Preparation of Modified Silane Composite Emulsion and Its Effect on Surface Properties of Cement-Based Materials

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Abstract: A new type of waterproofing composite emulsion with high silane content and good economic efficiency was synthesized by sol synthesis. The effects of the amount and proportion of the compound emulsifier, amount of tetraethyl orthosilicate, and mixing time on the properties of the emulsifier were investigated. The optimum conditions for the synthesis of a tetraethyl orthosilicate/isobutyl triethoxysilane emulsion were determined. The composite emulsion was characterized by infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, and energy-dispersive spectrometry, along with a series of microscopic testing techniques. It was verified that the composite emulsion was coated on the surface of the paste to form a hydrophobic protective layer. The results show that the composite emulsion can achieve a permeability and impervious effect after coating the concrete material, and microhardness tests prove that the composite emulsion will not reduce the surface hardness of cement-based materials.

Keywords: silane waterproof materials; cement-based materials; infrared spectroscopy; thermogravimetric analysis

1. Introduction

As one of the most used materials in the construction industry, research on the durability of concrete, and its working and mechanical properties in the process of its production and application, has attracted more and more attention in recent years [1,2]. Some studies show that, in addition to the external environment and external load, damage to the concrete itself, including holes and microcracks, is the main factor causing a reduction of durability [3–5]. Through these types of damage, harmful substances and ions can invade into the concrete with water as the carrier, resulting in neutralization, freeze–thaw loss, sulfate erosion, and other durability reductions [6–8]. Therefore, controlling water intrusion is one of the main measures used to improve the durability of concrete [9,10].

On the basis of not changing the concrete base material, the current method to prevent moisture from invading the concrete interior is to carry out waterproofing treatment on the concrete surface [11–13]. Among many waterproof materials, compared to traditional asphalt, such as epoxy resin, polyurethane, and acrylic resin, silane material can penetrate into the concrete interior and will not block the pores of the concrete, which has the effect of gas permeability and impermeability [14–16]. Concrete with air permeability can make the water inside the concrete in the process of evaporation be smoothly discharged, reducing the risk of concrete cracking [16]. In recent years, silane material has attracted the attention of researchers and engineers. Through a large number of experiments, it has been found that isobutyl triethoxysilane has good hydrophobicity [17]. Silane emulsion can enhance silane stability and reduce volatilization, but can also reduce the effective silane ratio,
thereby reducing the effect of silane material to some extent [18]. At the same time, the
effect of silane on the surface of early age concrete will affect the concrete early to a certain
extent, as it is harmful to the development of concrete surface strength due to the hydration
of concrete [19].

Tetraethyl orthosilicate (TEOS) is prone to hydrolytic action to form polysilicic acid.
Studies have shown that polysilicate has a certain volcanic ash effect and can react
with the cement hydration product Ca(OH)₂ for two hydration reactions to generate
hydrated silicate gel [20,21]. The Si–O bond after hydrolysis of TEOS can also be linked to
–OH on the surface of cement-based material, which is helpful to improving the surface
strength of concrete. Because TEOS is easy to hydrolyze, its long-term effect is not stable
when it is used directly in cement-based materials, and it will cause a certain kind of
environmental pollution.

Combined with the advantages and disadvantages of isobutyl triethoxysilane emul-
sion and TEOS, in this paper an attempt is made to prepare a new composite silane material
that is waterproof and breathable and that can improve the surface strength of cement-
based materials by sol–gel synthesis. TEOS and isobutyl silane emulsion were synthesized
by the sol–gel synthesis method, and results show that the waterproof effect, gas permeabil-
ity, and surface strength of concrete are enhanced by this method, all of which contribute
to the further improvement of concrete durability.

2. Experiment
2.1. Preparation of TEOS/Isobutyl-Triethoxysilane Emulsion
2.1.1. Materials
Isobutyl-triethoxysilane monomer and TEOS were used in experiments with polyethy-
lene glycol (PEG) as a dispersant. Span 80, peregal O (PPG O), sodium lauryl sulfate
(SLS), and sodium dodecyl benzene sulfonate (SDBS) were used to prepare the composite
emulsifier. Deionized water was used throughout the experiments. The materials used in
this experiment are described in detail in Table 1.

