

Research Article

Effect of TiO₂ Nanoparticles on Physical and Mechanical Properties of Cement at Low Temperatures

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Low temperature negatively affects the engineering performance of cementitious materials and hinders the construction productivity. Previous studies have already demonstrated that TiO₂ nanoparticles can accelerate cement hydration and enhance the strength development of cementitious materials at room temperature. However, the performance of cementitious materials containing TiO₂ nanoparticles at low temperatures is still unknown. In this study, specimens were prepared through the replacement of cement with 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% TiO₂ nanoparticles and cured under temperatures of 0°C, 5°C, 10°C, and 20°C for specific ages. Physical and mechanical properties of the specimens were evaluated through the setting time test, compressive strength test, flexural strength test, hydration degree test, mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) analysis, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM) in order to examine the performance of cementitious materials with and without TiO₂ nanoparticles at various curing temperatures. It was found that low temperature delayed the process of cement hydration while TiO₂ nanoparticles had a positive effect on accelerating the cement hydration and reducing the setting time in terms of the results of the setting time test, hydration degree test, and strength test, and the specimen with the addition of 2 wt.% TiO₂ nanoparticles showed the superior performance. Refined pore structure in the MIP tests, more mass loss of CH in TGA, intense peak appearance associated with the hydration products in XRD analysis, and denser microstructure in SEM demonstrated that the specimen with 2 wt.% TiO₂ nanoparticles exhibited preferable physical and mechanical properties compared with that without TiO₂ nanoparticles under various curing temperatures.

1. Introduction

Pavement structures, owing to their nature of closely contacted with the environment, are highly influenced by environmental factors such as low temperatures in cold regions, specifically. Cement, as one of the most widely used pavement materials, is widely used in pavement engineering because of its low price and easy availability. However, previous studies have demonstrated that low temperature prolongs the setting time of cement and reduces the strength of cement, resulting in lower construction productivity in cold regions [1].

To minimize these negative impacts associated with low temperature, accelerators of cement hydration are used as additives in concrete to reduce the setting time and enhance the strength development [2]. Commonly, chloride salts are the most widely used and cost-effective accelerators [3].

However, in some areas which suffered from chemical attacks such as chloride-induced corrosion, addition of these chloride accelerators should be avoided to reduce the occurrence of corrosion of steel reinforcement and strength loss of concrete. Hence, numerous studies have been carried out to develop nonchloride accelerator instead to remove the possibility of corrosion, especially in aggressive environments. Calcium nitrate [4, 5], aluminate [6], and lithium salts [7] can change the setting time and strength of cement through their chemical properties. In addition, limestone powder [1, 8] and silica fume [9] can be used as physical accelerators to modify the cement at low temperatures.

Nanoparticles, owing to its ultrafine size and high surface area to volume ratio, can accelerate the cement hydration process and enable the formation of a denser microstructure, thereby improving the durability and mechanical properties

of cementitious materials [10, 11]. Therefore, nanoparticles could be considered as an alternative choice to serve as accelerators for cementitious materials under low temperatures. Numerous studies have been conducted on the utilization of nanoparticles, including nano-SiO₂ [12–22], nano-CaCO₃ [17, 23, 24], nano-Al₂O₃ [16, 20, 25], nano-TiO₂ [14, 16, 26–38], nano-Fe₂O₃ [10, 13], and nano-CuO [13, 39], in cementitious materials to improve their durability and mechanical properties. Nano-SiO₂ is the most commonly used nanoparticle, while nano-TiO₂ is comparatively favorable for pavement structures in terms of air-cleaning property. With respect to TiO₂ nanoparticles, the study by Nazari et al. showed that partial replacement of cement with TiO₂ nanoparticles reduced the setting time, enhanced the hydration process, and increased the flexural strength of concrete at the temperature of 20°C, while the flexural strength reduced when the content of TiO₂ nanoparticles was more than 4% [26–29]. Lee et al. reported that, through the addition of TiO₂ nanoparticles, the early-age hydration of cement was accelerated, the setting time was reduced, and the compressive strength was increased at 23 ± 2°C [31, 32]. Pimenta Teixeira et al. indicated that high temperature (40°C and 60°C) facilitated the hydration of cement paste containing TiO₂ nanoparticles and improved the early-age compressive strength [34]. Mohseni et al. found that the incorporation of TiO₂ nanoparticles enhanced the compressive strength of self-compacting mortar at ambient temperature and with the increase in the content of TiO₂, the compressive strength also exhibited an upward trend [16]. However, Zhang et al. examined that, at 20 ± 3°C, the compressive strength and flexural strength of concrete decreased with the increasing dosage of TiO₂ nanoparticles [33]. Feng et al. discovered that, at room temperature, the microstructure of cement paste became denser with the incorporation of TiO₂ nanoparticles and a new type of hydration product was examined [30]. In addition, due to photocatalytic action of TiO₂ nanoparticles, these particles are commonly mixed into construction materials to obtain the property of air cleaning [36–38].

Most of these studies were carried out under ambient temperature, and very few studies have investigated the influence of SiO₂ nanoparticles and Al₂O₃ nanoparticles on properties of cementitious materials under low temperatures [18–20]. The effect of TiO₂ nanoparticles on the performance of cementitious materials under low temperatures was still undiscovered, and whether TiO₂ nanoparticles still possess its characteristics under low temperatures was still unknown. Better understanding the knowledge of nanoparticles under low temperatures can promote the practical application of nanoparticles in cold regions. The aim of the current study was to evaluate the effect of TiO₂ nanoparticles on the physical and mechanical properties of cement under low temperatures, and low temperatures of 0°C, 5°C, and 10°C were selected in this paper with the ambient temperature 20°C as a reference temperature. Furthermore, the influences of TiO₂ on the pore size distribution, microstructure, and thermal property were studied when the specimens were cured under varying temperatures at specific ages.

2. Materials and Tests

2.1. Materials and Specimen Proportions. Raw materials used in this study include cement, TiO₂ nanoparticles, and natural river sand. Type I ordinary Portland cement (P.O) 42.5 conforming to ASTM C150 specification [40] and TiO₂ nanoparticles with the average particle size of 15 nm were used. The chemical and physical properties of cement and TiO₂ nanoparticles, provided by the suppliers, are listed in Table 1 and Table 2, respectively. The particle size distribution of the sand used was 0.63–1.25 mm, 0.315–0.63 mm, and 0.16–0.315 mm, with a sand grading of 2:4:2. Polycarboxylic-type water-reducing agent complied with ASTM C494-type F [41] was used to keep a favorable workability.

