Mortar, Concrete Waterproofing Agent" [31]. The cured cement mortar test block was dried and transferred to a laboratory, where the temperature was 20 ± 3 °C and the humidity was above 80%. Then, the molding surface, with a size of 25 mm x 160 mm, was used for coating, and cracks were induced after the emulsion was completely absorbed. The induced crack test was conducted with a concrete flexural testing machine (the maximum force value was 1000 kN), with the method shown in Figure 1. The opposite side of the coated surface was used as the loading surface, wherein the coated surface was facing down and was loaded at a loading speed of 0.1 m/min until cracks appeared; then, a crack width gauge was used to measure the width of the cracks. If the width was not sufficient, the sample was further loaded until cracks appeared. The induced cracks required for this test were approximately 0.1, 0.3, and 0.5 mm, as shown in Figure 2. This test only studied the water absorption of one crack, so only one crack and its surrounding water-absorbing surface with a size of 20 mm x 25 mm were taken, and the rest was sealed with epoxy resin. Finally, a water absorption test was performed to measure the water absorption at different time points.

2.6. Observation of the Micro Morphology of Cement Paste (SEM)

The cement paste test block, which had been cured for 28 days, was placed in an oven for drying. Then, a molding surface was taken and coated with waterproof material. After the waterproof material was completely absorbed by the cement paste, a small test block with a diameter of 5–10 mm under the coated surface was used. Water mist was sprayed on the surface of the small test block, which had not darkened in color, and was then dried as a sample for SEM.
Figure 1. Sketch and real map of the induced crack. (a) Sketch map; (b) Real map; (c) Concrete flexural testing machine.

Figure 2. Schematic diagram of different crack widths. (a) 0.1 mm; (b) 0.3 mm; (c) 0.5 mm.

2.7. X-ray Diffraction (XRD) Test

The 28-day-cured cement paste test block was placed in an oven for drying. A molded surface was then coated with waterproof material. After the waterproof material was completely absorbed by the cement paste, the surface powder of the coated surface was then ground through a 0.04 mm sieve. X-ray diffraction analyzer (Bruker D8, Bruker, Karlsruhe, Germany) was used to analyze the mineral composition of the sample via XRD with a Cu target, a voltage of 3 kW, a scanning range of 5°–80°, and a scanning speed of 5°/min.

2.8. Comprehensive Thermal Analysis (TGA) Test

The surface powder of the coated surface, prepared the same way as above, was then ground through a 0.04 mm fine screen. TGA tests were then conducted. The heat loss of Ca(OH)₂ of the sample at 0–1300 °C was analyzed using an SDTQ600 integrated thermal analyzer from the TA Company (New Castle, DE, USA). The gas atmosphere was nitrogen with a purity of 99.99%, and the heating rate was 10 °C/min.

3. Results and Discussion

3.1. The Influence of Graphene Oxide/Silane Composite Emulsion on the Waterproof Performance of Concrete After Abrasion

Penetration depth is a basic index to test the waterproof performance of materials. The penetration depth of the waterproof material measured by the water spray color method is shown in Figure 3, and the specific value of the penetration depth is shown in Table 5.

It can be seen from Figure 3 that the color of the concrete coated with silane waterproof material changed after it was sprayed with water, and there was a certain thickness of light-white on the surface of the concrete, which was formed after the water-repellent layer formed by the silane material met water. It can be seen from Table 6 that the penetration depth of silane emulsion and graphene oxide/silane composite emulsion was greater than 5 mm, indicating that both the silane emulsion and composite emulsion have a good...
waterproof effect. When the concrete surface peeled off, it did not penetrate further than the waterproof material. Thus, the silane waterproof material had a strong waterproof effect. It can be seen from the table that the penetration depth of the composite emulsion was higher than that of the silane emulsion, indicating that the waterproof effect of the composite emulsion was better than that of the silane emulsion.