Table 1. Details of silane monomer used in experiments.

| Silicone Monomer | Molecular Formula | Manufacturer | Purity |
|------------------|-------------------|--------------|--------|
| Isobutyl-triethoxysilane | (CH₃)₃CHCH₂Si(OCH₃)₃ | Sigma (Shanghai, China) | Chemical level |
| TEOS | Si(OCH₃)₄ | | |
| Span 80 | C₂₄H₄₄O₆ | Shanghai Aibi Chemical Reagent Co., Ltd. (Shanghai, China) | |
| PPG O | RO-(CH₂CH₂O)ₙ-HR | | |
| PEG | HOC₂H₄OₙH | | |
| SLS | C₁₂H₂₅SO₄Na | | |
| SDBS | C₁₈H₂₉NaO₃S | | |

2.1.2. Preparation Process
TEOS/isobutyl-triethoxysilane emulsion (Figure 1) was prepared as follows. First, a
certain amount of oily emulsifier, isobutyl-triethoxysilane (accounting for 35% of the total
solution mass), and a certain amount of PEG were mixed to prepare a stable oil phase using
a homogenizing machine. In addition, a certain amount of water-based emulsifier and
distilled water (accounting for 30% of the total solution mass) were mixed to create a stable
aqueous phase. Next, an oil phase was added dropwise into the aqueous phase in a flask at
40 °C while stirring at high speed for a while. Subsequently, a certain amount of TEOS was
added dropwise. The final compound emulsion was obtained after 4 h of reaction time and
followed by cooling to room temperature.
Figure 1. Synthesis process of tetraethyl orthosilicate (TEOS)/isobutyl-triethoxysilane compound emulsion.

2.1.3. Effect of Emulsifiers on Compound Emulsion

The value of the hydrophilic–lipophilic balance (HLB) of the oil/water system emulsion was kept in the 8–18 range [22]. Thus, HLB plays an important role in synthesizing compound emulsifiers constituted by lipophilic and hydrophilic emulsifiers. The type and proportion of emulsifier can be determined through studying the HLB. The HLB values for the different emulsifiers used are shown in Table 2.

Table 2. Hydrophilic–lipophilic balance (HLB) values for different emulsifiers used.

| Emulsifier | SLS | SDBS | Span 80 | PPG O |
|------------|-----|------|---------|-------|
| HLB       | 40  | 10.6 | 4.3     | 16.5  |

The HLB for the compound emulsifiers was calculated using [23]

$$HLB_0 = \frac{W_A HLB_A + W_B HLB_B}{W_A + W_B}$$ (1)

where $HLB_0$ is the HLB value for the compound emulsifier, $W_A$ the amount of emulsifier A (%), $W_B$ the amount of emulsifier B (%), $HLB_A$ the HLB value of emulsifier A, and $HLB_B$ the HLB value of emulsifier B.

It was confirmed that the HLB of the compound emulsifier was 10; the compound dosage of two different kinds of emulsifiers was calculated using Equation (1). The effects of compound emulsifier dosages are shown in Table 3.

Table 3. Effect of compound emulsifier dosages.

| Compound Emulsifier | Dosage Ratio | Static Situation |
|---------------------|--------------|------------------|
| Span 80 and SDS     | 4:1          | Layered          |
| Span 80 and SDBS    | 1:9          | Layered          |
| Span 80 and PPG O   | 1:1          | Stable           |

The most stable composite ratio was obtained with Span 80 and PPG O, two kinds of emulsifiers combined at a 1:1 ratio.
2.1.4. Effect of Addition Time Period of TEOS on Compound Emulsion

As the oil phase was added dropwise into the aqueous phase in a flask at 40 °C while stirring at high speed for 5 h, 35% TEOS was added dropwise at different times to prepare the TEOS/isobutyl-triethoxysilane emulsion. The effect of addition times is shown in Table 4.