In this study, the laboratory experiments were accomplished in two steps. In the first step, effects of TiO₂ nanoparticles of different dosages of 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% on the physical and mechanical properties of the specimens cured under temperatures of 0°C, 5°C, 10°C, and 20°C were evaluated. The optimum dosage of TiO₂ nanoparticles that exhibited the superior performance in terms of strength, setting time, and hydration degree was selected as a representative to investigate the reason why TiO₂ nanoparticles could accelerate cement hydration. In the second step, the influence of optimum TiO₂ nanoparticles on the pore structure, hydration products, and microstructure of cement pastes under different curing temperatures was studied.

Cement mortar specimens were prepared for the test of mechanical strength. Mortar specimens included the ordinary mortar specimen without TiO₂ nanoparticles and mortar specimens with the cement replacement of 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% TiO₂ nanoparticles, respectively. 50 × 50 × 50 mm cube specimens for the compressive strength test and 40 × 40 × 160 mm prism specimens for the flexural strength test were prepared.

TiO₂ nanoparticles were uniformly dispersed in 30% of water using ultrasonication firstly. Then, cement and sand were mixed together for about 1 minute, and after that, the well-dispersed TiO₂ nanoparticles were added and mixed for another 1 minute before the rest of the water was added. Mortar was then placed into molds and cured under temperatures of 0°C, 5°C, 10°C, and 20°C with a constant relative humidity of 95% until testing. The water to binder ratio of specimens was 0.5. With regard to the control of curing temperature, automated control chambers with an adjustable temperature range of 0–50°C were employed in the tests. It should be emphasized that the raw materials and molds used were precooled first in order to achieve the temperatures close to the target curing temperature after the mixing process.

In addition, cement paste specimens with the same water to binder ratio of mortar specimens were also prepared and cured under the same curing conditions, and the small pieces cut from the 50 × 50 × 50 mm cube paste specimen were used in the tests of hydration degree, MIP, TGA, XRD, and SEM analysis.

It should be noted that the test process was carried out at room temperature. When the specimens reached the testing

TABLE 1: Chemical and physical properties of ordinary Portland cement.

Chemical composition	Content (%)
CaO	59.48
SiO ₂	18.73
Al ₂ O ₃	5.12
Fe ₂ O ₃	3.45
MgO	4.02
SO ₃	2.83
LOI	2.51
Specific gravity(g/cm ³)	3.15
Specific surface area (m ² /g)	0.39

TABLE 2: Properties of TiO₂ nanoparticles.

	Diameter (nm)	Surface volume ratio (m ² /g)	Purity (%)
TiO ₂	10–25	200	99.8

age, they were taken out of the temperature-controlled curing chambers for testing, and the test process was completed within 30 minutes.

2.2. Physical and Mechanical Property Tests. Initial and final setting times of ordinary cement pastes and cement pastes with different additions of TiO₂ nanoparticles were measured in accordance with ASTM C191 [42] with a manually operated Vicat needle apparatus under varying curing temperatures. The initial setting time was determined as the time between the initial contact of cement and water and the time when the penetration depth was measured to be 25 mm, and the final setting time was calculated as the time between initial contact of cement and water and the time when the needle did not leave a complete circular impression on the surface. Repeated penetration tests were conducted on paste specimens by allowing the Vicat needle to penetrate into the paste. Cement paste used for this test should be prepared to satisfy a standard normal consistency according to ASTM C187 [43], and the cement paste should be of standard consistency when the measuring needle settles to a point 10 ± 1 mm below the original surface within 30 s after being released. Fresh cement pastes with various amounts of water were made until the standard consistency was achieved.

The compressive strength test was conducted on ordinary cement mortars and cement mortars containing different additions of TiO₂ nanoparticles according to ASTM C109 [44] by operating a hydraulic testing machine under a controlled rate of 1350 N/s, and flexural strength was determined in accordance with ASTM C293 [45]. These tests were carried out, respectively, at 3, 7, 28, and 56 days of curing under curing temperatures of 0°C, 5°C, 10°C, and 20°C, and the strength was determined by the average value of triplicate specimens.

To evaluate the hydration process of ordinary cement pastes and cement pastes with various TiO₂ nanoparticles under different curing temperatures, the nonevaporable

water chemically bounded in hydration products was calculated to determine the degree of cement hydration at 3, 7, 28, and 56 days of curing [12, 15]. A piece of cement paste was chosen and grinded into powder, and then, 2 g of this powder was dried at 105°C for 3 h until a constant weight was achieved; after that, the powder was ignited at 1000°C for 3 h, and then, the degree of hydration at a certain age can be calculated as the ratio of the non-evaporable water for paste cured at that age to the non-evaporable water for paste fully hydrated, as indicated in the following equation:

$$\alpha = \frac{m_{105} - m_{1000}}{0.25 \cdot m_{105}}, \quad (1)$$

where α is the hydration degree at a certain curing age, m_{105} and m_{1000} are the masses of the specimens after drying at 105°C and then heating at 1000°C, respectively, and $0.25m_{105}$ is considered as the amount of chemically bounded water for a fully hydrated cement paste.

2.3. MIP. In order to observe the influence of low temperature on the pore structure of cement pastes in the hydration process, based on the results of physical and mechanical tests already conducted in this study, the ordinary cement paste and cement paste containing the optimum dosage of TiO₂ nanoparticles were selected to measure the pore size distribution with mercury intrusion porosimetry (MIP) referring to ISO 15901-1 [46]. After 28 days of curing under different temperatures, cement paste specimens were broken into small square fragments with an approximate size of $5 \times 5 \times 5$ mm with the knife, and hardened cement slurry pieces chosen from the middle of the specimen were employed to measure the pore size distribution in order to ensure accuracy. The hardened cement slurry pieces should be soaked in ethanol to stop hydration. After soaking in ethanol for 24 h, the pieces were taken out from ethanol to fully evaporate the ethanol and dried at 105°C for 3 h in an oven to remove the water from the pores and ensure a stable weight before the mercury test. The pore pressure was in a range from 0.2 to 220 MPa, the density of mercury was 13.5335 g/mL, the angle of contact was 130°, and the surface tension was 0.485 N/m.

