Study on the mechanical properties and frost resistance of multiple modified concrete

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Abstract
To study the effects of graphene oxide (GO), fly ash, and steel fiber on the mechanical properties and durability of concrete, the mechanical properties, frost resistance, and internal pore structure of modified concrete are investigated by compression tests, freeze–thaw cycle tests, and industrial computed tomography (CT) tests. The test results show that the compressive strength of concrete with GO is better than that of mixed concrete, concrete mixed with only steel fiber, and ordinary concrete. Further, it is strongest at all ages when the GO content is 0.03%; the compressive strength of mixed concrete with 30% of fly ash is generally better than that with 15% and 45% of fly ash. In general, the frost resistance of concrete with only GO is better than that of ordinary concrete. With the increase in fly ash content, the internal porosity of concrete decreases, and its compressive strength increases accordingly; as GO increases, the porosity decreases and then increases, with the lowest porosity and the highest compressive strength of concrete at 0.03% of GO. With an increase in porosity, the mass loss and relative dynamic elastic modulus of concrete increase after 100 freeze–thaw cycles, which indicates that porosity directly affects the frost resistance of concrete.

1. Introduction
Since the 21st century, the rapid development of the construction industry in China has increased the demand for construction materials as well as the requirements for the performance of materials and the technology of construction. Therefore, the mechanical properties and durability of concrete are crucial for structural safety. Current research is mainly focused on improving concrete properties by adding composite materials, mineral admixtures, nanomaterials, etc.

Fly ash is a type of industrial waste that occupies a large amount of land when it is stacked. In China, its utilization has developed; however, there is still a certain gap compared to that in foreign countries [1]. To solve the problem of occupying land and reduce environmental pollution, the right amount of fly ash should be added into concrete under the conditions for engineering applications [2, 3]. As a new type of material, nanomaterials possess many characteristics, including size and surface effects. Because of their large specific surface area and strong interfacial interactions, nanomaterials can be effectively combined with cementitious materials, and their incorporation into concrete for application research has become one of the current trends of new materials [4–8]. Therefore, it is important to explore multifunctional nanomaterials to improve the performance of concrete [9–12].

A study by Xiao et al [13] showed that the slump of recycled concrete gradually decreased with an increase in the nano-SiO$_2$ admixture, and the slump loss was reduced by adding fly ash. Lei et al [14, 15] found that the flexural and compressive strength of concrete could be enhanced by adding graphene oxide (GO). According to Guo et al [16], the addition of GO could improve the microstructure of the interfacial transition region of recycled concrete, and thus, the mechanical properties of recycled concrete is improved. The research results of Yang et al [17] showed that the compressive and flexural strengths of cement paste and its ability to resist the
erosion of the external environment were the best when GO was dosed at 0.03%. Additionally, GO can thicken cement slurry, accelerate its solidification, and reduce the heat release of its hydration reaction [18].

In cold regions, freeze–thaw is often one of the main causes of the destruction of concrete; therefore, its resistance has become an important indicator of the durability of concrete in these regions, and it has gradually become the top priority of concrete durability research [19–21].

To investigate the effects of nanomaterials, GO, fly ash, and steel fiber, on the mechanical properties and frost resistance of concrete, 18 types of concrete with different mix proportions were designed. The mechanical properties, frost resistance, and internal pore structure of the modified concrete were studied by compressive tests, freeze–thaw cycle tests, and industrial computed tomography (CT) detection.

2. Experimental

2.1. Raw material

2.1.1. Cement

The cement used in the test was P·O 42.5, a type of ordinary Portland cement produced by Conch Group, and its indexes met the relevant regulations and test requirements. The main performance indexes are listed in table 1.

2.1.2. Aggregate

The fine aggregate used in the test was natural medium sand from the Bahe River in Xi’an, with a fineness modulus of 2.61. The coarse aggregate was calcareous gravel with particle size ranging from 4.75 mm to 19 mm.

2.1.3. Graphene oxide

An industrial grade GO-aqueous dispersion with a concentration of 10 mg ml⁻¹ was used in the test, and it was produced by Suzhou Tanfeng Technology Co., Ltd. The main technical parameters are listed in table 2.

