THE EFFECT OF NANO-TIO_2 ON THE DURABILITY OF ULTRA-HIGH PERFORMANCE CONCRETE WITH AND WITHOUT A FLEXURAL LOAD

GU CHUNPING*, **, WANG QIANNAN***, #LIU JINTAO*, **, SUN WEI***

*College of Civil Engineering and Architecture, Zhejiang University of Technology, Hangzhou 310023, China
**Key Laboratory of Civil Engineering Structures & Disaster Prevention and Mitigation Technology of Zhejiang Province, Zhejiang University of Technology, Hangzhou 310023, China
***Jiangsu Key Laboratory of Construction Materials, School of Materials sciences and Engineering, Southeast University, Nanjing 211189, China

#E-mail: jtliu@zjut.edu.cn

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In this study, the durability of nano-TiO_2 modified ultra-high performance concrete (UHPC) with and without a flexural load was experimentally investigated. Firstly, the mechanical properties of UHPC with various nano-TiO_2 contents were tested, and the results showed that UHPC with 1 wt. % nano-TiO_2 exhibited the best mechanical properties. Then, 1 wt. % nano-TiO_2 was added into UHPC to evaluate its effects on dry shrinkage, chloride ingress resistance, freeze-thaw resistance and carbonation resistance of UHPC. The effect of the flexural load on the durability of UHPC was also studied. The dry shrinkage of nano-TiO_2 modified UHPC was reduced compared with the control UHPC. The flexural load accelerated the chloride penetration process in the tensile region of the UHPC specimens, and the addition of nano-TiO_2 mitigated the negative influence of flexural load on the chloride ingress resistance of UHPC. Moreover, the addition of nano-TiO_2 particles also improved the freeze-thaw resistance of the flexural loaded UHPC by reducing the mass loss after enduring 800 freeze-thaw cycles. Carbonation was not detected in all UHPC specimens after being exposed to 60 % CO_2 for 180 days. Furthermore, the MIP results indicated that the addition of nano-TiO_2 refined the pore structure of the UHPC, which improved the mechanical properties and durability of the UHPC.

INTRODUCTION

Ultra-high performance concrete (UHPC) is a new type of cement-based material with a compressive strength exceeding 150 MPa [1, 2]. Due to the extremely dense microstructure, UHPC also exhibits very excellent durability, which allows for longer service life and lower life cycle cost. Hence, UHPC is considered as the potential material for future infrastructure constructions. It has been used for many applications in Europe, Asia, North America, etc. [3]. Thanks to the excellent durability, UHPC is suitable for new construction and the rehabilitation of structures in harsh environments, where durability is even more important than the mechanical properties of the UHPC. However, durability was rarely the main concern of previous studies on UHPC.

Recently, much attention was paid to the use of nanomaterials in cement-based materials to modify their performance [4]. Attempts were made to optimise UHPC with nanoparticles [5-11], such as nano-SiO_2, nano-Al_2O_3, nano-TiO_2, nano-$CaCO_3$, etc. The addition of nanoparticles in UHPC will significantly influence the early age hydration process of UHPC due to a nucleation effect [4, 6, 12-14]. Hence, the early age properties (e.g., mechanical properties and shrinkage) of the UHPC will be altered with the presence of nanoparticles. The long-term properties, i.e., durability, of the UHPC are also influenced by the nanoparticles. The addition of nano-SiO_2 could reduce the gas permeability of the UHPC by refining the microstructure of the UHPC [15]. Moreover, nano-SiO_2 was proven to be effective in reducing the corrosion rate and delaying the corrosion initiation of steel bars embedded in UHPC [9].

Compared with other nanoparticles, nano-TiO_2 is unique because of its self-cleaning and photocatalytic performance [16-18]. The use of nano-TiO_2 in cement-based materials could catalyse the degradation of NO_x in the air, helping to solve the air pollution problem. Nano-TiO_2 acts as a photocatalyst and is not consumed during the NO_x degradation reaction, so this process is long-lasting and renewable. It is an extremely economic solution for the air pollution problem. Hence, a few studies have tried to incorporate nano-TiO_2 in UHPC [18, 19], attempting to combine the advantages of nano-TiO_2 and UHPC together. The influences of nano-TiO_2 on the basic mechanical properties, electrical properties and microstructure of UHPC had been investigated primarily. Su *et al*. found that the addition of 2 wt. % nano-TiO_2

