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Case study

Mechanical properties of mortar and concrete incorporated with concentrated graphene oxide, functionalized carbon nanotube, nano silica hybrid aqueous solution

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ABSTRACT

The purpose of this study was to develop concrete with all advantages by using combinations of various nanomaterials (f-CNTs, NS, GO) and to evaluate the mechanical performance. The mixing method for the nanomaterials developed so far has been useful in the laboratory, but its application in an industrial scale is limited. Therefore, a method for mixing concentrated aqueous solution was proposed by applying a dispersion method based on the functional group ratio of the nanomaterials. The effectiveness of the concentrated aqueous solution was confirmed through UV-Vis and mortar strength tests. To evaluate the mechanical performance of concrete, the uniaxial compression and splitting tensile tests were performed. As a result, the splitting tensile strength increased by about 23% and the elastic modulus by about 10% according to the incorporation of nanomaterials. In the absence of GO, which plays a major role in improving dispersion in the concentrate method, the application of triple nanomaterials in the concentrate method is essential as the variation of the tensile strength data is large. As the nanomaterial was incorporated and the dispersion was improved, not only the strength was increased, but also the volume dilation and the yield point of the concrete were changed. Therefore, when nanomaterials are used in concrete, the applicability of the nanomaterial itself needs to be improved to expand its applicability. And the mechanical properties of concrete improved by nanomaterials should be considered when designing structural members.

1. Introduction

The demand continues to increase for high-rise, large-scale, and large spaces in buildings. To keep pace with this demand, research to reduce the cross-section and enable long spans through the high performance of building materials is steadily progressing. In particular, various studies are being conducted to overcome the limitations of concrete by securing high strength and ductility for concrete, which has excellent economic feasibility and can construct structures of various shapes. Until now, the materials used to improve the mechanical properties of concrete have been fiber reinforced concrete (FRC) such as steel fiber and polypropylene fiber. FRC has clearly verified its performance according to fiber incorporation [1–3]. However, in FRC, the fiber ball effect occurs during

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casting at the actual construction site, so the fiber reinforcement effect may not occur evenly over the entire section. In addition, there are problems such as reduction of slump and deterioration of workability during pouring [4]. Recently, since the development and mass production of nanomaterials are possible, research to fundamentally solve the aforementioned problems by applying them to concrete is increasing. Nanomaterials have the effect of improving the mechanical properties of cement paste and mortar. In recent studies, nanomaterials mainly used to improve the performance of cement composites are carbon nanotubes (CNTs), nano silica (NS) and graphene oxide (GO).

CNTs have the advantage of improving the mechanical properties even when a small amount is added [5]. In previous studies [6–9], it is reported that the compressive strength, tensile strength, and modulus of elasticity increase due to the bridge effect when CNTs were incorporated. In addition, when the optimal amount of CNTs were incorporated, the mechanical properties of the cement composite can be improved by improving the interfacial transition zone (ITZ) properties [10]. Aside from these, it has various effects such as improvement of electrical conductivity and an electromagnetic wave shielding effect [11,12]. The studies on functionalized CNTs with functional groups deposited on the surface to improve the dispersion of CNTs are being actively conducted. NS generates a pozzolan reaction when mixed with cement, promotes hydration, and enhances compressive and tensile strength [13–15]. Turkmenoglu et al. [16] evaluated the effect on elastic and inelastic behavior of high-strength concrete reinforced with NS and reported that the critical stress of concrete and other mechanical properties were improved. GO is also effective in improving flexural and compressive strength and durability [17,18], as well as affecting the dispersion of other nanomaterials [19–22]. In particular, GO may play a role in promoting hydration due to the effect of nucleation sites.

As mentioned above, nanomaterials have various performance enhancing effects of cement composites, and if these nanomaterials are used together, it is expected that concrete with all advantages will be developed, so research has been actively conducted recently. Du et al. [19] confirmed that the compressive strength of cement paste rapidly increased when CNTs and GO were mixed together, and an optimal ratio of GO and CNTs were derived that could create such a synergistic effect. Lu et al. [20] report that the dispersion of nanomaterials increases when CNTs and GO are incorporated. Liu et al. [22] confirmed that the compressive and flexural strengths of cement pastes were increased by mixing NS and GO together, and hybrid nanomaterials (NS, GO) increased the degree of hydration and the pozzolanic reaction, and analyzed the cause.

However, there are limitations to using these nanomaterials together. Although the aforementioned three nanomaterials (CNTs, NS, GO) improve the durability and mechanical properties of cement paste and mortar, their dispersion decreases due to agglomeration [23], which does not fully demonstrate the advantages of nanomaterials. In particular, when two or more materials are mixed together, the strength decreases rapidly when more than a certain ratio is mixed due to agglomeration [24]. To solve this problem when applying various nanomaterials, a study on the method and effect of preparing a highly concentrated aqueous solution of nanomaterials by separating the nanomaterials from the aqueous solution using a centrifuge after a pretreatment process such as high temperature and high pressure [25] has been conducted. Nevertheless, since this method is a very complicated process to be applied to concrete scale and actual structures, there is a limit to its application to construction sites. Therefore, there is a need for a method that can secure dispersion while minimizing the pretreatment process.