2.1.4. Fly ash, steel fiber, and water-reducing agent

First-grade fly ash produced by Henan Sitong Chemical Construction Co., Ltd was used in this test. The main components of this active mineral admixture were SiO₂, Al₂O₃, and small amounts of FeO, Fe₂O₃, CaO, MgO, SO₃, and TiO₂. Additionally, ST-01B retarding superplasticizer was used as the water-reducing agent. Shear wave-type steel fibers with dimensions of 35 mm (length) × 2 mm (width) × 0.8 mm (thickness) produced by Hebei Shengze Building Materials Co., Ltd were used in the test.

2.2. Mix proportion

The baseline mix proportions for the concrete design are listed in table 3. The numbered specimens in table 4 correspond to different dosage combinations and substitutions of modified materials, all based on the baseline mix proportion in table 3, and each number in table 4 corresponds to a different specific mix ratio, which is expressed in terms of the mass of each material component required to prepare a batch of concrete specimens.

In this test, fly ash was used to replace part of the cement, and the replacement rates were 15%, 30%, and 45%, respectively. GO admixtures (as a percentage of sand mass) were 0.01%, 0.03%, 0.05%, and 0.07%,

| Table 1. Main technical indexes of cement. |
|------------------------------------------|
| Ignition loss (%) | SO₃ (%) | MgO (%) | Specific surface area (cm² kg⁻¹) | Initial setting (min) | Final setting (min) | Stability | Chloride ion (%) |
|-------------------|---------|---------|----------------------------------|----------------------|---------------------|----------|-----------------|
| 3.49              | 2.41    | 2.32    | 349                              | 187                  | 246                 | Qualified | 0.032           |

| Table 2. Parameters of industrial GO-aqueous dispersion. |
|---------------------------------------------------------|
| Purity (wt%) | Thickness (nm) | Lamellar diameter (nm) | Number of layers | Specific surface area (m² g⁻¹) | Appearance |
|--------------|----------------|------------------------|------------------|-------------------------------|------------|
| >95          | 3.4–7          | 10–50                  | 6–10             | 100–300                       | Black-brown |

| Table 3. Mix proportion design of concrete. |
|--------------------------------------------|
| Cement (kg) | Sand (kg m⁻³) | Coarse aggregate (kg m⁻³) | Water (kg m⁻³) | Water-binder ratio |
|-------------|---------------|--------------------------|---------------|--------------------|
| 456         | 687           | 1030.5                   | 205           | 0.45               |
Table 4. Mix proportion.

