Effect of epoxy emulsion on properties of ultra-high toughness cementitious composites

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Abstract: The ultra-high toughness cementitious composites (UHTCC) was modified by different types of epoxy emulsion, the effect of the emulsion on working performance, mechanical properties and impermeability of UHTCC were studied. The result showed that compared with the control without epoxy emulsion, the type I and type II epoxy emulsion improved the working performance of UHTCC with low dosage. However, the type III epoxy emulsion exhibited an improvement effect on working performance of UHTCC only when the dosage was high. The addition of epoxy emulsion to UHTCC caused a decrease in compressive strength and flexural strength, but epoxy emulsion and hydration products formed an excellent energy absorption mechanism in the specimen and enhanced the elastic modulus of UHTCC. Type I and II epoxy emulsion had little effect on the tensile properties of UHTCC. Type III epoxy emulsion greatly increased the ultimate tensile strength of UHTCC, and the strain hardening phenomenon disappeared at low dosage level, however, the effect of strain hardening had been improved by increasing its dosage.

1. Introduction
Concrete has been an important material in construction filed for hundreds of years. The behavior of traditional concrete is weak in tension. The cracking was easily to be occurred in concrete under temperature stress and loosening pressure due to the low tensile strength and brittleness. Cementitious materials combining the optimization of the micro-mechanical parameters to achieve the high performance concrete, where the challenges still exist in the application of concrete [1]. This limitation of concrete is not suitable for important building structure. Engineered cementitious composites (ECC) or ultra-high toughness cementitious composites (UHTCC) was design by Li Victor C [2]. UHTCC is known for its excellent strain-hardening, and multiple cracking [3-5].

In recent years, to improve the performance of ordinary concrete. Researchers have attempted a long time to research a new type of building materials using polymer that shows excellent performance [6-7]. Polymer cement mortars have been used as repairing materials in the construction buildings for their excellent properties. They both have excellent mechanical properties and durability properties [8-10].

UHTCC is composed of cement, fine silica sand, fly ash, fiber, water and superplasticizer. One of the most important phases in UHTCC which have an effective role in determining the concrete characteristics is the interfacial transition zone (ITZ) of cement paste and fibers. The high tensile strain capacity of UHTCC is obtained by optimizing the micromechanical parameters, in which the fiber matrix interaction is customized to achieve strain hardening properties. [11-13]. So, polymer can be used...
in the design optimization of UHTCC to increase the ITZ between fiber and matrix. Some researchers have done related research in this direction [14-16]. However, there are still some problems that have not been explained clearly, and there are differences between different research results. Then, the research needs to do more in-depth work in order to explore the mechanism.

The approach we are introducing in this paper comprises the introduction of different type of epoxy emulsion and its dosage to produce organic-inorganic or film toughening structure in UHTCC. In order to investigate the effect of epoxy emulsion on different properties of UHTCC.

2. Experimental

2.1. Materials

2.1.1. Cement and SCMs. The ordinary Portland cement (P.O 42.5R) confirmed to GB 175–2007 [17] used in paper. Fly ash, micro beads and silica fume were used as auxiliary gelling materials. Fly ash with surface area of 3850 cm²/g and density of 2.8 g/cm³ was purchased from a plant of Sichuan province in China. The microbeads with surface area of 4030 cm²/g was produced by a plant in Sichuan. Silica fume was purchased from a plant in Shandong with a specific surface area of 10900 cm²/g. Figure 1 (a-c) showed the scanning electron micrograph of SCMs.

![Figure 1. SEM of SCMs: (a) Fly ash, (b) micro beads, and (c) silica fume.](image)

2.1.2. Aggregate. Quartz powder with a particle size of 38 µm (400 mesh) was used as fine aggregate.

2.1.3. Water reducing agent and epoxy emulsion. Polycarboxylic acid superplasticizer, solid content 40%, water reduction rate 25%, used as an additive with 1wt.% of cementitious material. Epoxy emulsion is divided into Type I, Type II and Type III, with a solid content (mass fraction) of 47%, which was produced by CSCEC new materials Co., Ltd.

2.1.4. Fiber. Polyvinyl alcohol fiber (PVA) is preferred as one of the raw materials for the preparation of UHTCC. The volume content of PVA fiber is 2.0% of UHTCC. The fiber properties are shown in Table 1.

| Tensile strength / MPa | Length / mm | Diameter / µm | Density / g·cm⁻³ | Elasticity modulus / GPa |
|------------------------|-------------|---------------|-------------------|-------------------------|
| 1600                   | 12          | 39            | 1.3               | 32.5                    |

2.2. Mixture and preparation

The mix design is shown in Table 2. The amount of epoxy emulsion in the control is 0(K0), K1, K2, and K3 correspond to three types of epoxy emulsions I, II, and III, respectively, and the dosage is 2wt.%, K4, K5, K6, and K7 correspond to epoxy emulsion III dosages of 3wt.%, 4wt.%, 5wt.%, and 6wt.%, respectively.