Table 4. Effect of adding TEOS to compound emulsion at different addition times.

| Addition Time Period | Emulsion State |
|----------------------|----------------|
| Stirring for 1 h     | Stable         |
| Stirring for 2 h     | Layered        |
| Stirring for 3 h     | Layered        |
| Stirring for 4 h     | Layered        |

With increasing mixing time, the emulsion will be affected by the demulsification of mixer blades. It was found that the compound emulsion had little effect on the preparation process when adding TEOS after 1 h of high-speed stirring at 40 °C. A stable compound emulsion was obtained for a reaction followed by cooling to room temperature, and the content of the silane in the emulsion significantly increased.

2.1.5. Effect of Added Amount of TEOS on Compound Emulsion

It was found that the gel time of the compound emulsion was reduced while the ratio of TEOS increased. Because of the hydrolysis of TEOS, some of the water was consumed. Considering 7 days of absorption of the coating, the best result was a TEOS-to-isobutyl-triethoxysilane ratio of 1:1. The effects of adding TEOS are shown in Table 5.

Table 5. Effects of adding TEOS on compound emulsion.

| Mass Ratio of TEOS and Isobutyl-Triethoxysilane | Static Situation | Gelation Time         |
|-------------------------------------------------|------------------|-----------------------|
| 1:2                                             | Stable           | Approximately 2 months|
| 1:1                                             | Stable           | Approximately 1 month  |
| 2:1                                             | Layered          | Approximately 15 days  |

2.2. Preparation of Cement-based Materials

In this paper, the cement-based materials used to verify the effect of composite emulsion were mainly concrete of strength grade C40 and C50 that are commonly used in engineering and cement paste with a water–cement ratio of 0.4. The mixing ratio of cement-based materials is shown in Table 6.

Table 6. Mixing ratios of cement-based materials (kg/m³).

| Cement-Based Materials | Strength Grade | Water–Cement RATIO | Mixing Ratio (kg/m³) |
|------------------------|----------------|--------------------|----------------------|
|                        |                |                    | Cement | Sandstone | Aggregate | Water |
| Concrete               | C40            | 0.5                | 320    | 653       | 1267      | 160   |
|                        | C50            | 0.4                | 380    | 579       | 1269      | 152   |
| Cement paste           | -              | 0.4                | 1350   | -         | -         | 540   |

Ordinary Portland cement (PO 42.5) with the chemical composition shown in Table 7 was used in the experiments. River sand with a fineness of 2.9 was used in the concrete, Chinese ISO standard sand (GBS 08-1337. ISO standard sand, China, 2019.) was used in the cement paste, and basalt with a particle size of 5–20 mm was used in the concrete aggregate.
Table 7. Composition of PO 42.5 cement (%).

|         | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | f-CaO |
|---------|------|-------|-------|-----|-----|-----|------|-------|
|         | 21.9 | 4.5   | 3.5   | 64.0 | 2.9 | 2.4 | 0.5  | 0.92  |

3. Performance Characterization and Methods

3.1. Fourier-Transform Infrared Spectroscopy

Cement paste blocks coated with different waterproofing silanes were measured using Fourier-transform infrared (FTIR) spectroscopy (TENSOR 27, Bruker, UK; scanning range, 0–8300 cm⁻¹; wavelength accuracy, 0.01 cm⁻¹). The chemical groups of the cement paste blocks were analyzed and compared before and after the coating of the silanes. The quality of the bond between different silane waterproofing coatings and the cement-based materials was investigated, which revealed the underlying mechanism for the waterproofing coating effect.

3.2. Thermogravimetric Analysis and Differential Scanning Calorimetry

The cement-paste–powder samples with different coatings were measured using a comprehensive thermal analysis instrument (TA, SDTQ600, New Castle, DE, USA; determination range, 0.1 g to 200 mg; temperature range, room temperature to 1500 °C; heating rate, 5 °C/min), including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability of the cement-paste–powder samples and the mass loss in different temperature ranges were analyzed and compared before and after coating. The reactions of Ca(OH)₂ from cement with different waterproofing silanes were characterized.