| Specimen | Cement (kg) | Sand (kg) | Coarse aggregate (kg) | Water (kg) | GO (kg) | Go content | Fly ash (kg) | Fly ash content | Steel fiber (kg) | Superplasticizer (kg) |
|----------|-------------|-----------|-----------------------|------------|---------|-------------|--------------|-----------------|------------------|---------------------|
| C-01     | 12.56       | 22.26     | 33.39                 | 5.03       | 0.0022  | 0.01%       | 2.22         | 15%             | 0.81              | 0.065               |
| C-02     | 12.56       | 22.26     | 33.39                 | 4.58       | 0.0067  | 0.03%       | 2.22         | 0.81            | 0.065              |
| C-03     | 12.56       | 22.26     | 33.39                 | 4.14       | 0.0111  | 0.05%       | 2.22         | 0.81            | 0.065              |
| C-04     | 12.56       | 22.26     | 33.39                 | 3.69       | 0.0156  | 0.07%       | 2.22         | 0.81            | 0.065              |
| C-05     | 10.34       | 22.26     | 33.39                 | 5.03       | 0.0022  | 0.01%       | 4.43         | 30%             | 0.81              | 0.065               |
| C-06     | 10.34       | 22.26     | 33.39                 | 4.58       | 0.0067  | 0.03%       | 4.43         | 0.81            | 0.065              |
| C-07     | 10.34       | 22.26     | 33.39                 | 4.14       | 0.0111  | 0.05%       | 4.43         | 0.81            | 0.065              |
| C-08     | 10.34       | 22.26     | 33.39                 | 3.69       | 0.0156  | 0.07%       | 4.43         | 0.81            | 0.065              |
| C-09     | 8.13        | 22.26     | 33.39                 | 5.03       | 0.0022  | 0.01%       | 6.65         | 45%             | 0.81              | 0.065               |
| C-10     | 8.13        | 22.26     | 33.39                 | 4.58       | 0.0067  | 0.03%       | 6.65         | 0.81            | 0.065              |
| C-11     | 8.13        | 22.26     | 33.39                 | 4.14       | 0.0111  | 0.05%       | 6.65         | 0.81            | 0.065              |
| C-12     | 8.13        | 22.26     | 33.39                 | 3.69       | 0.0156  | 0.07%       | 6.65         | 0.81            | 0.065              |
| C-13     | 14.77       | 22.26     | 33.39                 | 5.25       | 0       | 0%          | 0            | 0%              | 0.81              | 0.065               |
| C-14     | 14.77       | 22.26     | 33.39                 | 5.25       | 0       | 0%          | 0            | 0%              | 0.81              | 0.065               |
| C-15     | 14.77       | 22.26     | 33.39                 | 5.03       | 0.0022  | 0.01%       | 0            | 0               | 0.065              |
| C-16     | 14.77       | 22.26     | 33.39                 | 4.58       | 0.0067  | 0.03%       | 0            | 0               | 0.065              |
| C-17     | 14.77       | 22.26     | 33.39                 | 4.14       | 0.0111  | 0.05%       | 0            | 0               | 0.065              |
| C-18     | 14.77       | 22.26     | 33.39                 | 3.69       | 0.156   | 0.07%       | 0            | 0               | 0.065              |
respectively, and steel fibers were mixed at a fixed rate of 25 kg m$^{-3}$. The specific mix ratios are shown in Table 4, where specimens C-01 to C-12 represent GO-fly ash–steel fiber mixed concrete (15% fly ash in C-01 to C-04, 30% in C-05 to C-08, 45% in C-09 to C-12, and the content of GO from C-01 to C-12 varied), C-13 is steel fiber concrete, C-14 is ordinary concrete, and C-15 to C-18 are concrete with GO only.

2.3. Test method

2.3.1. Mechanical test

In this study, cubic concrete specimens with dimensions of 100 × 100 × 100 mm were naturally cured and tested for compressive strength using the microcomputer–controlled electro-hydraulic servo universal testing machine MTS at the ages of 7, 14, and 28 days, respectively, to study the variation in the mechanical properties of concrete with different amounts of fly ash and GO and the variation in the compressive strength values of concrete at each age during the curing period. The test was performed according to GB/T 50081-2002.

2.3.2. Fast freeze–thaw test

The freeze–thaw cycle test was performed on the concrete cube with a side length of 100 mm using the fast-freeze method, and the test procedure was based on GB-T50082-2009, during which the mass loss, compressive strength loss, and dynamic modulus of elasticity were measured to judge the frost resistance of concrete.

2.3.3. Meso test

Industrial CT scanning is one of the techniques for the non-destructive testing and evaluation of concrete; it enables a 360° inspection of concrete specimens. The scanned images are reconstructed, and the pores are extracted using post-processing software, which provides information on the porosity and pore distribution within the concrete, allowing the structural characteristics of the concrete to be analyzed.

In this test, to analyze the internal aggregate-mortar distribution and porosity, a Multiscale-Voxel 450 industrial CT was used for the non-destructive testing of concrete cube specimens with dimensions of 100 × 100 × 100 mm after 28 days of natural curing.

3. Results and discussion

3.1. Compressive strength

The compressive strength of concrete at different ages is shown in Figure 1 and Table 5. From C-14 to C-18, the compressive strength of concrete with only GO increased. Afterward, it decreased as the GO content increased from 0% to 0.07%, with the compressive strengths of 7 d, 14 d, and 28 d peaking at 0.03% GO content, increasing by 33.15%, 10.88%, and 17.72%, respectively, compared to that of ordinary concrete (C-14).

Although there was a tendency for the compressive strength to decrease after GO exceeded 0.03%, it was still generally higher than that of ordinary concrete, which shows that GO had a good effect on improving the early compressive strength of concrete. The enhancement of the concrete strength was mainly due to the appropriate number of nanomaterials, which can improve the C–S–H gel structure and pore structure within the cementitious matrix, as well as the aggregate and mortar interface properties [22–26]. The strengthening effect of GO on the compressive strength of concrete has also been studied in reference [27], Chen et al pointed out that the nucleation effect due to the addition of GO could enhance the hydration degree of cement.