2.4. Thermal Gravimetric Analysis (TGA). The mass variation of a material exposed to steadily growing heating temperature can be obtained using thermogravimetric analysis. Because the decomposition temperatures of different constituents in a material are different, the content of the corresponding constituents can therefore be determined. In this study, to quantify the CH content of the ordinary cement paste and cement paste modified with optimum dosage of TiO₂ nanoparticles under different curing temperatures, corresponding specimens at 28 days of age were grinded into powder and 2 g of powder was heated with the temperature rising from 20°C to 1000°C at a rate of 10°C/min under a nitrogen environment.

2.5. X-Ray Diffraction (XRD). X-ray diffraction can be utilized to identify the main mineral phases of the cementitious material during hydration. The phases of ordinary cement paste and cement paste with optimum dosage of TiO₂ nanoparticles under varying curing temperatures were analyzed at 28 days of age. The XRD test was conducted to scan the specimens between 5° and 90° (2θ) with a step of 0.02° (2θ) using Cu Kα radiation, at a scan rate of 1° per minute.

2.6. SEM. Microstructural images of ordinary cement paste and cement paste containing the optimum dosage of TiO₂ nanoparticles under various curing temperatures were acquired at 28 days of age by scanning electron microscopy (SEM). After 28 days, the specimen was broken into pieces and the middle part was used in this test. This part was immersed into ethanol to stop hydration, and then, it was dried and sprayed with gold to be conductive prior to SEM testing.

3. Results and Discussion

3.1. Physical and Mechanical Properties

3.1.1. The Setting Times. The initial and final setting times of ordinary cement paste and pastes with different proportions of TiO₂ nanoparticles at various curing temperatures are shown in Figure 1. It is examined from the results that both the initial setting time and the final setting time were extended as the curing temperature reduced. The setting times of cement pastes cured at 0°C were notably longer than those cured at ambient temperature regardless of the content of TiO₂ nanoparticles. With the increase in the curing temperature, the setting time showed an obvious downward trend. The initial setting time of pastes cured at 0°C was three times longer than that of pastes cured at 5°C, nearly five times in comparison with that of pastes cured at 20°C, while pastes cured at 10°C had the initial setting time 9–20% longer compared to that cured at 20°C, almost the same. Similar trends were observed in the final setting time. This is because low temperature restrains the pace of the cement hydration and cement pastes require much longer time to set especially at 0°C. Although the hydration process is demonstrated to proceed at a slower rate in previous study [1, 8], low temperature still has a significant impact on the dissolution of clinkers and their reaction with water, resulting in delay in setting time.

Another phenomenon can also be noticed that, with the increasing content of TiO₂ nanoparticles, the setting time of cement pastes was shortened steadily despite the variation in curing temperature. This is due to the fact that, in addition to the filler effect, nanoparticles itself can act as activator to promote the hydration of cement due to its high activity. TiO₂ nanoparticles, despite chemically inert with cement constituents, can provide extra space for hydrated products to precipitation due to its large surface area to volume ratio, thereby accelerating the cement hydration and shortening the setting time.

3.1.2. Degree of Hydration. Hydration degree of ordinary cement paste and pastes with varying addition of TiO₂ nanoparticles determined by chemically bounded water at different curing temperatures is shown in Figure 2. From the results, it can be seen that the hydration degree of cement was improved with the increase in the curing age because the hydration products could be produced with time growing. It is also worth noting that the hydration degree of cement increased gradually at the early age, while the hydration of cement increased at a relatively slower rate after 7 days.

This phenomenon is mainly attributed to the fact that low temperature generally suppresses the hydration process, causing the slow rate of hydrated product generation. At low temperatures, the dissolution of clinkers will be slowed down and the lower temperature indicates the slower rate of dissolution. Also, low temperature impedes the mutual movement of molecular reaction and accordingly delays the process of the hydration reaction, resulting in poor development of hydration products, which can be reflected in strength gain and microstructure development. It is generally considered that a hydrated cement particle is composed of an anhydrous cement core and a hydrated cement shell, and the core turns smaller with the shell turning thicker as the hydration proceeds. The reason why the hydration degree showed a slower increase after 7 days might be that the diffusion rate of Ca²⁺ and OH⁻ through the hydrated cement shell decreases as more hydration products will be produced with time and therefore delays the increase of the hydration degree.

On the contrary, with the increase of TiO₂ nanoparticles, the hydration degree of cement pastes was improved firstly, then the improvement was not very evident, and this trend was similar regardless of the curing temperature. TiO₂ nanoparticles, owing to its large surface area to volume ratio, can provide an extra space for the precipitation of hydration products; therefore, the hydrated shell will not get thicker and thicker with time compared to that without TiO₂ nanoparticles, since the thicker the hydrated cement shell reflects the lower the diffusion rate of ions through the shell; finally, the hydration process can be accelerated. With the increasing content of TiO₂ nanoparticles, the nucleation site provided by the total surface area for growth of hydration products also increases, therefore more hydration products will be deposit on the surface of TiO₂ nanoparticles, and the hydration degree will be improved.

3.1.3. Mechanical Strength. The compressive strength and flexural strength of ordinary cement mortar and mortars with different proportions of TiO₂ nanoparticles at various curing temperatures are shown in Figure 3. It is noted that both the two strengths showed a downward trend as the curing temperature decreased and low temperature had an undesirable impact on the strengths especially at 3 days. On the contrary, the strength was steadily enhanced with the growth of the curing time regardless of the variation in temperature. The strength of the specimens increased fast