improved the compressive and flexural strength of UHPC without fibres by around 5 % and 20 % respectively [19]. When UHPC was fibre reinforced, the addition of nano-TiO_2 only made very small difference on the compressive and flexural strength of UHPC. The efficiency of the fibre reinforcement was the key factor which influenced the mechanical properties of the fibre reinforced UHPC. The study of Li *et al*. showed that the presence of nano-TiO_2 refined the pore structure of UHPC, and restricted the size of $Ca(OH)_2$ in UHPC, hence the compressive and flexural strength of UHPC with 2.32 vol. % TiO_2 improved by 18.05 % and 47.07 %, respectively [18]. In addition, nano-TiO_2 improved the electrical conductivity property of UHPC. When the content of nano-TiO_2 is 3.88 vol. %, the electrical resistivity of UHPC deceased by 13.61 % [18].

Apart from the mechanical and electrical properties, the long-term properties of nano-TiO_2 modified UHPC is also very important for its further applications in harsh environments. However, related studies have not been conducted yet. Hence, this paper is aimed at studying the mechanical properties, dry shrinkage and durability of UHPC modified with nano-TiO_2 particles. The effect of flexural load, which is very common in reality, on the durability of nano-TiO_2 modified UHPC was also addressed in the paper. Mercury intrusion porosimetry (MIP) tests were performed to investigate the pore structure of nano-TiO_2 modified UHPC.

EXPERIMENTAL

Raw materials and mix proportion

Portland cement (P·II 52.5R), fly ash (FA) and silica fume (SF) were used for the UHPC preparation. FA was a substitute for part of the cement and could improve the workability of the UHPC. Natural sand was used as the aggregate, and the size was smaller than 2.36 mm. A polycarboxylic superplasticiser was employed to modify the workability of the UHPC. Steel fibres were copper coated, and the diameter and length were 0.2 mm and 13 mm, respectively. The nano-TiO_2 particles were in the anatase phase. The average diameter of the nano-TiO_2 particles was 20 nm, and the specific surface area were 160 $m^2 \cdot g^{-1}$.

The mix proportions of UHPCs are shown in Table 1. In order to make the comparison clearer, the proportions were given in a percentage form. Six UHPC mixtures with different amounts of nano-TiO_2 particles were prepared for the mechanical tests. The sum of the binders (Cement + FA + SF) were set to be 1.0. The volume fraction of the steel fibres was 2 %. The water to binder (w/b) ratio was controlled to be 0.16, and the total binder content was about 960 $kg \cdot m^{-3}$ for all the mixtures. The experimental data for UHPC-T0 in the paper was cited from our previous studies [20, 21], in which the same materials and experiment programme were adopted.

Preparation of the specimens

The superplasticiser was mixed with water first, then the nano-TiO_2 particles were ultrasonically dispersed in the mixed solution for 15 min, forming a nano-TiO_2 suspension. The cement, FA, SF, sand and fibres were mixed in a cement mortar mixer for 2 min at a low speed. Then the nano-TiO_2 suspension were added in the mixer, and mixed at a low speed for another 1 min and then at a high speed for 5 min. The fresh UHPC mixtures were cast in steel moulds with a size of 40 × 40 × 160 mm. The specimens were demoulded after 1 day and placed in a standard curing (20°C, RH > 95 %) room for 90 days.

Mechanical tests

The mechanical tests, including compressive and flexural strength tests, were carried out according to the Chinese standard GB/T17671-1999. The flexural tests were performed on 40 × 40 × 160 mm specimens with three-point bending. Two portions of the specimen broken in the flexural tests acted as samples for the compressive strength tests.

Dry shrinkage

The dry shrinkage tests were performed following the Chinese standard GB/T 50082-2009. The size of the specimens was also 40 × 40 × 160 mm. After standard curing for 3 days, the specimens were placed in a room, in which the temperature and the humidity were controlled at 20 ± 2 °C and 60 ± 5 %, respectively. The specimens' length variation was measured at different ages (3, 7, 14, 28, 45, 60, 90, 120, 150 and 180 days) with dial gauges.

Table 1. Mix proportion of UHPCs.