When the fly ash content was 15%, the compressive strength of the mixed concrete at each age decreased first and then increased with an increase in the GO admixture and reached the minimum value at 0.05% of the GO admixture. C-05 to C-08 showed that the compressive strength at 7 d increased with the addition of GO when the fly ash admixture was 30%. The compressive strength at 14 d and 28 d increased and then decreased and reached the maximum value at 0.05% of the GO admixture. From C-09 to C-12, the compressive strength of the mixed concrete with 45% of fly ash admixture decreased with an increase in the GO admixture at all ages.

The compressive strength of concrete with only GO was better than that of mixed concrete, steel fiber concrete, and ordinary concrete, and it was strongest at all ages when the GO content was 0.03%. The compressive strength of mixed concrete with 30% of fly ash (C-05 to C-08) was generally better than that with 15% and 45% of fly ash. When fly ash was mixed at 15%, the compressive strength of the concrete at all ages increased with a relatively high GO dose (0.07%). When fly ash was mixed at 45%, the compressive strength at all ages increased with a relatively small GO dose (0.01%).

3.2. Frost resistance

3.2.1. Mass loss

Table 6 shows the mass loss rate of the concrete with only GO after 25, 50, 75, and 100 freeze–thaw cycles, and when the mass loss rate is negative or 0, it is indicated by ‘—’.
Figure 1. Compressive strength of concrete at different ages.

(a) GO-fly ash-steel fiber mixed concrete (Fly ash content: 15%)

(b) GO-fly ash-steel fiber mixed concrete (Fly ash content: 30%)

(c) GO-fly ash-steel fiber mixed concrete (Fly ash content: 45%)

(d) Concrete with GO only

Table 5. Compressive strength of concrete at different ages.

| Specimen | Compressive strength (MPa) | Specimen | Compressive strength (MPa) |
|----------|----------------------------|----------|----------------------------|
|          | 7 d | 14 d | 28 d | 7 d | 14 d | 28 d |
| C-01     | 31.67 | 36.70 | 41.73 | C-10 | 30.10 | 36.23 | 43.63 |
| C-02     | 30.77 | 35.13 | 41.00 | C-11 | 29.90 | 35.43 | 40.63 |
| C-03     | 29.03 | 34.67 | 40.97 | C-12 | 27.60 | 35.03 | 39.40 |
| C-04     | 36.71 | 39.92 | 44.19 | C-13 | 38.20 | 42.45 | 47.87 |
| C-05     | 31.67 | 36.70 | 45.53 | C-14 | 37.83 | 46.93 | 52.13 |
| C-06     | 33.20 | 38.74 | 46.11 | C-15 | 49.03 | 49.20 | 58.20 |
| C-07     | 35.17 | 40.50 | 46.67 | C-16 | 50.37 | 52.03 | 61.37 |
| C-08     | 35.57 | 39.27 | 44.80 | C-17 | 48.37 | 50.47 | 57.60 |
| C-09     | 35.13 | 38.10 | 45.97 | C-18 | 41.83 | 48.23 | 52.00 |

Table 6. Mass loss rate of concrete after the freeze–thaw cycles (%).

| Specimen | 25 cycles | 50 cycles | 75 cycles | 100 cycles |
|----------|------------|------------|------------|------------|
| C-13     | —          | 0.20       | 0.92       | 1.22       |
| C-14     | —          | 0.16       | 0.64       | 1.09       |
| C-15     | —          | 0.52       | 0.36       | 0.99       |
| C-16     | 0.08       | 0.40       | 0.45       | 0.83       |
| C-17     | —          | 0.08       | 0.20       | 0.39       |
| C-18     | —          | 0.04       | 0.20       | 1.04       |
According to the data in table 6, the mass loss rate of concrete continuously increases as the number of freeze–thaw cycles increases. At 25 freeze–thaw cycles, most of the concrete specimens showed negative values of mass loss, which means that their mass increased after 25 freeze–thaw cycles, probably due to the gradual absorption of water into the internal pores of the concrete at the beginning of the freeze–thaw process. After 25 freeze–thaw cycles, the rate of concrete mass loss increased, with the gradual spalling of the specimen surface.