![Figure 3](image-url)  
**Figure 3.** Penetration depth of uncoated group and coated waterproof material. (a) Uncoated; (b) Silane emulsion; (c) Graphene oxide (GO)/silane composite emulsion.

| W/C | Uncoated | Silane Emulsion | GO/Silane Composite Emulsion |
|-----|----------|-----------------|-------------------------------|
| 0.4 | -        | 8.97            | 9.36                          |

The capillary water absorption of concrete treated with different waterproof materials is shown in Figures 4–7. It can be seen from Figure 4 that as the depth of wear increases, the water absorption of the composite emulsion-coated concrete also increases, indicating that the waterproof effect of the composite emulsion decreases after the concrete is worn and damaged. It can be seen from Figures 5–7 that with the increase in the depth of wear, the water absorption of the blank group and the concrete coated with different waterproof materials have a certain increase, but regardless of the depth of the concrete wear, with concrete coated with composite emulsion, the water absorption is the lowest, indicating that the composite emulsion has the best waterproof effect. From Figures 5–7, it can also be seen that as the depth of wear increases, the difference between the water absorption of the silane emulsion-coated concrete and the water absorption of the composite emulsion becomes larger and larger, indicating that the composite emulsion has a greater impact on wear. The protective performance of concrete is better than that of silane emulsion.

![Figure 4](image-url)  
**Figure 4.** Influence of composite emulsion on the water absorption of concrete at different wear depths.
Figure 5. Influence of different waterproof materials on the water absorption of concrete after abrasion.

Figure 6. Influence of different waterproof materials on the water absorption of concrete after wearing of 3 mm.

Figure 7. Influence of different waterproof materials on water absorption of concrete after wearing 5 mm.

Table 7 provides the capillary water absorption coefficients of concrete coated with different waterproof materials at different abrasion depths calculated by Equation (1), and water absorption ratio of different wear depth for 48 h by Equation (2). It can be seen from the table that the capillary water absorption coefficient of the concrete coated with the composite emulsion is the smallest, which further shows that the composite emulsion has the best waterproof effect. When the concrete wear was 5 mm, the capillary water
absorption coefficient of the concrete coated with silane emulsion was \(47 \text{ g m}^{-2} \text{h}^{-1/2}\), 67.4% lower than that of the concrete without waterproof material treatment with an abrasion of 0 mm. The capillary water absorption coefficient of composite emulsion-coated concrete was \(35 \text{ g m}^{-2} \text{h}^{-1/2}\), which was 75.7% lower than that of concrete without waterproof material treatment with an abrasion of 0 mm. Through data comparison, it was found that after the concrete was worn 5 mm, both the silane emulsion and the composite emulsion had excellent waterproof performance, and the waterproof performance of the composite emulsion was better than that of the silane emulsion.

Table 7. Capillary water absorption coefficient of concrete coated with different waterproof materials under different wear depths (g m\(^{-2}\) h\(^{-1/2}\)).

| Item                        | Capillary Water Absorption Coefficient (g m\(^{-2}\) h\(^{-1/2}\)) | Average Water Absorption Ratio of Different Wear Depth for 48 h (%) |
|-----------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
|                             | Wearing 0 mm | Wearing 3 mm | Wearing 5 mm |                                |                                 |
| Uncrated                    | 144          | 220          | 264          |                                | -                               |
| Silane emulsion             | 25           | 35           | 47           |                                | 15.4                            |
| GO/silane composite emulsion| 16           | 28           | 35           |                                | 13.2                            |

According to the standard of “Mortar, Concrete Waterproofing Agent” [31], when the water absorption ratio of the test block was less than 65% in 48 h, the waterproof material coated on the test block was the first-class product, while the water absorption ratio of the test block coated with composite emulsion in this test was less than 15% over 48 h, far exceeding the requirements of the first class product.

3.2. The Influence of Composite Emulsion on the Waterproof Performance of Cement Mortar Test Block with Crack Damage

For cracked test blocks, the protective effect of silane emulsions and composite emulsions has a great relationship with their bonding mechanism with cement-based materials [32,34–37]. After the silane waterproof material enters the cement-based material, the ethoxy group of the silane monomer itself is hydrolyzed to form silanol. The silanol undergoes dehydration and condensation on the concrete capillary wall to form a water-repellent silicone resin layer with a waterproof effect. When the test block is cracked, the water-repellent layer will reduce the speed of water transmission along the cracking surface, thereby reducing the amount of water intrusion. The composite emulsion has a better waterproof effect than the silane emulsion. This is because the graphene oxide provides sites for the silane molecules, and the small silane molecules attach to the surface of the graphene oxide [38–42], so that the silane is distributed inside the cement-based material. It is more uniform and denser; thus, that the number of small silane molecules distributed on the cracked surface of the cement-based material is greater, the distribution is more uniform, and the waterproof ability is better than that of silane emulsion.