3.3. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy

The micro-structure of the cement-paste blocks coated with different waterproofing silanes was observed using scanning electron microscopy (SEM) (ZEISS, IGM 300/VP, Jena, Germany). The Si content on the surface of the cement-paste test blocks was examined before and after coating using energy-dispersive X-ray spectroscopy (EDS) (EISS, IGM 300/VP, Jena, Germany) (both spot and surface scanning).

3.4. Particle-Size Measurements and Distributions

Both the isobutyl-triethoxysilane emulsion and compound emulsion were measured to obtain the average particle size using a laser particle-size analyzer (Jinan Runzhi Technology, Rise-2008, Jinan, China). The distribution of the two emulsion types was observed with an inverted fluorescence microscope (Olympus, IX71-F22FL/PH, Tokyo, Japan).

3.5. Capillary Water-Absorption Test

A one-dimensional capillary water-absorption test was conducted to measure the weight of each block with absorption times of 0, 1, 2, 4, 6, 8, 12, 24, 36, and 48 h. According to the changes in every sample, a water-absorption coefficient was calculated using [24]

\[
\Delta W = A \times t^{1/2}
\]

where \( A \) is the water absorption coefficient (g·m⁻²·h⁻⁰.⁵), \( \Delta W \) is the amount of water absorbed during the absorption time (g·m⁻²), and \( t \) is the water-absorption time (h).

3.6. Gas Permeability Test

The gas permeability of concrete blocks (150 mm × 150 mm × 150 mm) coated with different waterproofing silanes was measured to determine the breathing properties of concrete before and after coating using the Auto-Clam Permeability System (Amphora Autoclam, Ireland, UK). According to the measured gas pressure reduction, the index for gas permeability of concrete was calculated.
3.7. Microhardness Test

The effect of coating composite emulsion on the surface hardness of cement-based materials was tested by a microhardness tester (Airma, FALCON 400, Shenzhen, China). Twenty points were evenly selected on the coating surface of the paste test block, and the selection rules were as follows.

The diagonal length of indentation was \( L_1 > L_2 > 20 \mu m \) (to reduce the visual reading error), the distance between two longitudinal points \( d > 2L_1 \) or \( 50 \mu m \), the distance between two adjacent transverse points \( d \), and the height difference \( h = 10 \mu m \). The schematic is shown in Figure 2.

![Figure 2. Point group of microhardness.](image)

The points with dense parts in the figure were selected, and the average value was calculated as the average Vickers hardness of the corresponding test block. The effect of composite emulsion on the surface hardness of cement-based materials was reflected by the Vickers hardness.

4. Results and Discussion

4.1. Chemical Characterization

FTIR spectra for cement-paste blocks with different coating materials are shown in Figure 3. The peak at 1100 cm\(^{-1}\) corresponds to the Si–O–C bending vibration, which indicates that test silane combined well with the cement paste [25]. In particular, in the block coated with isobutyl-triethoxysilane emulsion and the compound emulsion, the presence of Si–O–C shows that this kind of silane waterproof material is well combined with cement paste. The peak at 3500 cm\(^{-1}\) corresponds to the Si–OH bending vibration, which is a hydrophobic group that facilitates waterproofing [25].

The isobutyl-triethoxysilane and compound emulsions were compared after coating with TEOS. The peaks near 3000 cm\(^{-1}\) correspond to the –CH\(_3\) and –CH\(_2\)– bending vibrations [25], which confirms that the isobutyl-triethoxysilane and compound emulsions form a protective layer on the surface of the cement paste.