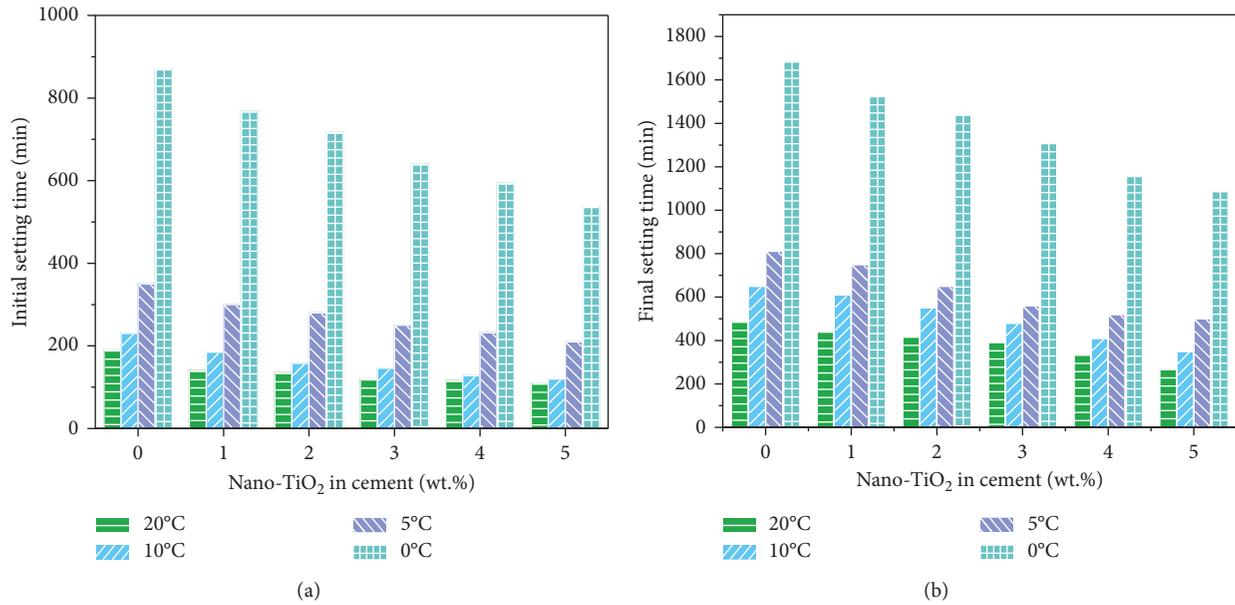


FIGURE 1: (a) Initial setting time of cement pastes; (b) final setting time of cement pastes.

before 7 days while after 7 days the increase rate slowed down, and finally at 56 days, the maximum strength was exhibited. Meanwhile, it is discovered that, with the incorporation of TiO₂ nanoparticles, the strength firstly showed a fast increase compared with the ordinary mortar until the dosage of TiO₂ nanoparticles reached up to 2 wt.% and then the rate of this increase slowed down.

The strength of cement mortar is mainly attributed to the uniform distribution and density of the hydrated product, mainly gels of calcium silicate hydrate (C-S-H), from the hydration of the tricalcium silicate (C₃S) and dicalcium silicate (C₂S). Nevertheless, the hydration rate at low temperatures is lower, therefore insufficient hydration products will be generated to shorten the distance between them and fill the pores in the matrix, and accordingly much more time will be needed for the formation of a dense microstructure compared to the time required at ambient temperature. Moreover, the diffusion of Ca²⁺ and OH⁻ through the hydrated shell during the hydration process is slowed down at low temperatures, which in turn delays the strength gain. This may be the reason that, at 3 days, although the cement hydration was still carried on at 0°C, the retardation in hydration resulted in the generation of few hydrated products, leading to approximately no strength gain.

The effect of TiO₂ nanoparticles on the strength of mortars in this study was evident. It is clear that the strength of mortars was improved rapidly until the content of TiO₂ nanoparticles is up to 2 wt.%, and this improvement was more remarkable in flexural strength. As is mentioned above, the strength of the cement mortar is closely related to the amount of ettringite and C-S-H gels, and the existence of nanoparticles facilitates the cement hydration, thereby producing more hydration products. In addition to the filler property of nanoparticles to fill the pores in C-S-H gels, it is well known that nanoparticles

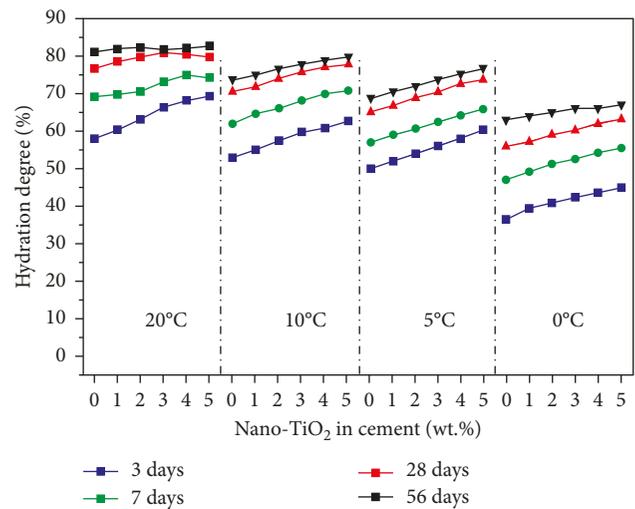


FIGURE 2: Hydration degree of cement pastes.

have a large surface area to volume ratio, and hence, the additional surface area turns to be an appropriate place for hydration products to precipitate. Besides, nanoparticles enable the formation of a bond between itself and C-S-H gels, as a result the strength can be accordingly improved. However, there is also an undesirable effect due to the large ratio of surface area to volume, since nanoparticles are liable to glue together and many nanoparticle clusters which are very weak in strength will be generated, leading to a heterogeneous microstructure [47]. This may be the reason why the hydration degree was still increased slightly while a limited increase in the strength of mortar was observed when the dosage of TiO₂ nanoparticles was over 2 wt.% in this study. This phenomenon may also be attributed to the fact that TiO₂ nanoparticles are enough to