Kim et al. [26] recently conducted a study to minimize the pretreatment process and improve durability and mechanical performance by suggesting the optimal mixing ratio of CNTs, NS, and GO to solve this problem. They proposed the optimal mixing ratio of nanomaterials based on chemical bonding according to the ratio of functional groups of nanomaterials to ensure optimal dispersion without any pretreatment other than ultrasonic dispersion for multiple mixing of nanomaterials in cement paste. As a result, the dispersion and mechanical properties were the highest at a certain level of GO (0.04 wt%). In this study, it was confirmed that the performance of cement paste was improved by improving the dispersion with the optimal ratio of nanomaterials. However, in order to apply this method to concrete scale, the sonication method for the entire volume of mixing water performed in this study has limitations when mixing a large amount of concrete. In addition, since a small amount of aqueous solution has to be prepared when sonicating for dispersion is performed, the specimen for material testing is produced in a very small size ($5 \times 5 \times 10$ mm^3), so it is difficult to use it in actual buildings. Because the mixing water used is also limited to deionized (DI) water, it is necessary to expand the research scope for application to the concrete scale.

The purpose of this study is to extend the study at the cement paste level to mortar and concrete containing fine and coarse aggregates by confirming the continuity of the effect of nanomaterials and the mechanical properties of nano concrete. For application to real structures rather than laboratory-level specimens, a new concentrated nanomaterial aqueous solution manufacturing method was developed by applying the nanomaterial dispersion manufacturing method based on the functional group ratio proposed in previous studies [26].

2. Research significance

Although many studies have been conducted to improve the performance of cement composites by incorporating nanomaterials, studies on the mechanical properties of concrete containing aggregates are lacking due to limitations such as dispersion of aqueous solutions of nanomaterials, and it is difficult to use on the construction site. In this study, the scale is extended in the material performance evaluation for cement composites, and the methodology for applying structural members and locally to structures is presented. The method presented in this study incorporates GO as a method to improve the dispersion for the application of various nanomaterials (f-CNTs, NS) without going through a complicated pretreatment process, and uses a concentrated aqueous solution of nanomaterials to expand the scope of nanomaterials application.

3. Materials and test methods

3.1. Preparation of triple nanomaterial admixture

Three types of nanomaterials were used in this study: CNTs (f-CNTs), NS, and GO. The most important variable in the preparation of the three nanomaterial dispersion solutions is the amount of GO. According to the results of previous studies [24,26], the change in the amount of GO had an effect on the dispersibility of CNTs and NS, which was linked to the improvement of compressive and tensile strength. Therefore, in this study, the amount of CNTs and NS was fixed and the amount of GO was increased in order to confirm the change in strength according to the dispersion of nanomaterials in mortar and concrete.

Hamzaoui et al. [27] reported that the optimal amount of CNT was 0.01 wt% in the mortar, and in the study of Kim et al. [26], the optimal amount of CNT was 0.01 wt% and the amount of NS was 1.0 wt% in the triple nanomaterial composite. In this case, the dispersion was found to be the highest. Therefore, the amounts of CNTs and NS were planned to be 0.01 wt% and 1.0 wt%, respectively [26,27]. The amounts of GO were changed to 0.02, 0.04, and 0.06 wt%, and this was compared with the Ordinary Portland Cement (OPC) mixing without nanomaterials. The physical properties of the nanomaterials are shown in Tables 1–3, respectively.

The main purpose of this study is the effectiveness of the concentrate solution method for the large-capacity dispersion and practical preparation method of the triple nanomaterial. Two methods of mixing nanomaterials were utilized (Fig. 1). The first method involved preparation of an aqueous solution by mixing nanomaterials with the total mixing water mainly used in previous research. This method requires sonication of the nanomaterial to the total aqueous solution to be blended. Since the equipment mainly used for sonication has a limit in its capacity, not only the maximum mixing amount is limited, but also the time to prepare the aqueous nanomaterial solution is lengthened.

The second method proposed in this study is to prepare a concentrated aqueous solution of nanomaterials by mixing nanomaterials in 1/4 of the total mixing water, and to mix the concentrated aqueous solution of nanomaterials with the remaining mixing water. The mixing water used for the preparation of the concentrate is DI water to minimize the reaction with nanomaterials. In this way, the number of sonication cycles is reduced about 1/4 times compared to the first method. In addition, in this study, the efficiency of the concentrated aqueous solution was maximized by increasing the amount of aqueous solution by about 9 times during a single sonication, and it was attempted to compare the results with the material test results for the non-concentrated aqueous solution.

According to the results of previous studies [28,29], it was reported that if the sonication time is increased, the effect is not significant after ultra-sonication for a certain period of time. Accordingly, in this study, in the first method, ultrasonic treatment was performed for 15 min with reference to the time suggested in the previous study results; and in the second method, it was increased to 20 min. The mix proportion table for a single sonication for each aqueous solution preparation method was performed as shown in Table 4**.** Each mix identification (ID) is the name of the GCS (GO, f-CNTs, NS) composite designated by the amount of GO incorporated. The second section of the ID denotes that N is a non-concentrated aqueous solution, and C is a concentrated aqueous solution. For example, a concentrate containing 0.02 wt% of GO becomes 0.02 GCS-C.