Mix No.	Cement	FA	SF	Sand	Superplasticiser	w/b	Fibre (vol. %)	Nano-TiO_2
UHPC-T0	0.5	0.4	0.1	1.2	3.5%	0.16	2	0
UHPC-T0.5	0.5	0.4	0.1	1.2	3.5%	0.16	2	0.5 %
UHPC-T1	0.5	0.4	0.1	1.2	3.5%	0.16	2	1 %
UHPC-T2	0.5	0.4	0.1	1.2	3.5%	0.16	2	2 %
UHPC-T3	0.5	0.4	0.1	1.2	3.5%	0.16	2	3 %
UHPC-T5	0.5	0.4	0.1	1.2	3.5%	0.16	2	5 %

Chloride diffusion test

The chloride diffusion tests were performed based on NT Build 443-94. After 90 days standard curing, the specimens were water saturated and coated with epoxy resin, leaving one surface exposed. After that, the UHPC specimens were immersed in a 10 wt. % NaCl solution for 90 days. After immersion, the specimens were dried, and powder samples were collected from the exposed surface at different depths by drilling. The free chloride contents at different depths were determined by titration [22].

Freeze-thaw test

The freeze-thaw tests were conducted following the Chinese standard GB/T 50082-2009. The cured specimens were also saturated and placed in a freeze-thaw box, in which the temperature ranged from -20°C to 20°C. One freeze-thaw cycle lasted for about 4 hours. The relative dynamic elastic modulus and mass loss of the specimens were measured every 25 cycles.

Carbonation test

The carbonation tests were carried out according to the Chinese standard GB/T 50082-2009. Specimens were taken out of the curing room 2 days before the curing was finished, then the specimens were oven dried at 60°C for 2 days. The surfaces of the dried specimens were coated with wax, leaving one surface exposed. Then, the specimens were placed into a carbonation box, in which the temperature, humidity and CO_2 concentration were controlled at 20 ± 5°C, 70 ± 5 %, and 60 ± 3 %, respectively. The CO_2 concentration used in this study was three times higher than that regulated in the standard, so as to accelerate the carbonation process.

The loading strategy

The durability of the flexural loaded UHPC specimens was also investigated in the study. The loading device is demonstrated in Figure 1. The same type of loading device has been adopted in several studies relating to the durability of flexural loaded concrete specimens [23, 24]. The applied load was set to be 50 % of the ultimate flexural load of the UHPCs in this study. In the durability tests, both the compressive and tensile surfaces of the specimens were exposed to chlorides and CO_2, so that the effects of compressive and tensile stress on the chlorides and CO_2 resistance of UHPC specimens can be revealed.

MIP

MIP was applied to investigate the porosities and pore size distribution of the UHPC specimens. The matrix of the UHPC specimens were used as samples. Before the tests, the hydration of the samples was stopped by immersion in acetone, then the samples were oven dried for 3 days. The pore sizes that could be detected were between of 3 nm and 360 μm.

RESULTS AND DISCUSSION

Mechanical properties of UHPC

The mechanical properties of UHPCs containing nano-TiO_2 were investigated. The 90-day compressive and flexural strengths of the UHPC specimens are shown Figure 2. Both the compressive and flexural strengths of the UHPC were improved when the nano-TiO_2 content was lower than 1 wt. %. The improvement was attributed to the nucleation effect and the filling effect of the nano-TiO_2 particles [12, 26]. The addition of nanoparticles could promote cement hydration in cementitious materials, which is favourable for the strength improvement of cementitious materials [27, 28]. In addition, the nano-TiO_2 particles could fill in the nano-size pores in UHPC, and further improve the mechanical properties of the UHPC. When the nano-TiO_2 content was higher than 1 wt. %, the mechanical properties of the UHPC deceased. This may result from the relatively poor dispersion of nano-TiO_2 particles when more nanoparticles were added. The agglomerations of nano-TiO_2 particles acted as weak zones in UHPC.