4.2. Thermogravimetric Analysis of Silane Waterproofing Materials

The cement hydration products were C–S–H (calcium silicate hydrated), C–H(Ca(OH)\(_2\)), and AFt(3CaO·Al\(_2\)O\(_3\)·3CaSO\(_4\)·32H\(_2\)O) [26]. Hence, during the process (0–135 °C), when the cement paste released heat, weight loss was mainly associated with these substances (see Figure 4). It was found that the degradation process included three phases between 20 and 900 °C. The first phase occurred between room temperature and 300 °C, with...
weight loss due to the evaporation of absorbed water. In addition, the dehydration of hydrated calcium silicate gel and dehydration of ettringite changed into a low-sulfur-type calcium aluminate [27]. The second step took place between 300 and 600 °C, and brucite was mainly converted to periclase, and calcium di-hydroxide water was deoxidized to calcium oxide [27]. The third phase occurred between 600 and 900 °C, where the process slowed down by converting calcium silicate into silica fume [27].

Figure 3. FTIR transmission spectra of cement paste for different coating materials.

Figure 4. TGA and DSC curves of cement paste with different coating processes. (a) Cement paste after coating with compound emulsion; (b) Cement paste after coating with TEOS; (c) Cement paste after coating with isobutyl-triethoxysilane emulsion; (d) Cement paste only.
The weight-loss rates for the cement-paste blocks at different temperatures with different silanes are shown in Table 8. It can be found that the area of the DSC curve of the paste coated with waterproof material is obviously smaller than that of the untreated reference paste in the temperature range from 300 to 500 °C. The mass-loss rate of the corresponding TGA curve more intuitively reflects this result. Polysilicate forms after the hydrolysis of TEOS combines with calcium hydroxide to produce a second hydration reaction. The isobutyl-triethoxysilane emulsion combines with a hydroxyl from the calcium hydroxide on the concrete surface via dehydration synthesis, which forms a dense waterproof layer [28,29]. Thus, through the above tests, it can be proved that the prepared compound emulsion can be combined with the cement-based surface layer and react with the surface layer Ca(OH)$_2$ to a certain extent.

Table 8. Percentage of weight loss after heating of cement paste using different coating methods (%).

| Samples                              | 20–300 °C | 300–500 °C |
|--------------------------------------|-----------|------------|
| Compound emulsion                    | 10.92     | 4.24       |
| TEOS                                 | 11.59     | 4.14       |
| Isobutyl-triethoxysilane emulsion    | 9.38      | 4.12       |
| Reference                            | 11.21     | 4.74       |

4.3. SEM and EDS

The surface morphologies of a cement paste block after undergoing different coating processes are shown, magnified (1500 times) via SEM, in Figure 5. For the reference block (Figure 5d) without coating treatment, the internal compactness of the sample block is poor, and there are many voids. The distribution of dense and small particles can be seen on the surface of the coating with TEOS (Figure 5b). TEOS has little effect on the surface morphology of the cement paste because of its high permeability. However, for the cement-paste block after coating with the compound emulsion (Figure 5a) and isobutyl-triethoxysilane emulsion (Figure 5c), an obvious layered structure was formed to cover the surface. The EDS results for cement paste with different coating materials are shown in Table 9. The silicone contents of the spot-scanned and surface-scanned surfaces show that the substance covering the surface of the paste was silane waterproof material. Overall, these results confirm that the compound emulsion can be successfully combined with cement-based materials.

4.4. Particle-Size Analysis

The silane emulsion is a heterogeneous and multi-phase system. In the oil/water system of the isobutyl-triethoxysilane emulsion, the isobutyl-triethoxysilane monomer combined with water molecules using the emulsifier, which ensured the permeability and simultaneously increased the adhesion to the concrete surface. However, for the isobutyl-triethoxysilane emulsion, the silane content was only approximately 50%. Upon increasing the silane monomer content further, the stability of the emulsion decreased. In this study, TEOS, with its excellent permeability and low molecular weight, was introduced to produce a compound emulsion that could increase the silane content and improve distribution density (see Figure 6), the distribution density of isobutyl-triethoxysilane emulsions was shown in Figure 7, this also ensures that the particles of the compound emulsion are not too large. The average particle sizes for the different silane waterproofing materials are shown in Table 10. Although the particle sizes of the compound emulsion increased, its permeability depth could reach more than 5 mm after mixing with TEOS.