During the freeze–thaw process, the mass loss rate of steel fiber concrete (C13) was slightly higher than that of ordinary concrete (C14), whereas the frost resistance of concrete with only GO (C15 to C18) was generally better than that of ordinary concrete. At relatively low GO contents (0.01% and 0.03%), there was a relatively high mass loss of concrete before 50 freeze–thaw cycles; however, the latter frost resistance was better. When the GO content was 0.05% (C17), the most significant improvement in frost resistance occurred.

3.2.2. Compressive strength loss

Tables 7 and 8 show the compressive strength and loss rate of concrete with only GO during freezing and thawing, respectively.

As shown in tables 7 and 8, the strength loss increases with the number of freeze–thaw cycles. The strength loss rate of steel fiber concrete (C13) was significantly higher than that of ordinary concrete (C14), while the strength loss rate of concrete with only GO (C15 to C18) was generally lower than that of ordinary concrete, indicating that the admixture of GO improved the frost resistance of the concrete. When it reached 100 cycles of freezing and thawing, the overall rate of the strength loss of concrete with only GO was approximately 20%, and it was the lowest at 0.07% of GO (C18).

As shown in figure 2, during the freeze–thaw period, the compressive strength of the GO concrete first increases and then decreases with the continuous addition of GO and reaches the peak value (C16) when the amount of GO is 0.03%. The pattern of strength change with GO content was the same as that before freeze–thaw, and with the increase in the freeze–thaw cycles, the strength of concrete with different GO contents decreased.

There were several tiny cracks and pores in the concrete. Therefore, under freeze–thaw cycles, water entered these pores, cracked them, and froze, increasing the volume of pore water and imposing a certain stress on the concrete, which will disappear in the process of ice melting. Under the action of multiple freeze–thaw cycles, the interior of the concrete was repeatedly loaded and the pores were further connected. The stress concentration in the concrete resulted in the destruction of the cementitious material and the spalling on the weak surface and corners of the specimens, reducing the strength of the specimens after the freeze–thaw cycles. Therefore, as the number of freeze–thaw cycles increased, the strength loss rate increased.

3.2.3. Relative dynamic modulus of elasticity

The relative dynamic modulus of elasticity of the concrete with only GO and ordinary concrete at 0, 25, 50, 75, and 100 freeze–thaw cycles are shown in table 9.

As shown in table 9, the relative dynamic modulus of elasticity of the concrete decreases with the increase in freeze–thaw cycles. After 100 freeze–thaw cycles, this modulus was above 70% for all concrete with only GO.

| Specimen | 0 cycles | 25 cycles | 50 cycles | 75 cycles | 100 cycles |
|----------|----------|-----------|-----------|-----------|------------|
| C-13     | 47.87    | 40.70     | 38.34     | 36.69     | 36.28      |
| C-14     | 52.13    | 47.05     | 44.88     | 41.91     | 40.81      |
| C-15     | 58.20    | 52.48     | 51.21     | 48.51     | 46.20      |
| C-16     | 61.37    | 55.63     | 54.17     | 49.77     | 47.78      |
| C-17     | 57.60    | 52.01     | 51.25     | 46.73     | 45.68      |
| C-18     | 52.00    | 47.41     | 44.87     | 44.14     | 42.09      |

| Specimen | 25 cycles | 50 cycles | 75 cycles | 100 cycles |
|----------|-----------|-----------|-----------|------------|
| C-13     | 14.98     | 19.90     | 23.35     | 24.21      |
| C-14     | 9.74      | 13.91     | 19.61     | 21.71      |
| C-15     | 9.83      | 12.00     | 16.65     | 20.62      |
| C-16     | 9.35      | 11.73     | 18.90     | 22.15      |
| C-17     | 9.70      | 11.02     | 18.88     | 20.70      |
| C-18     | 8.82      | 13.71     | 15.13     | 19.06      |
compared to only 65.4% for ordinary concrete, which indicates that GO has a certain effect on the freeze–thaw resistance of concrete. When the content of GO was 0.03%, the relative dynamic elastic modulus of concrete was higher than that of the other contents of concrete, indicating that concrete with this amount of GO had the best resistance to the freeze–thaw cycles. Further, the larger the dynamic elastic modulus, the greater the compactness of the concrete; therefore, the compactness of the concrete mixed with GO was better, and the optimum content was 0.03%.