3.3. Microscopic Morphology Analysis

Figure 8 shows the capillary water absorption of the blank test block under different crack widths. It can be seen from the figure that as the width of the crack increased, the water absorption of the test block gradually increased, indicating that the existence of cracks will accelerate the transmission of water. The larger the crack, the faster the transmission speed. Figures 9–11 show the effect of different waterproof materials on the water absorption of cement mortar test blocks under different crack widths. It can be seen from these figures that no matter what the crack width was, the best waterproof effect was always the composite emulsion. When the crack width was 0.1 mm, the waterproof effect of the silane emulsion and the composite emulsion was basically the same, but with the increase in the crack width, the difference in water absorption between the two became larger and larger, indicating that the composite emulsion was useful for the cement mortar test because the waterproof effect of the block was better than that of the silane emulsion.
coated with different waterproof materials under different crack widths. It can be seen from the table that when the crack widths were 0.1, 0.3 and 0.5 mm, the capillary water absorption coefficient of the cement mortar test block coated with composite emulsion was about 10% in 48 h after the crack within 0.5 mm better waterproof performance than the silane emulsion.

It was found through the test that the water absorption capacity of the coated composite emulsion had excellent waterproof performance, and the composite emulsion has shown that for the cement mortar test block with cracks, the silane emulsion and the composite emulsion were 92.1%, 89.8%, and 86.1% lower than that of the blank group. The data indicated that the capillary water absorption coefficients of the silane emulsion-coated cement mortar was reduced by 93.6%, 93.1%, and 91.4%, respectively, compared with the blank group;
The uniformity of the distribution of silane molecules. This conclusion [43] has been confirmed in previous studies.

Table 8. Capillary water absorption coefficient of cement mortar test blocks with a crack width of 0.1 mm.

| Item                  | Capillary Water Absorption Coefficient (g·m⁻²·h⁻¹) |
|-----------------------|---------------------------------------------------|
| Silane emulsion       | 205 309 465 13.9                                   |
|GO/silane composite    | 167 207 288 10.8                                   |
| Uncoated              | 2593 3023 3351 -                                    |

Figure 8. Capillary water absorption of uncoated blocks under different crack widths.

Figure 9. Influence of different waterproof materials on the water absorption of cement mortar with a crack width of 0.1 mm.

Figure 10. Influence of different waterproof materials on the water absorption of cement mortar with a crack width of 0.3 mm.

Figure 11. Influence of different waterproof materials on the water absorption of cement mortar test blocks with a crack width of 0.5 mm.
Table 8 shows the capillary water absorption coefficient of cement mortar test blocks coated with different waterproof materials under different crack widths. It can be seen from the table that when the crack widths were 0.1, 0.3 and 0.5 mm, the capillary water absorption coefficient of the cement mortar test block coated with composite emulsion was reduced by 93.6%, 93.1%, and 91.4%, respectively, compared with the blank group; the capillary water absorption coefficients of the silane emulsion-coated cement mortar test blocks were 92.1%, 89.8%, and 86.1% lower than that of the blank group. The data show that for the cement mortar test block with cracks, the silane emulsion and the composite emulsion had excellent waterproof performance, and the composite emulsion has better waterproof performance than the silane emulsion.

| Item                     | Capillary Water Absorption Coefficient (g·m⁻²·h⁻¹/²) | Average Water Absorption Ratio of Different Crack Width for 48 h (%) |
|--------------------------|-----------------------------------------------------|------------------------------------------------------------------|
|                          | 0.1 mm  | 0.3 mm  | 0.5 mm  |                                      |                                                   |
| Uncoated                 | 2593    | 3023    | 3351    |                                      |                                                   |
| Silane emulsion          | 205     | 309     | 465     | 13.9                                  |                                                   |
| GO/silane composite emulsion | 167    | 207     | 288     | 10.8                                  |                                                   |

It was found through the test that the water absorption capacity of the coated composite emulsion test block in this test was about 10% in 48 h after the crack within 0.5 mm appeared, which is far more than the requirements for first-class products.