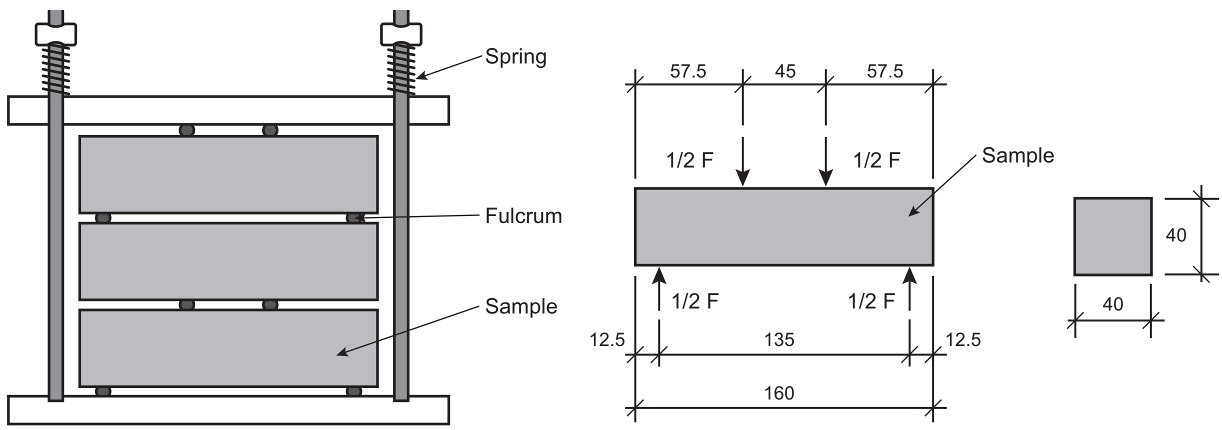


Figure 1. Illustration of the loading device (unit: mm) [25].

As the same as the other nanoparticles, the addition of the nano-TiO_2 particles also accelerated the mechanical properties development of the UHPC at the early ages. The comparison of the mechanical properties of UHPC-T0 and UHPC-T1 is shown in Figure 3 and Figure 4. The 1-day and 3-day compressive and flexural strength of UHPC-T1 were much higher than that of UHPC-T0. The presence of nanoparticles provided much more nucleation sites for the products of hydration reaction, hence it accelerated the hydration process of the UHPC at the early age.

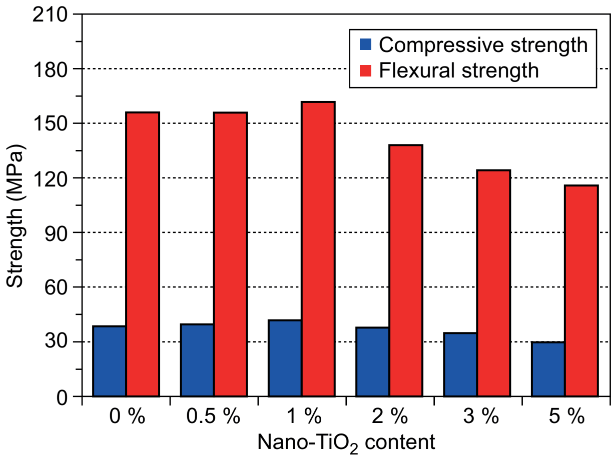


Figure 2. The effect of nano-TiO_2 content on the compressive and flexural strength of the UHPCs.

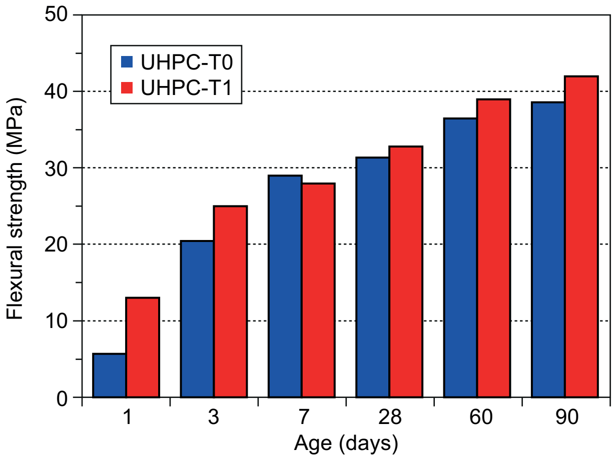


Figure 3. Effect of nano-TiO_2 particles on the development of the flexural strength of the UHPC.

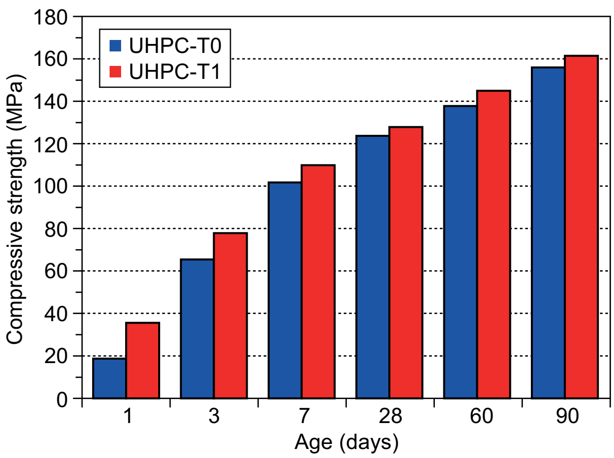


Figure 4. Effect of nano-TiO_2 particles on the development of the compressive strength of the UHPC.