Both the mass loss and relative dynamic modulus elasticity show that GO has potential to increase the freeze-thaw resistance of concrete, this is in consistent with some researchers’ work [28, 29].

3.3. Pore structure

3.3.1. Two-dimensional tomographic analysis

Concrete cube specimens with different mix proportions (C-01, C-05, C-09, C-14, and C-18) were selected for CT scanning, and the scanned data were imported into Voxel Studio Recon software for pre-reconstruction processing. The 2D tomographic images obtained are shown in figure 3.

The distribution of the internal pores (black areas), aggregates, and mortar of the concrete at each mix ratio is shown in the figures above. The mixed concrete showed bright white spots in the industrial CT test, as shown in figure 3 (a) to (c), because of the presence of metallic substances (steel fibers), in contrast to the concrete with a single GO admixture, as shown in figure 3 (d) to (h). The scanning tomogram of the concrete with steel fibers showed that the steel fibers were generally well distributed.

3.3.2. Three-dimensional extraction of the pores in concrete

After pre-reconstruction using Voxel Studio Recon software, the next post-processing step was performed using the visualization Avizo software to obtain the pore number, pore volume, porosity, and 3D pore distribution of concrete. The 3D pore distribution for each concrete mix ratio is shown in figure 7. The specific pore volume percentages and pore parameters obtained by the industrial CT post-processing are shown in tables 10 and 11, respectively.
According to Figure 4 (a) to (c) and Table 11, with the continuous addition of fly ash, the internal porosity of concrete decreases. As shown in Figure 4 (d) to (h) and Table 11, the porosity decreases and then increases with the continuous addition of GO, and reaches a minimum when the GO admixture is 0.03%, and it increases significantly when GO is 0.07%, which may be due to the aggregation phenomenon triggered by the excessive addition of GO.

In this paper, the pores were classified into 7 categories according to single pore volume: \( V \leq 0.01 \text{ mm}^3 \), \( 0.01 \text{ mm}^3 < V \leq 0.05 \text{ mm}^3 \), \( 0.05 \text{ mm}^3 < V \leq 0.1 \text{ mm}^3 \), \( 0.1 \text{ mm}^3 < V \leq 0.5 \text{ mm}^3 \), \( 0.5 \text{ mm}^3 < V \leq 1 \text{ mm}^3 \), \( 1 \text{ mm}^3 < V \leq 5 \text{ mm}^3 \), and \( V > 5 \text{ mm}^3 \). From the 8 different mix proportion concrete (C-01, C-05, C-09, C-14 to C-18) selected in Table 10, it is shown that the number of pores within 0.01 mm\(^3\) accounts for above 50%, followed in order by 0.01 mm\(^3\) to 0.05 mm\(^3\), 0.05 mm\(^3\) to 0.1 mm\(^3\), 0.1 mm\(^3\) to 0.5 mm\(^3\), 0.5 mm\(^3\) to 1 mm\(^3\), 1 mm\(^3\) to 5 mm\(^3\), and \( V > 5 \text{ mm}^3 \). The number of pores \( (0.5 \text{ mm}^3 \text{ to } 1 \text{ mm}^3, 1 \text{ mm}^3 \text{ to } 5 \text{ mm}^3, \text{ and } > 5 \text{ mm}^3) \) accounts for less than 2.5%.

Combining tables 5 and 11, it is seen that the higher the compressive strength of concrete with only GO, the smaller the corresponding concrete porosity. When the GO admixture was 0.03% (C16), the concrete had the lowest porosity and the highest concrete compressive strength. The compressive strength and porosity of concrete mixed with the GO-fly ash-steel fibers also showed a similar pattern. This leads to the conclusion that

Table 10. Proportion of pore number in different mix proportion (%).