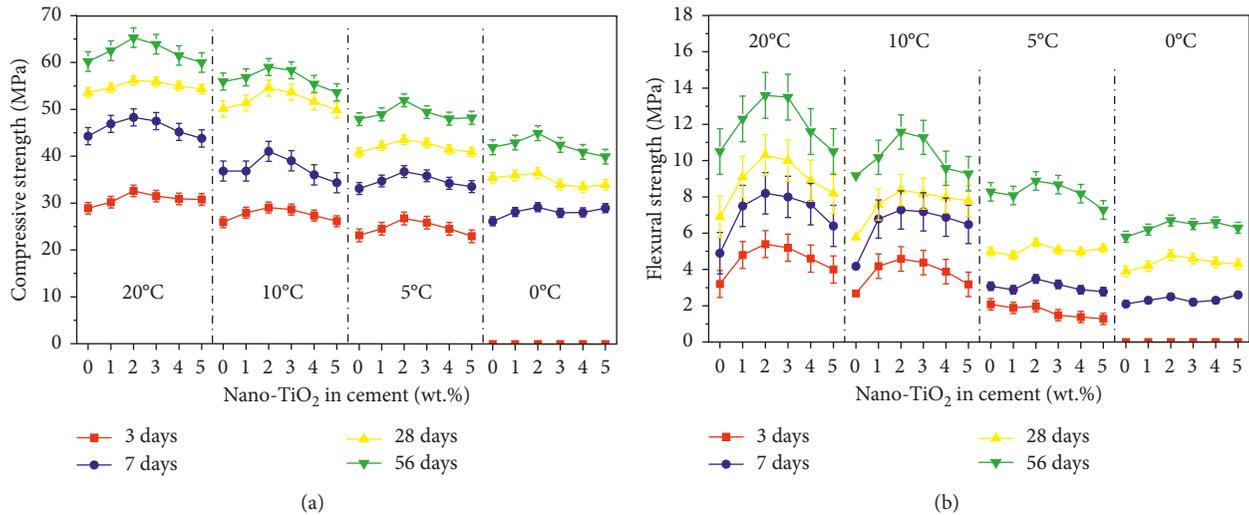


FIGURE 3: (a) Compressive strength of cement mortars; (b) flexural strength of cement mortars.

combine with the free lime, resulting in a loss in strength due to leaching of excessive silica [28].

It should be worthy to note that, although the strength was enhanced by TiO₂ nanoparticles, the enhancement was still not very pronounced at low temperatures. Because at low temperatures, the overall rate of cement hydration reduced, the strength development mainly due to the generation of C-S-H gels is accordingly postponed.

Based on the results of the setting time test, hydration degree test, and mechanical strength test, the specimen with 2 wt.% TiO₂ nanoparticles showed the superior performance, therefore the optimum dosage was considered as 2 wt.%. In the following experiments, the specimens with 2 wt.% TiO₂ nanoparticles and the ordinary specimen were selected to illustrate the mechanism why TiO₂ nanoparticles can accelerate the hydration of cement under low temperatures.

3.2. Pore Structure. Integral curves and differential curves of pore size distribution of specimens without and with 2 wt.% TiO₂ nanoparticles at different temperatures are shown in Figure 4. These two curves can be utilized to illustrate the pore distribution in specimens. The highest point in the integral curves of pore distribution is the total specific pore volume of the specimen, and the smaller the total pore volume indicates the lower porosity of the specimen. The pore diameter corresponding to the peak in the differential curves of pore distribution is considered as the most probable pore size, which accounts for the largest proportion of the pore size in the specimen compared to the rest of pore sizes, and the larger the most probable pore size indicates the bigger mean pore size [33].

From the test results in Figure 4(a), it can be seen obviously that specimens with TiO₂ nanoparticles had smaller pore volume size in comparison with those without nanoparticles, and with 2 wt.% TiO₂ nanoparticles, the total pore volume decreased by 12.1%, 11.5%, 10.1%, and 7.3%, at 20°C, 10°C, 5°C, and 0°C, respectively. Also, we noticed that, with 2 wt.% TiO₂ nanoparticles in the specimen, the volume of

harmless pore (<20 nm) and few-harm pore (20–50 nm) increased, while the volume of harmful pore (50–200 nm) and multiharm pore (>200 nm) reduced, indicating that TiO₂ nanoparticles could refine the pore structure and reduce the porosity [48]. On the contrary, it was observed that, at low temperatures, the harmful and multiharmful pores increased while the harmless and few-harm pores decreased, which demonstrated that low temperature had an adverse effect on the development of the pore structure. From Figure 4(b), the most probable pore sizes in specimen containing TiO₂ nanoparticles were also smaller compared to the ordinary specimen, indicating that the size of gel pores was reduced due to the addition of TiO₂ nanoparticles [49]. Viewed from these two indexes, it can be found that the incorporation of 2 wt.% TiO₂ nanoparticles optimized the pore distribution in specimens, although the overall effectiveness was inhibited by low temperatures. This may be the reason why specimens modified with 2 wt.% TiO₂ nanoparticles showed superior performance in mechanical strength, since the strength of the specimen is closely associated with its porosity and microstructure.

For specimens without TiO₂ nanoparticles, the total specific pore volume became larger as the curing temperature declined and the most probable pore size also became bigger, indicating that low temperature deteriorated pore structures of specimens and increased their porosity. Therefore, the strength of the specimen was damaged by low temperatures. TiO₂ nanoparticles, due to its specialty, can fill the pores in the cement specimen and act as a core for hydration products to precipitate, thus making a homogeneous and dense structure, which may explain the corresponding variation in strength.

However, even with the addition of TiO₂ nanoparticles, the pore structure of the cement specimen can hardly be improved at 0°C. The main reason for this phenomenon is that low temperature suppresses the hydration reaction of each constituent of cement and reduces the mutual movement between molecules, especially at 0°C, resulting in the