Dry shrinkage

Considering UHPC with 1 wt. % TiO_2 exhibited the best mechanical properties, the dry shrinkage and durability tests were only performed on the control UHPC (UHPC-T0) and UHPC with 1 wt. % TiO_2 (UHPC-T1). During the hardening process, the shrinkage of the UHPC actually includes dry shrinkage, autogenous shrinkage and chemical shrinkage. Hence, the measured dry shrinkage was actually the total shrinkage of the UHPC. But it should be noted that the shrinkage measurements began at 3 days after casting, so the dry shrinkage was predominant during the test period. The shrinkage of UHPC-T0 and UHPC-T1 is shown in Figure 5. It can be seen that the 180-day dry shrinkage of UHPCs was in the range of 500 × 10^{-6} – 600 × 10^{-6}, which was close to that of normal concrete. The addition of nano-TiO_2 particles lowered the shrinkage of the UHPC. The addition of nanoparticles could accelerate the hydration process at an early age, so the hydration degree of UHPC-T1 would be higher than UHPC-T0 at 3 days, and the microstructure of UHPC-T1 would be denser, which inhibited the water release from the UHPC. Correspondingly, the dry shrinkage of UHPC-T1 was lower than that of UHPC-T0. The lower shrinkage could reduce the tensile stress development and cracking potential in the UHPC structures.

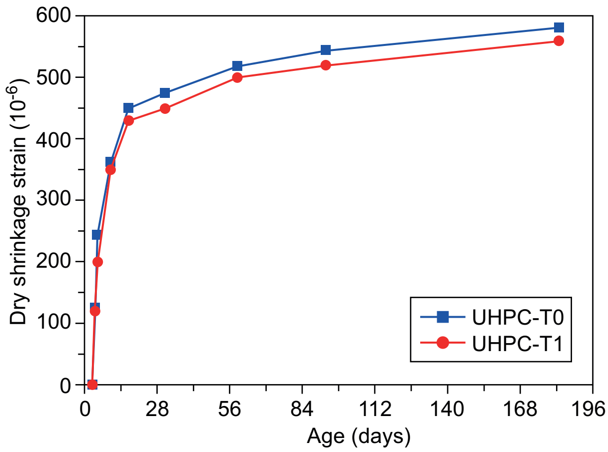


Figure 5. Effect of nano-TiO_2 particles on the dry shrinkage of the UHPC.

Chloride ingress resistance of the UHPC

In chloride environments, the service life of the UHPC structures is largely determined by its chloride ingress resistance. After 90 days immersion, the chloride profiles in UHPCs with and without a flexural load are shown in Figure 6. The values in the figure represent the average chloride concentration at different depths. It can be seen that, after 90 days immersion, the chloride diffusion depth in all UHPC specimens were less than 5 mm. When the UHPC specimens were non-loaded, the chloride concentrations of UHPC-T0 and UHPC-T1 specimens at a depth of 0-5 mm were almost the same. Under a flexural load, the chloride concentration in the tensile region of the UHPC specimens increased, while the chloride concentration in the compressive region decreased. This implied that the tensile stress negatively influenced the chloride ingress resistance of the UHPC. The tensile stress could induce damage, i.e., microcracks, into the UHPC, hence accelerating the chloride penetration process in the tensile region of the UHPC specimens.

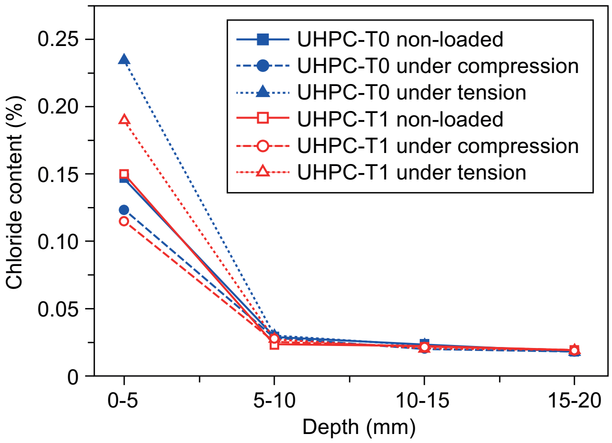


Figure 6. Chloride profiles in UHPC-T0 and UHPC-T1 under a flexural load after 90 days immersion.