| Pore volume | C-1 | C-5 | C-9 | C-14 | C-15 | C-16 | C-17 | C-18 |
|-------------|-----|-----|-----|------|------|------|------|------|
| \( V \leq 0.01 \text{ mm}^3 \) | 66.29 | 59.88 | 71.16 | 83.44 | 75.22 | 54.43 | 59.90 | 68.33 |
| \( 0.01 \text{ mm}^3 < V \leq 0.05 \text{ mm}^3 \) | 14.29 | 16.78 | 11.15 | 7.13 | 9.27 | 16.02 | 15.32 | 10.96 |
| \( 0.05 \text{ mm}^3 < V \leq 0.1 \text{ mm}^3 \) | 6.14 | 7.56 | 4.84 | 2.65 | 2.51 | 8.96 | 7.97 | 5.25 |
| \( 0.1 \text{ mm}^3 < V \leq 0.5 \text{ mm}^3 \) | 11.11 | 13.61 | 0.47 | 5.54 | 7.81 | 15.46 | 13.82 | 12.80 |
| \( 0.5 \text{ mm}^3 < V \leq 1 \text{ mm}^3 \) | 0.89 | 0.98 | 1.02 | 0.53 | 0.91 | 2.10 | 1.33 | 1.63 |
| \( 1 \text{ mm}^3 < V \leq 5 \text{ mm}^3 \) | 0.93 | 0.86 | 1.05 | 0.48 | 1.01 | 2.11 | 1.28 | 0.82 |
| \( V > 5 \text{ mm}^3 \) | 0.36 | 0.33 | 0.31 | 0.23 | 0.27 | 0.91 | 0.57 | 0.20 |

Table 11. Parameters related to pores after CT scanning.

| No. | Number of pores | Porosity (%) | No. | Number of pores | Porosity (%) |
|-----|----------------|--------------|-----|----------------|--------------|
| C-01 | 23 350 | 0.925 | C-15 | 22 378 | 0.828 |
| C-05 | 39 838 | 0.865 | C-16 | 13 342 | 0.729 |
| C-09 | 38 126 | 0.832 | C-17 | 16 321 | 0.937 |
| C-14 | 41 074 | 0.914 | C-18 | 57 131 | 1.026 |
the compressive strength of concrete with only GO varies inversely with the porosity. Furthermore, when the GO admixture was 0.01% (C-01, C-05, C-09), the porosity of the concrete decreased as the fly ash was continuously mixed; thus, the compressive strength increased. This indicates that the presence of GO resulted in a more compacted microstructure and thus enhanced the compressive strength [30, 31]. Two explanations have been proposed, one claims that the pore-filling effect of the GO refined the pore structure [32, 33], the other is that GO induced more hydration products to fill the pores [34, 35].

Combining tables 6 and 9, it can also be seen that the greater the porosity, the greater the concrete mass loss and relative dynamic elastic modulus loss after 100 freeze–thaw cycles, which indicates that the porosity directly affects the frost resistance of concrete.

4. Conclusion

In this study, 18 different ratios of concrete were designed, including 12 different ratios of mixed concrete (GO-fly ash-steel fiber) with 15%, 30%, and 45% of fly ash and 0.01%, 0.03%, 0.05%, and 0.07% of GO, respectively, four ratios of concrete with only GO, and two control groups, ordinary concrete and concrete with only steel fiber. The mechanical properties, frost resistance, and internal pore structure of the modified concrete were investigated using compressive tests, freeze–thaw cycle tests, and industrial CT tests. The test results are as follows:

1. The compressive strength of concrete mixed with only GO is better than that of mixed concrete, concrete mixed with only steel fiber, and ordinary concrete, and under all ages, it is the maximum when the GO content is 0.03%; the compressive strength of the mixed concrete with 30% of fly ash is better than that with 15% and 45% of fly ash.

2. The frost resistance of concrete with only GO is generally better than that of ordinary concrete. When the GO content is 0.05%, the mass loss rate of concrete after 100 freeze–thaw cycles is the lowest; when the GO content is 0.07%, the strength loss rate is the lowest; when the GO content is 0.03%, the loss of relative elastic modulus is the lowest.

3. With the increase in fly ash admixture, the internal porosity of concrete decreases, and its compressive strength increases accordingly; as the GO admixture increases, the porosity decreases and then increases, with the lowest porosity and the highest compressive strength of concrete at 0.03% of the GO admixture. With the increase in porosity, the mass loss and relative dynamic modulus of elasticity of concrete increase after 100 freeze–thaw cycles, which indicates that porosity directly affects the frost resistance of concrete.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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