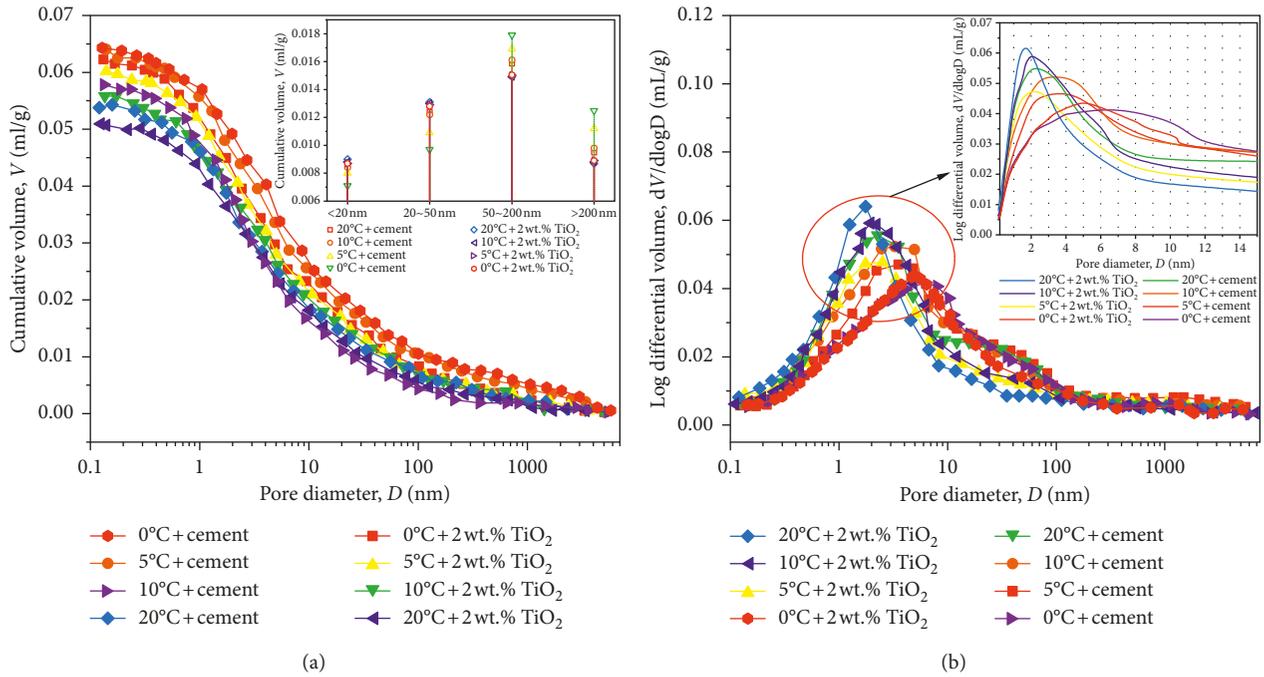


FIGURE 4: (a) Integral curves of pore size distribution of specimens; (b) differential curves of pore size distribution of specimens.

overall reduction of the hydration reaction and ultimately leading to poor development of the pore structure.

3.3. Thermal Gravimetric Analysis. According to findings of previous researchers, it is generally considered that, between 30 and 120°C, the evaporable water in hardened cement paste is eliminated, the decomposition of calcium hydroxide (CH) takes place between 400 and 550°C, and the decarbonation of calcium carbonate (CaCO₃) appears between 700 and 900°C [50]. Based on this theory, thermal gravimetric analysis was conducted on ordinary cement paste and paste with 2 wt.% TiO₂ nanoparticles cured at different curing temperatures for 28 days to examine the mass loss of the specimens subjected to an elevated temperature, and CH content are presented in Figure 5. To be exact, a portion of CH may participate in the process of carbonation along with C₃S, C₂S, and C-S-H [51]. However, it is quite difficult to quantify the mass loss of CH during the carbonation process, and as a result, CH content calculated from the mass loss in the temperature domain of 400–550°C is generally selected as an index to describe the hydration degree of pastes. The content of CH can be determined from the following equation:

$$W_{CH} = (W_1 - W_2) \frac{M_{CH}}{M_H}, \quad (2)$$

where W_{CH} is the percentage content of CH, W_1 and W_2 are the mass losses of specimens at 400°C and 550°C, respectively, and M_{CH} and M_H are the molar masses of CH and water, which are 74.10 g/mol and 18.02 g/mol, respectively.

The results indicated that the content of CH in cement pastes was steadily increased as the curing temperature went up from 0°C to 20°C regardless of with or without TiO₂ nanoparticles, demonstrating that low temperature inhibited

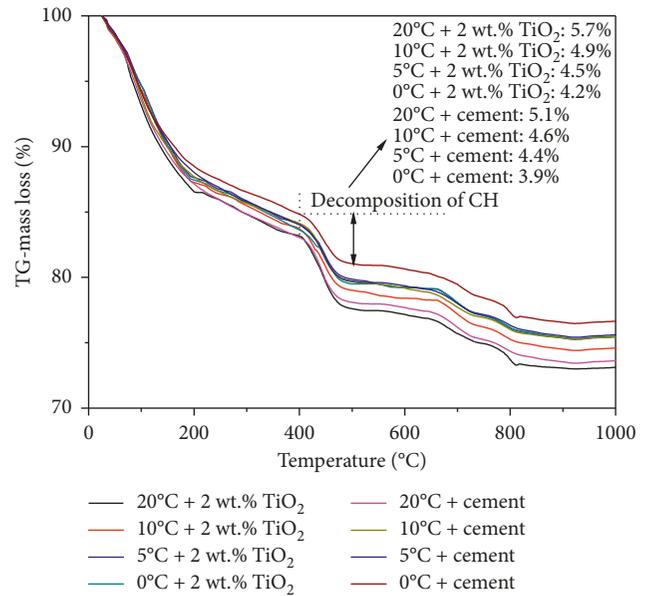


FIGURE 5: TG mass loss in percentage for cement pastes cured at various temperatures.

the process of cement hydration. On the contrary, cement pastes with TiO₂ nanoparticles had more CH in content compared to the ordinary cement pastes because TiO₂ nanoparticles could enhance the hydration of cement due to its characteristic of high ratio of surface area to volume. The thermal gravimetric test results conformed to the strength test very well, since the formation of more CH due to the hydration reaction of C₃S and C₂S directly illustrated more generation of C-S-H gels, leading to the improvement in strength.

3.4. X-Ray Diffraction. The XRD analysis was conducted on ordinary cement paste and paste with 2 wt.% TiO₂ nanoparticles under different curing temperatures at 28 days of age, and the results are shown in Figure 6. From Figure 6(b), it can be observed that diffraction peaks of TiO₂ nanoparticles appeared at 25.33°, 36.25°, and 42.33°, indicating that TiO₂ nanoparticles did not participate in the hydration of cement but only provided extra space for the attachment of hydration products, such as calcium hydroxide (CH), C-S-H gels, and ettringite. What should be worthy to note is that, despite the variation in curing temperature, diffraction peaks of CH at 29.63°, 47.73°, and 48.77° were more intense in cement paste containing 2 wt.% TiO₂ nanoparticles compared to those corresponding peaks in ordinary cement paste exhibited in Figure 6(a). Meanwhile, the diffraction intensity of C-S-H gels and ettringite at 23.22°, 39.20°, and 39.65° in cement paste containing 2 wt.% TiO₂ nanoparticles also became stronger, demonstrating that the role of TiO₂ nanoparticles in accelerating the hydration of cement.

Combined with Figures 2 and 5, the XRD diffraction agreed with the results of hydration degree and thermal gravimetric analysis. The hydration degree was enhanced with 2 wt.% TiO₂ nanoparticles, as more CH and C-S-H gels were generated during the hydration process with the increase in diffraction peaks of CH and C-S-H gels. And with the reduction in curing temperature, the amount of CH and C-S-H gels declined and the corresponding diffraction peaks also decreased, which in turn verified the results of hydration degree.