Compared with the control UHPC, the addition of nano-TiO_2 particles reduced the chloride concentration in the tensile region of UHPC specimens. The negative influence of the tensile stress on the chloride ingress resistance of the nano-TiO_2 modified UHPC was less significant than that of the control UHPC. This was due to the fact that nano-TiO_2 could improve the toughness of the concrete. Li *et al*. stated that the toughness improvement of the nano-TiO_2 modified UHPC resulted from two reasons [18]. One is the nucleation effect of the nanoparticles, which enhanced the compactness of the matrix; the other is the nano-core effect [29]. Because of the high specific surface area and surface energy, the hydration products will deposit on the nano-fillers. Hence the nanoparticles could act as nano-cores, which could lead to crack deflection, thus inhibiting crack expansion to achieve the toughening effect [30]. The damage caused by the flexural load in the tensile region of the nano-TiO_2 modified UHPC would be more minor than that in the control UHPC. Consequently, the chloride concentration in the tensile region of the nano-TiO_2 modified UHPC was relatively lower. It can be anticipated that the nano-TiO_2 modified UHPC structures may have a longer service life in chloride environments.

Freeze-thaw resistance of the UHPC

The freeze-thaw resistance of UHPC is the key property that influences the serviceability of UHPC structures in cold regions. The influences of the flexural load on the mass loss and the relative dynamic elastic modulus of UHPC-T0 and UHPC-T1 subjected to freeze-thaw action are shown in Figure 7 and Figure 8, respectively. The mass loss was lower than 0.5 % and the relative dynamic elastic modulus was higher than 96 % for all non-loaded UHPC specimens after enduring 800 freeze-thaw cycles. Compared with non-loaded UHPCs, the loaded UHPCs have higher mass losses and lower relative dynamic elastic modulus after the freeze-thaw tests. The flexural load reduced the freeze-thaw resistance of the UHPC. The addition of nano-TiO_2 particles did not show any obvious influence on the freeze-thaw resistance of the UHPC. When non-loaded, UHPC-T0 and UHPC-T1 almost had the same mass loss

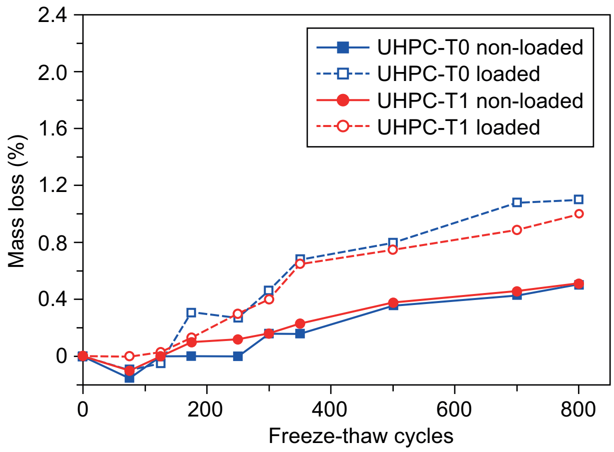


Figure 7. Mass loss of UHPC-T0 and UHPC-T1.

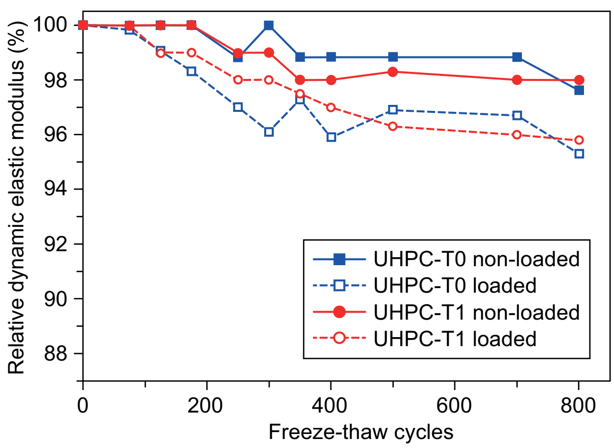


Figure 8. Relative dynamic elastic modulus of UHPC-T0 and UHPC-T1.

after 800 freeze-thaw cycles. When the UHPC specimens were flexural loaded, the mass loss of UHPC-T1 was a little lower than that of UHPC-T0. Whether loaded or not, the relative dynamic elastic modulus of UHPC-T0 and UHPC-T1 were almost the same. So generally, the addition of nano-TiO_2 particles slightly improved the freeze-thaw resistance of flexural loaded UHPC by reducing the mass loss under the freeze-thaw action.