Preparation: cement, fly ash, micro-beads, and quartz powder were added to the mixer and stirred for
120 s. Then, water, superplasticizer and epoxy emulsion were added to the mixed powder and stirred for 180 s. Finally, PVA was added in batches and stirred at high speed for 240 s until the mixture was uniform. After being formed for 24 hours, the specimens were demolded and cured to 3 d, 7 d, and 28 d. The curing temperature was 20±1 °C and the relative humidity was 95%.

### Table 2. Mixture proportion of control.

| Mix proportion |  |
|----------------|----------------|
| Cement / (kg·m⁻³) | 700 |
| m(fly ash) / m(cement) | 0.64 |
| m(silica fume) / m(cement) | 0.33 |
| m(microbeads) / m(cement) | 0.11 |
| m(quartz powder) / m(binder) | 0.29 |
| m(superplasticizer) / m(binder) | 0.02 |
| m(water) / m(binder) | 0.21 |

### 2.3. Test methods

The slump and slump flow value were used to measure the working performance of fresh mixture, according to the Chinese Standards GB/T 50080–2016 [18]. The compressive and flexural strength of specimens at the ambient temperature according to the Chinese Standards GB/T 50081–2002 [19]. The size of the specimens is 100mm×100mm×100mm and 100mm×100mm×400mm, respectively. The elastic modulus according to the Chinese Standards GB/T 50081–2019 [20]. The specimen size is 100mm×100mm×300mm, using dial indicator and displacement sensor, and the gauge distance is 150mm. Tensile properties of UHTCC according to the Chinese Standards GB/T50081-2019. The axial deformation is measured by an electronic extensometer with a gauge distance of 50 mm, and a loading rate of 0.1mm/min.

### 3. Results and Discussion

#### 3.1. Compressive strength and flexural strength

Figure 2 shows the compressive strength of UHTCC. The compressive strength of the epoxy emulsion-added UHTCC increased with curing age, however, the compressive strength was decreased significantly comparing with the control. The water-binder ratio of the material system was increased, and the homogeneity of the system was destroyed with the introduction of the epoxy emulsion. Compared with the control at the curing age of 3days, the compressive strength of specimens with type I, type II, and type III epoxy emulsions decreased by 11.6%, 14.3%, and 16.1%, respectively. The development trend of the compressive strength had changed at the age of 7d and 28d. The compressive strength of the specimens added with type I and II epoxy emulsions was equivalent, while the compressive strength of the specimens added with type III epoxy emulsion was higher than the former two. Different types of epoxy emulsions showed different effects on the compressive strength of UHTCC. Considering the results of working performance mentioned before. The hydration of the coated particles was delayed due to the coating system formed by the epoxy emulsion and the cementitious material. The compressive strength of the specimens was reduced by the increased microscopic distance between the hydration products. However, the delayed effect of type III epoxy emulsion was decreased, which making the compressive strength of the specimens develop faster in the later stage [13].

The compressive strength of specimens showed a tendency to decrease first and then rise with the increase of the content of type III epoxy emulsion, and 4wt.% was the lowest point of the change trend. The results show that the discontinuity of the material system is larger at dosage of 4wt.% and the continuity and compressive strength of the specimens are improved after the dosage is exceeded 4wt.%.

The content of type III epoxy emulsion had a complex effect on UHTCC compressive strength. When using this type of epoxy emulsion, it is necessary to pay attention to adjusting its mass ratio and determine the appropriate content.
Figure 2. The compressive strength of UHTCC.

Figure 3. The flexural strength of UHTCC.

Figure 4. The elastic modulus of UHTCC.

Figure 2 shows the results of the flexural strength test of specimens. As expected, the flexural strength of the specimens after the addition of the epoxy emulsion showed an upward trend with the extension of curing age. However, compared with the control, the flexural strength of the epoxy emulsion-added specimens was significantly decreased, and the reduction rate of specimens using type III epoxy emulsion was the lowest among the three types of epoxy emulsion. Indicating that better organic-inorganic crosslinked and film toughening structure were formed in the specimens with introduction of type III epoxy emulsion [10, 20]. This is consistent with the analysis results of the compressive strength of specimens. The flexural strength of the single-doped type III epoxy emulsion shows a similar trend to the compressive strength. This mainly attributed to the effect of the type III epoxy emulsion on the mechanical properties of the material is relatively stable.