3.5. SEM Analysis. Microstructural images of ordinary cement paste and paste with 2 wt.% addition of TiO₂ nanoparticles cured under various temperatures at 28 days of age are shown in Figures 7 and 8. Microstructures of ordinary cement paste at different curing temperatures can be noticed in Figure 7. In light of mechanical strength and porosity results, compressive and flexural strengths of specimens cured at 0°C were lower in comparison with those of specimens cured at higher temperatures, and pore distribution was comparatively coarser at 0°C. Accordingly, the image of cement paste at 0°C shown in Figure 7(a) indicated a loosely packed microstructure with less hydration products, which was in agreement with the abovementioned tests. With the increase in the curing temperature, more hydrated products containing CH crystal and C-S-H gels were generated as indicated in Figures 7(b)–7(d), more C-S-H gels were found in SEM images, and the microstructures turned to be much denser.

With the incorporation of 2 wt.% TiO₂ nanoparticles, the hydration process was accelerated, and more hydration products were produced as seen in Figure 8, and as the additional space for precipitation of hydration products, it is not difficult to find that C-S-H gels and ettringite were generated on the surface of TiO₂ nanoparticles with the increasing curing age, thereby promoting the formation of a denser and closely bonded microstructure. However, the overall improvement by

TiO₂ nanoparticles was still weakened by low temperatures, and the pastes cured at 20°C had a denser microstructure with more C-S-H gels and ettringite bonded together than those cured at low temperatures, especially 0°C. These evolution of SEM images indicated that TiO₂ nanoparticles, despite chemically inert with cement, could accelerate the hydration of cement paste, thus improving the strength development under low temperatures due to its special performance.

4. Conclusions

The present study evaluated the physical and mechanical properties of cementitious materials without and with various dosages of TiO₂ nanoparticles under curing temperatures of 0, 5, 10, and 20°C, and microstructural analysis was employed to explain and verify the physical and mechanical test results. The following conclusions can be drawn based on the experimental results:

- (1) Low temperature had an undesirable impact on the setting time of cement pastes while with the incorporation of TiO₂ nanoparticles, the setting time of pastes remarkably reduced, and the more addition of TiO₂ nanoparticles, the shorter the setting time.
- (2) It was discovered that the hydration degree was enhanced with the increase in curing time and curing temperature, and TiO₂ nanoparticles had the ability to accelerate the hydration of the cement.
- (3) To increase the dosage of TiO₂ nanoparticles not necessarily enhanced the strength development of cement mortar, and the optimal addition was 2 wt.% in this study, and the strength showed a downward trend when the dosage of TiO₂ nanoparticles was over 2 wt.%.
- (4) The results of MIP indicated that, with the incorporation of 2 wt.% TiO₂ nanoparticles, the pore volume and most probable pore size turned smaller, demonstrating a much denser microstructure of cement.
- (5) TiO₂ nanoparticles, although inert with cement, could accelerate the hydration of cement, thereby promoting the formation of more hydration products, which could be confirmed by the XRD test conducted on cement paste at 28 days of age.
- (6) With the addition of TiO₂ nanoparticles, no new hydrate was generated in the cement pastes, but compared with ordinary cement pastes, the diffraction peaks of hydration products were more intense. Low temperatures decelerated cement hydration with weak diffraction peaks in all the cement pastes.
- (7) Morphology obtained by the SEM test on ordinary cement paste and paste with 2 wt.% TiO₂ nanoparticles cured under different temperatures at 28 days of age explained the experimental results. The specimen with TiO₂ nanoparticles showed a comparatively denser microstructure with the closely bonded C-S-H gels and ettringite.

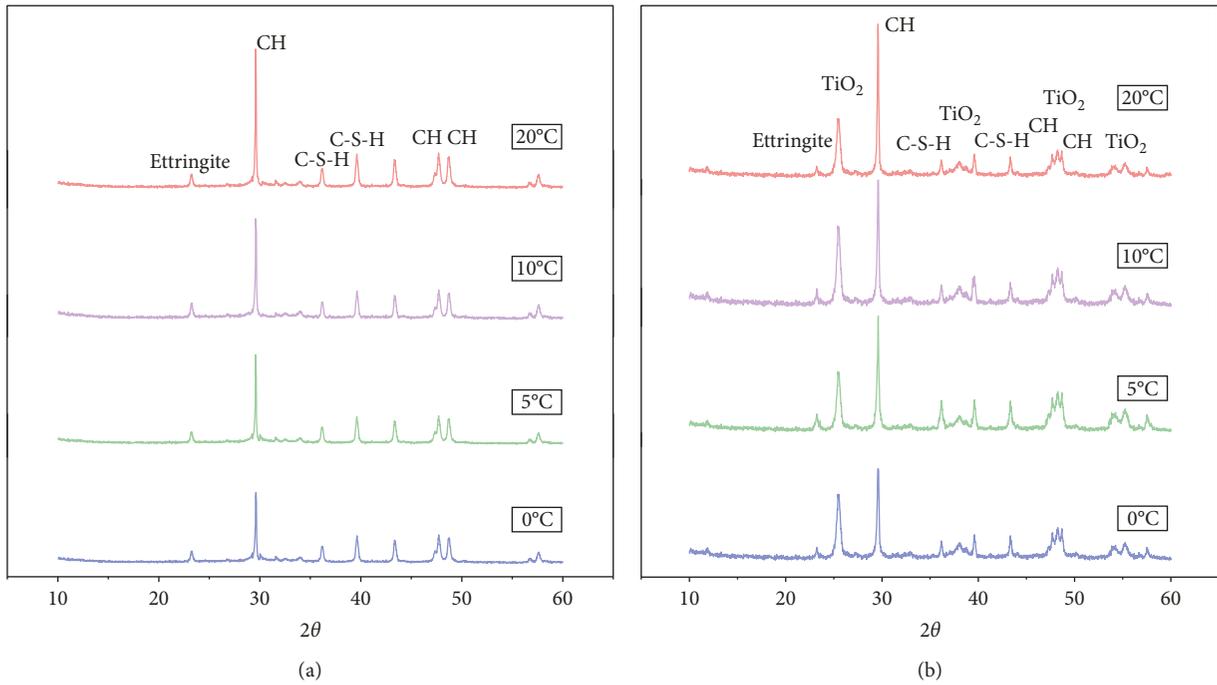


FIGURE 6: (a) XRD patterns of ordinary cement pastes at various temperatures; (b) XRD patterns of cement pastes with 2 wt.% TiO_2 nanoparticles at various temperatures.