4.5. Effect on Capillary Water Absorption of Concrete

Figure 8 shows that the capillary water absorption of concrete, with and without treatment of the surface with different silanes, varies with time. The measured coefficient for capillary water absorption is shown in Table 11. The waterproofing was highest for the
compound emulsion, in which the coefficient of capillary suction decreased by 84.1% for strength grade C40 and 83.1% for strength grade C50.

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Figure 5. SEM images (magnified 1500 times) of cement paste for different coating processes. (a) Cement paste after coating with compound emulsion; (b) Cement paste after coating with TEOS; (c) Cement paste after coating with isobutyl-triethoxysilane emulsion; (d) Cement paste only.

Table 9. EDS results for cement paste with different coating materials.

| Samples                          | Content of Silicon (at.%) |
|---------------------------------|---------------------------|
|                                 | Spot Scanning | Surface Scanning |
| Compound emulsion               | 14.12          | 10.23            |
| TEOS                            | 7.34           | 7.21             |
| Isobutyl-triethoxysilane emulsion| 11.64          | 8.28             |
| Reference                        | 4.04           | 4.81             |

Table 10. Average particle sizes of different waterproofing silanes.

| Silane Waterproofing Material             | Average Particle Size (µm) |
|------------------------------------------|-----------------------------|
| Isobutyl-triethoxysilane emulsion        | 5.12                        |
| Compound emulsion                        | 6.31                        |
Table 9. EDS results for cement paste with different coating materials.

| Samples                      | Spot Scanning | Surface Scanning |
|------------------------------|---------------|------------------|
| Compound emulsion            | 14.12         | 10.23            |
| TEOS                         | 7.34          | 7.21             |
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| Reference                    | 4.04          | 4.81             |

**Particle Size Analysis**

The silane emulsion is a heterogeneous and multi-phase system. In the oil/water system of the isobutyl-triethoxysilane emulsion, the isobutyl-triethoxysilane monomer combined with water molecules using the emulsifier, which ensured the permeability and simultaneously increased the adhesion to the concrete surface. However, for the isobutyl-triethoxysilane emulsion, the silane content was only approximately 50%. Upon increasing the silane monomer content further, the stability of the emulsion decreased. In this study, TEOS, with its excellent permeability and low molecular weight, was introduced to produce a compound emulsion that could increase the silane content and improve distribution density (see Figure 6), the distribution density of isobutyl-triethoxysilane emulsions was shown in Figure 7, this also ensures that the particles of the compound emulsion are not too large.

The average particle sizes for the different silane waterproofing materials are shown in Table 10. Although the particle sizes of the compound emulsion increased, its permeability depth could reach more than 5 mm after mixing with TEOS.

Figure 6. Morphology (magnified 400 times) of the compound emulsion.

Figure 7. Morphology (magnified 400 times) of the isobutyl-triethoxysilane emulsion.

Table 11. Coefficients of capillary water absorption for different contrastive groups (g·m⁻²·h⁻⁰·⁵).

| Strength Grade | Compound Emulsion | TEOS | Isobutyl-Triethoxysilane Emulsion | Reference |
|----------------|-------------------|------|-----------------------------------|-----------|
| C40            | 38                | 58   | 48                                | 240       |
| C50            | 20                | 36   | 25                                | 118       |
### 4.6. Gas Permeability Analysis

The gas permeabilities for concrete using different coatings are shown in Figure 9 and the indexes of gas permeability for concrete with different coatings were determined (see Table 12). The indexes of gas permeability were 0.0332, 0.0414, and 0.0305 ln/min after coating with isobutyl-triethoxysilane emulsion, compound emulsion, and TEOS, respectively, when the strength grade was C40. The permeability of concrete was somewhat reduced, but was less than 0.1 ln/min, which means it still had excellent gas permeability [30,31]. It is mainly due to the infiltration of silane emulsion into the cement-based materials, which can participate in the hydration reaction of the surface layer of the cement-based materials, but does not completely block the concrete pores or form a dense mold material on the surface of the cement-based materials. As a result of the solvent volatilization and the micro-gap between the polymer chains, the water vapor inside the concrete can be exchanged to the outside world, retaining the “breathing property” of the concrete. The previous experimental results confirm the waterproofing and anti-carbonation properties for these coating materials on concrete. It was also found that the compound emulsion had little effect on the breathing property of the cement-based materials. This was still the case when the strength grade was C50.