Figure 12 shows the microscopic appearance of the blank group and the cement paste test block treated with silane emulsion and composite emulsion under a scanning electron microscope with a magnification of 10,000×. It can be seen from Figure 12a that the internal surface of the test block was flat and smooth. Figure 12b,c show some floccules on the surface of the test block. The floccule is the microstructure of the hydrophobic layer formed by the silane waterproof material, which shows that the silane waterproof material can be closely combined with the cement-based material and has a good waterproof effect. Comparing Figure 12b,c, it can be found that in addition to the flocculent structure on the surface of the cement paste coated with the composite emulsion, there were also some clustered structures, combined with the binding mechanism of graphene oxide and silane. The cluster structure is a structure formed by silane molecules connected to graphene oxide, thereby increasing the thickness of the hydrophobic layer, and improving the uniformity of the distribution of silane molecules. This conclusion [43] has been confirmed in previous studies.

Figure 12. The micromorphology of uncoated group and block coated with silane emulsion and composite emulsion. (a) Uncoated; (b) Silane emulsion; (c) GO/silane composite emulsion.
3.4. XRD Analysis Result

Figure 13 is the XRD pattern of the blank group and the cement paste sample coated with silane emulsion and composite emulsion, in which \( p \) represents \( \text{Ca(OH)}_2 \). It can be seen from the figure that the intensity of the \( \text{Ca(OH)}_2 \) diffraction peak in the cement paste sample coated with silane emulsion and composite emulsion is significantly lower than that in the blank group. Comparing the blank group and the cement paste samples coated with silane emulsion and composite emulsion, the integrated areas of the strongest \( \text{Ca(OH)}_2 \) diffraction peak at a 2-\( \theta \) of 18.05° are 5307, 634, and 1199, respectively. Data comparison found that after coating with waterproof material, the content of \( \text{Ca(OH)}_2 \) in the cement paste sample was significantly reduced. Combined with the bonding mechanism of permeable silane waterproof material and cement-based material, these results show that the silane waterproof material was in cement paste. A water-repellent layer was formed inside, which had a good waterproof effect.

![Figure 13. XRD pattern of uncoated group and silane emulsion and composite emulsion test block.](image)

3.5. Analysis of Thermogravimetric Results

Figure 14 is the thermal weight loss analysis of the blank group and the cement paste coated with silane emulsion and composite emulsion after being calcined at 1300 °C. The weight loss between 400 and 500 °C is mainly due to \( \text{Ca(OH)}_2 \) dehydration and decomposition to produce calcium oxide [44]. From the XRD analysis, it can be seen that the content of \( \text{Ca(OH)}_2 \) in the cement paste coated with silane emulsion and composite emulsion was reduced. From the thermogravimetric analysis graphs, it can be seen that the thermogravimetric loss of cement paste coated with silane emulsion and composite emulsion was between 400–500 °C more than that of the uncoated group, indicating that the cement paste coated with silane emulsion and composite emulsion had other substances reacting in addition to the decomposition of \( \text{Ca(OH)}_2 \) at 400–500 °C. Studies have shown that the Si–OC chemical bond decomposes at 400–500 °C [45]. According to the bonding mechanism of silane and cement-based materials, we believe that the substance that reacted between 400 and 500 °C was the hydrophobicity formed by the silane waterproof material. Therefore, it is proved that the silane waterproof material is closely connected with the cement-based material and has a good waterproof effect.

![Figure 14. Thermogravimetric analysis of uncoated cement paste, and coated with a silane emulsion and composite emulsion.](image)
4. Conclusions

The penetration depth of silane emulsion and composite emulsion can reach 5–10 mm, which has a good waterproof effect.

The capillary water absorption coefficient of concrete coated with composite emulsion is $35 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1/2}$, which is 75.7% lower than that of concrete without waterproof material treatment with an abrasion of 0 mm, indicating that when concrete is damaged by abrasion, the composite emulsion still has a good waterproof performance.

With a crack width of 0.5 mm, the capillary water absorption coefficient of the cement mortar test block coated with composite emulsion is 91.4% lower than that of the blank group, and the capillary water absorption coefficient of the cement mortar test block coated with silane emulsion is 86.1% lower than that of the blank group. The data show that for cement mortar test blocks with cracks, the silane emulsion and composite emulsion have excellent waterproof performance, and the waterproof performance of composite emulsion is better than that of silane emulsion.

Through SEM, XRD, and TGA tests, it was found that the composite emulsion can form a hydrophobic layer with a certain thickness inside the cement-based material, thereby achieving a good waterproof effect.

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