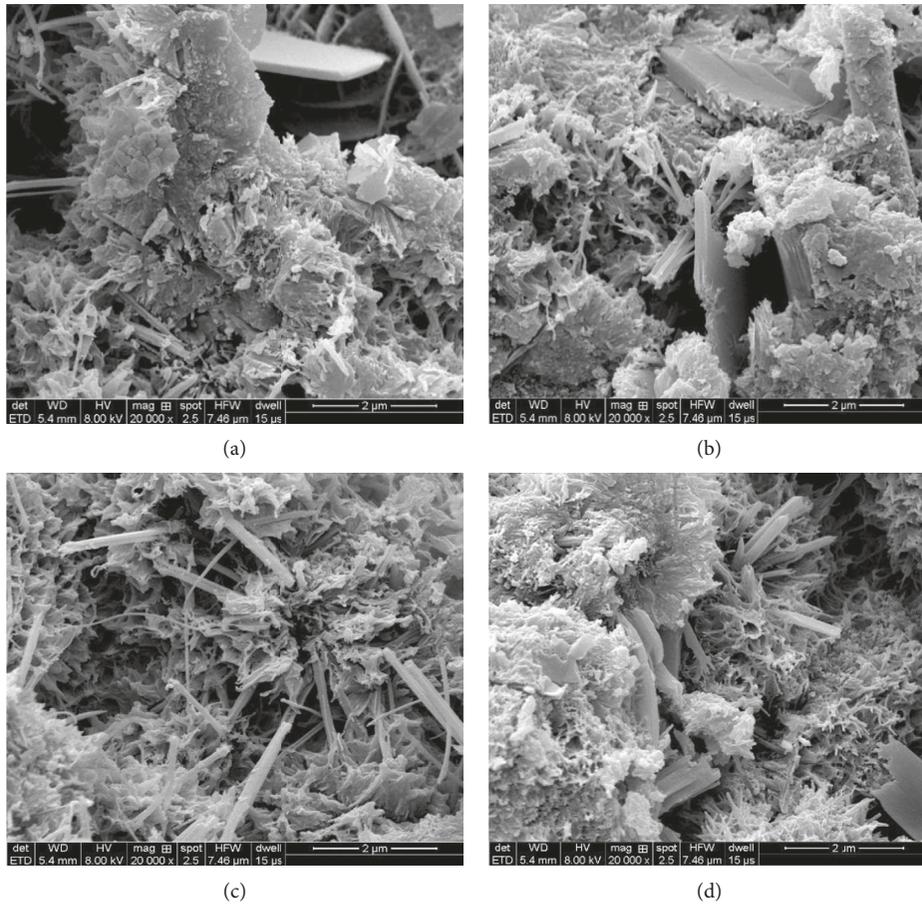


FIGURE 7: SEM images of ordinary cement pastes cured at (a) 0°C, (b) 5°C, (c) 10°C, and (d) 20°C at 28 days.

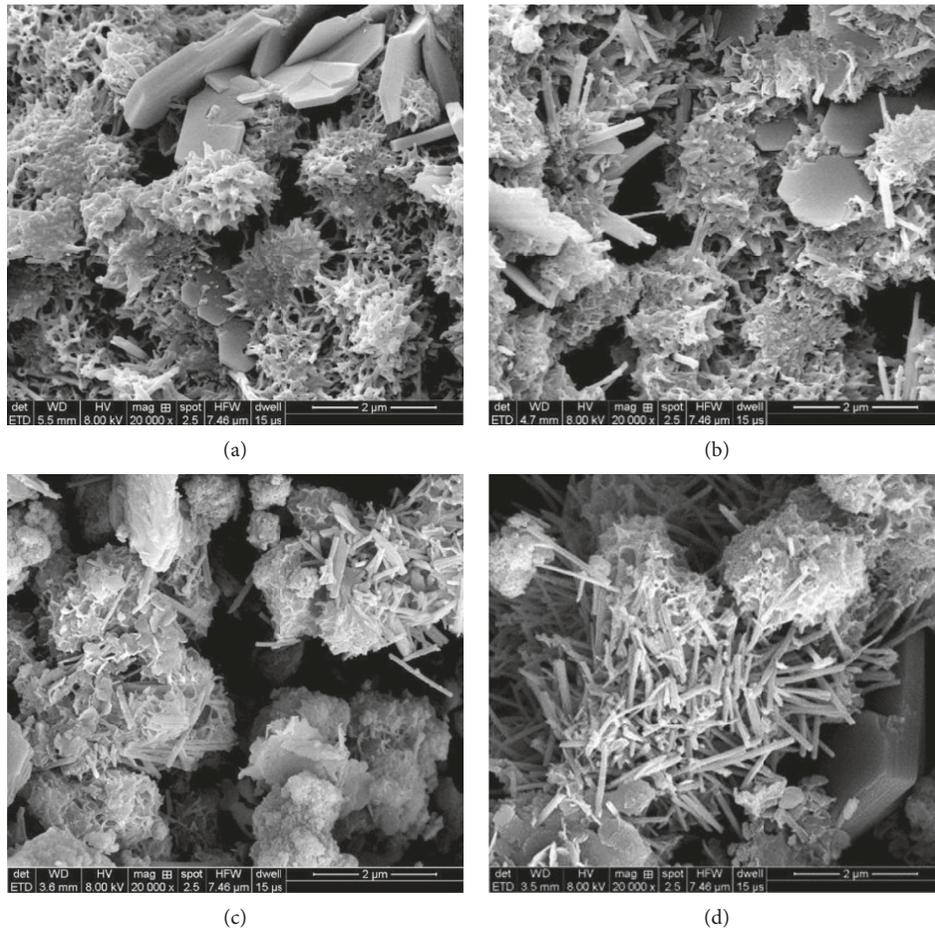


FIGURE 8: SEM images of cement pastes containing 2 wt.% TiO₂ nanoparticles cured at (a) 0°C, (b) 5°C, (c) 10°C, and (d) 20°C at 28 days.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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