It can be noticed that the UHPC only degraded a little after enduring 800 freeze-thaw cycles. Normally, concrete with a moderate compressive strength will fail within 300 freeze-thaw cycles, and the hydraulic pressure and osmotic pressure are considered to be the causes for the freeze-thaw damage of normal concrete. But for UHPC, because of the refined pore structure, the freeze point of water in pores of UHPC may lower than -20°C, which means the water did not freeze during the freeze-thaw tests. Hence, the hydraulic pressure and osmotic pressure would not be aroused. It was considered that the mismatch of the thermal expansion coefficients of the aggregate and the matrix is the cause of the freeze-thaw damage in the UHPC [20]. According to Sellevold and Bjøntegaard, the thermal expansion coefficient of cement paste is dependent on the internal relative humidity [31, 32]. Although the addition of nano-TiO_2 particles accelerated the early age hydration of the UHPC, the internal relative humidity in the UHPC at late ages will not be significantly influenced by the nano-TiO_2 particles, as well as the thermal expansion coefficient of UHPC matrix. Thus, the freeze-thaw resistance of UHPC-T0 and UHPC-T1 did not show much difference. However, if the UHPC were suffering from more freeze-thaw cycles and more microcracks were generated, it would be expected that the nano-core and toughening effects of the nano-TiO_2 particles might take effect and inhibit the propagation of the micro-cracks, resulting in the improved freeze-thaw resistance of the UHPC.

Carbonation of the UHPC

All the UHPC specimens were placed in the carbonation box for 6 months. However, carbonation was not detected in any of the UHPC specimens, including the flexural loaded UHPC specimens. The microstructure of the UHPC is extremely dense, hence it is very difficult for CO_2 to penetrate into the UHPC. In other words, carbonation would not act as the main cause for the degradation of the reinforced UHPC structures.

MIP results

The pore size distributions of the 90 days standard cured UHPC-T0 and UHPC-T1 samples are shown in Figure 9. It can be seen that most of the pores in the UHPC were smaller than 10 nm, and the total porosities of the UHPC-T0 and UHPC-T1 samples were 1.85 % and 1.66 %, respectively. The low porosity and small pore size are the reasons for the excellent mechanical properties and durability of the UHPC. Compared with UHPC-T0, the porosity of the UHPC-T1 sample was lower and the most probable pore size was even smaller. Due to the nucleation and filling effect, the addition of nano-TiO_2 particles refined the pore structure of the UHPC. This is also one of the reasons for the improved mechanical properties and chloride ingress resistance of the nano-TiO_2 modified UHPC.

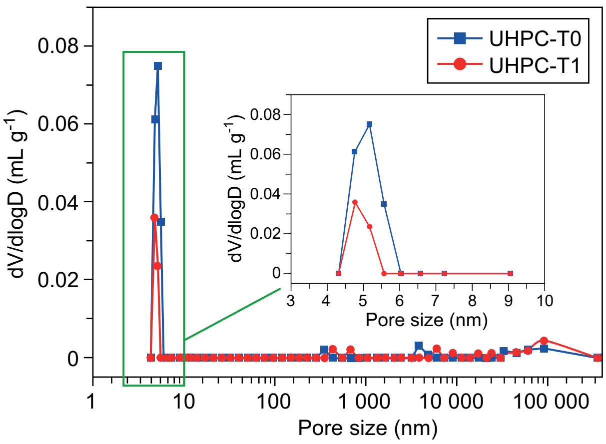


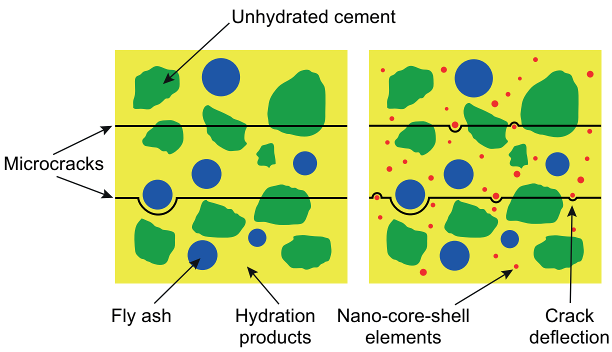
Figure 9. Pore size distribution of the UHPC-T0 and UHPC-T1 samples with 90 days standard curing.