![Figure 8](image-url)  
**Figure 8.** Effects of capillary water absorption of concrete for different coating: (a) C40; (b) C50.

| Strength Grade | Coefficient of capillary water absorption | Permeability Index |
|---------------|------------------------------------------|-------------------|
| C40           | 0.0332                                   | 0.0305            |
| C50           | 0.0414                                   | 0.0323            |

| Coating Material | Average Particle Size (μm) |
|------------------|---------------------------|
| Compound Emulsion| 5.12                      |
| TEOS             | 6.31                      |
| Isobutyl-triethoxysilane Emulsion| 7.21 |

![Table 10](image-url)  
**Table 10.** Average particle sizes of different coating materials.

![Table 11](image-url)  
**Table 11.** Effects of capillary water absorption of concrete, with and without the compound emulsion, in which the overall amount of the discrete type of data is relatively large. The addition of TEOS mitigated this problem. TEOS from Figure 10 can have an excellent hydrophobic effect, but it does not take place in the chemical reaction and the micro-gap between the polymer chains, the water vapor inside the concrete can be exchanged to the outside world, retaining the “breathing property” of the concrete. The permeation of the compound emulsion is ma...
Table 12. Indexes of gas permeability for concrete with different water-to-binder ratios using different coatings.

| Strength Grade | Compound Emulsion | TEOS | Isobutyl-triethoxysilane Emulsion | Reference |
|----------------|-------------------|------|-----------------------------------|-----------|
| C40            | 0.0414            | 0.0305 | 0.0332                          | 0.0438    |
| C50            | 0.0322            | 0.0287 | 0.0323                          | 0.0432    |

4.7. Microhardness Analysis

Through the microhardness test, it can be found that isobutyl-triethoxysilane emulsion can have an excellent hydrophobic effect, but it does not take place in the chemical reaction of cement hydration. The hydrophobic effect affects the progress of cement hydration, which reduces the surface hardness of the cement-based material. As can be seen from Figure 10 and Table 13, the overall amount of the discrete type of data is relatively large. The addition of TEOS mitigated this problem. TEOS-hydrolyzed SiO$_2$ can react with the cement hydration product Ca(OH)$_2$ to produce a calcium silicate hydrogel with higher strength [20,21], thus improving the surface hardness of cement-based materials. Therefore, the surface hardness of cement-based materials can be improved to a certain extent by the compound silane emulsion.

Figure 10. Surface hardness of cement paste for different coatings.

Table 13. Surface average Vickers hardness of cement paste for different coatings (MPa).

| Samples                                | Average Vickers Hardness (MPa) |
|----------------------------------------|--------------------------------|
| Compound emulsion                      | 41.2                           |
| TEOS                                   | 43.1                           |
| Isobutyl-triethoxysilane emulsion      | 37.2                           |
| Reference                              | 39.6                           |

5. Conclusions

Through the research performed in this study, the preparation method of modified silane composite emulsion was confirmed and the surface properties of cement-based materials were tested.
• The key points in the preparation of the composite emulsion were determined, including the type and amount of emulsifier (a mass ratio of Span80 to PPG O of 1:1), addition time (after an emulsion reaction period of 1 h), and amount of TEOS (accounting for 35% of the total solution mass), to ensure the stability of the composite emulsion.
• The composite emulsion was coated on the surface of cement-based materials, which formed a hydrophobic film on the surface of cement-based materials that can improve the waterproofing effect of cement-based materials without affecting its permeability.
• The surface hardness of the composite emulsion can be improved by coating it on the cement-based materials, due to the introduction of TEOS into the composite emulsion, which reduces the possibility of reducing the surface hardness of cement-based materials by the use of traditional silane silicas.

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