3.2. Elastic modulus

Elastic modulus is one of the important contents of HUTCC research, and an important parameter for structural design. The elastic modulus test results of specimens curing age up to 28 days are shown in figure 4. Compared with the reference group, the elastic modulus of the samples increased with the addition of epoxy emulsion, and the elastic modulus of the specimen with type II epoxy emulsion reached 29.6GPa. Indicating that the type II epoxy emulsion owns obvious improvement effect on the elastic modulus of the specimens at the same dosage. Combining the analysis results of the compressive and flexural strength, the strength of UHTCC was reduced by epoxy emulsion. However, the mechanism of energy absorption in specimens was increased by the formation of the organic-inorganic crosslinked structure. The special structure resulted in the increasing of loading in elastic phase, which improving the elastic modulus of specimens [7, 20].
3.3. Tensile properties

Ultimate tensile strength and ultimate tensile strain of tensile specimens curing up to 28d are shown in Figure 5 (a-b), where \( f_c \) represents the ultimate tensile strength and \( \varepsilon_c \) represents ultimate tensile strain. The ultimate tensile strength of the specimens with the addition of type I and type II epoxy emulsions basically unchanged comparing with the control. But, the ultimate tensile strength of the specimens with type III epoxy emulsion with a growth rate of 12.3%. The ultimate tensile strength of the specimen with type I epoxy emulsion was the same as that of the control, but the corresponding ultimate tensile strain had increased by 23.3%. The failure location of the two type specimens were different (as shown in Figure 6). The failure location of control and the specimens with type I epoxy emulsion were located at the horn position and central position respectively. The ultimate tensile strain of specimens with type II epoxy emulsion decreased by 6.7% comparing with control, the failure location was located at central position. The maximum tensile strain drops of the specimen added with type III epoxy emulsion was 90%, and the failure location was located at the horn position of the specimen. Indicating that type I and type II epoxy emulsion had little effect on the ultimate tensile strength, but had a significant effect on the ultimate tensile strain. The strain hardening ability of UHTCC was enhanced by type I and type II epoxy emulsion under the condition of enhancing the ultimate tensile strength, and the specimen exhibited catastrophic fracture.

The ultimate tensile strength of the specimen showed rising trend with increasing the content of the type III epoxy emulsion, and the ultimate tensile strain of the specimen exhibited the similar trend. The ultimate tensile strain of the specimen increased rapidly from 0.4% to 1.3% with the content reaching 4.0%. The ultimate tensile strain of the specimen is only 16.7% different from that of the control with the content reaching 6.0%. These analyses showed that there is a threshold for the content of type III epoxy emulsion in UHTCC. If the value was not reached threshold, the addition of the epoxy emulsion only increased the ultimate tensile strength. The tensile properties of the specimens were improved after the dosage of type III epoxy emulsion reached the threshold value.

Further observing the failure way of the specimen, it was found that there are two kinds of failure ways: multi-slot crack and single-slot crack (as shown in Figure 7). The cracks of destroyed specimens were tested and counted. The main cracks for multi-slot cracking were generally between 0.7 and 0.9 mm, the micro-cracks were between 0.06 and 0.09 mm, which mainly occurred in the central position of the specimens (as shown in Figure 6). The single-slot fracture crack was about 2 mm, which mainly occurred in the horn position of the specimens. It can also be obtained that multi-slot cracking mainly occurred during failure of UHTCC owning better tensile properties, and the location of failure is mostly in the central position of the specimens. The results had important feedback significance for adjusting the tensile properties of UHTCC.
Figure 7. Schematic diagram of multi-slot crack.

4. Conclusion

The effects of adding different types of epoxy emulsion on UHTCC performance were studied, and the following conclusions were obtained.

(1) The addition of epoxy emulsion to UHTCC caused a decrease in compressive strength and flexural strength. The introduction of epoxy emulsion enhanced the elastic modulus of UHTCC. The effect of type II epoxy emulsion was obvious, and the elastic modulus of the sample with increasing amount of type III epoxy emulsion showed a trend of decreasing first and then increasing.

(2) The addition of type I and type II epoxy emulsion in UHTCC had a relatively low variation in the ultimate tensile strength, but a significant change in ultimate tensile strain. The ultimate tensile strain of the specimen K1 reached 3.7%. Type III epoxy emulsion greatly increased the ultimate tensile strength of the specimen, while the ultimate tensile strain of the specimen decreased rapidly, and the strain hardening phenomenon disappeared. However, the strain hardening effect appeared along with further increasing the dosage of the type III epoxy emulsion in HTCC.

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