DISCUSSION

Because of the excellent mechanical properties and durability, the applications of UHPC are promising in civil structure construction. The addition of nano-TiO_2 could endue the UHPC with the self-cleaning and photocatalytic performances, making UHPC even more sustainable. The results of this study showed that the addition of 1 wt. % nano-TiO_2 particles did not show much influence on the long-term durability of the non-loaded UHPC; Moreover, when the flexural load was applied, the nano-TiO_2 particles improved the durability of the UHPC to some extent.

As the same as the other nanoparticles, the nano-TiO_2 particles refined the pore structure of the UHPC because of the filling effect and the nucleation effect [33, 34]. For normal concrete, the nanoparticles and the surrounded hydration products could fill in the space between the cement particles and reduce the capillary porosity of concrete. However, for UHPC, because of the dense particle packing, capillary pores hardly existed [2, 3]. Hence, the addition of nanoparticles mainly makes the hydration products denser, which improves the mechanical properties and aggressive agents (i.e., chloride and CO_2) resistance of UHPC. Because of the dense microstructure of the UHPC, the presented experiment programme has not totally revealed the influence of the nano-TiO_2 particles on the durability of the UHPC when the flexural load was not exerted. But for UHPC under a flexural load, the effect of the nano-TiO_2 particles on the durability of flexural loaded UHPC was identified in the presented study, especially for the chloride ingress resistance of the UHPC.

Under the flexural load, microcracks occurred in the tensile side of the UHPC specimens, so that the chloride contents in the tensile region were higher and the freeze-thaw resistance of the flexural loaded UHPC was reduced. Based on the experimental results of the chloride diffusion tests, it can be inferred that the characteristics of the microcracks in the control and nano-TiO_2 modified UHPCs were different from each other. As discussed in Section 3.3, the nano-core effect of the nanoparticles was considered as the underlying mechanism for the difference [29, 30]. As shown in Figure 10a, the cracks generated by the load would go straight through the paste of the control UHPC due to its high brittleness, and if the FA particles exist in the paste, the crack would go around the FA particles, as the FA particles are spherically shaped and are of high strength. As for the nano-TiO_2 modified UHPC, the nano-core-shell elements, which are nano-TiO_2 particles surrounded by hydration products, are uniformly distributed in the nano-TiO_2 modified UHPC paste. They could also deflect the cracks, resulting in more torturous cracks [30], as shown in Figure 10b. The crack deflection process could absorb more energy, and then the crack propagation could be inhibited. Generally, the toughness of the UHPC was improved by the incorporation of the nano-TiO_2 particles. Hence, under a flexural load, the nano-TiO_2 modified UHPC showed better chloride ingress resistance in the tensile region.



a) Control UHPC b) Nano-TiO_2 modified UHPC

Figure 10. Nano-core effect of nano-TiO_2 particles in the UHPC.

CONCLUSIONS

The mechanical properties, dry shrinkage, durability and pore structure of nano-TiO_2 modified UHPC were studied in the paper. Based on the presented results, the following conclusions can be drawn.

- The compressive and flexural strength of the UHPC were improved when the nano-TiO_2 content was no more than 1 wt. %. However, the compressive and flexural strength of the UHPC deceased with the excessive addition of nanoparticles. The dry shrinkage of the nano-TiO_2 (1 wt. %) modified UHPC was a little lower than the control UHPC, which is a benefit for the cracking control of the UHPC structures.
- After immersion in 10 wt. % NaCl solution for 90 days, the chloride penetration depth in the UHPC was lower than 5 mm. The flexural load accelerated the chloride penetration process in the tensile region of the UHPC specimens. The chloride concentration in the tensile region of the nano-TiO_2 modified UHPC was lower than that of the control UHPC. The addition of 1 wt. % nano-TiO_2 particles helped to mitigate the adverse influence of the flexural load on the chloride ingress resistance of the UHPC.
- The control and nano-TiO_2 modified UHPCs both had excellent freeze-thaw resistance. The flexural load accelerated the damage process in the UHPC under the freeze-thaw action, while the addition of 1 wt. % nano-TiO_2 particles slightly improved the freeze-thaw resistance of the UHPC within 800 freeze-thaw cycles.
- Carbonation cannot be detected in the UHPC specimens after 180 days exposure to 60 % CO_2. Long-lasting tests are needed for further investigation.
- The addition of 1 wt. % nano-TiO_2 particles refined the pore structure of the UHPC. Compared to the control UHPC, the porosity of the nano-TiO_2 modified UHPC was reduced, and the most probable size became finer.

Acknowledgement

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