3.2. Mixing procedure

The mixing table according to the change of the mixing method is shown in Table 5 below. The first letter 'M′ of Mix ID is mortar and 'C′ is concrete. In the case of concrete, the third term of the identification is omitted because the concentrate is used in all cases. Mortar was mixed in accordance with KS ISO 679:2009 [30] and ASTM C348–21 [31], and the concrete was formulated according to RILEM TC 150 ECM [32]. The materials used for the formulation were Portland cement, DI water, and standard sand. Concrete was mixed using tap water, fine aggregate, and coarse aggregate. In this study, 25 mm maximum size coarse aggregates were utilized, which is common in concrete mixes.

According to the scale change of the cement composite, different equipment was used for the mixer. The mortar mixer used a 40-L capacity mortar mixer, and the concrete mixer used a twin-screw spiral mixer. The mixing procedure is shown in Fig. 2. The mortar was prepared by first adding water into the mixer, then mixed with the entire amount of cement. After that, the entire amount of standard sand is added. When mixing concrete, the aggregate and cement were dry-mixed first. After that, tap water and concentrated aqueous solution of nanomaterials were dropped.

3.3. Test method

The dispersion of the triple nanomaterial was evaluated by UV–VIS (Thermo Scientific, Genesys 180, USA). The range of UV–VIS absorption spectroscopy is 190–1000 nm. The compressive strength tests were performed with a 50 mm × 50 mm × 50 mm specimens in accordance with ASTM C349–18 [33], and according to ASTM C348–21, 40 mm × 40 mm × 160 mm specimens were fabricated for the flexural strength test, and a compressive strength tests were performed with two pieces after the flexural test. Six specimens were

Table 1
Physical properties of f-CNTs.

Diameter (nm)	Length (μm)	Specific surface area (m^2/g)	Purity (wt%)
5–15	10–30	> 200	> 95

Table 2
Physical properties of GO.

Thickness (nm)	Layer diameter (μm)	Purity (%)
~ 1	0.2–10	> 98

Table 3
Physical properties of NS.

Average particle size (nm)	Specific surface area (m^2/g)	Purity (%)
110	> 23	> 99

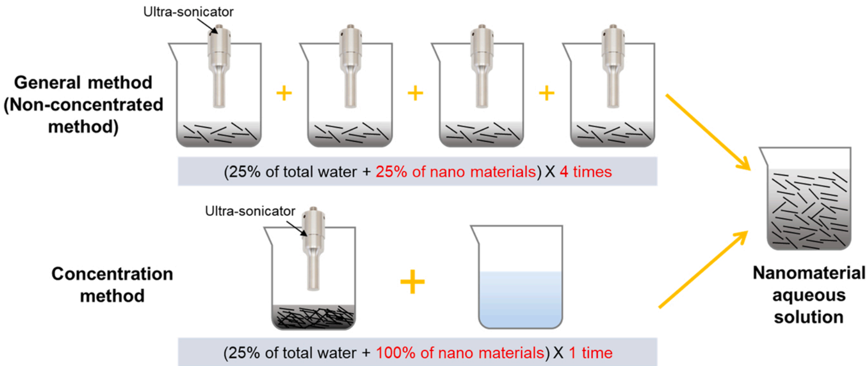


Fig. 1. Concept of nanomaterial aqueous solution manufacturing method.

Table 4
Single ultrasonic dispersion mixing ratio for each type of aqueous solution.

Type of aqueous solution	Mix ID	Water (g)	CNTs (g)	NS (g)	GO (g)	Ultra-sonication time
Non-concentrated solution	0.02GCS-N	30	0.01 (0.01)*	1.0 (1.0)*	0.02 (0.02)*	15 min
	0.04GCS-N				0.04 (0.04)*	
	0.06GCS-N				0.06 (0.06)*	
Concentrated solution	0.02GCS-C	270	0.483 (0.01)*	48.3 (1.0)*	0.966 (0.02)*	20 min
	0.04GCS-C				1.932 (0.04)*	
	0.06GCS-C				2.898 (0.06)*	

*weight percent of nanomaterials to cement (unit: wt%)

used in the compressive strength tests for each non-concentrated solution and 18 samples for the concentrated solution. When preparing a mortar flexural tensile strength specimen, it is practically difficult to evaluate it with a sufficient number of specimens because it requires a fairly large number of ultrasonic treatments when mixed with a non-concentrated solution. Therefore, in this study, the flexural tensile strength was evaluated only when it was formulated as a concentrate.

For the concrete strength test, the compressive strength and splitting tensile strength tests were performed. The compressive strength test was performed by manufacturing Φ100 mm × 200 mm specimens according to ASTM C39/39 M-21 [34] and KS D 2403 [35]. Splitting tensile strength test was also performed by manufacturing a Φ100 mm × 200 mm specimen. The loading plate for splitting tensile strength test was made equal to the length of the specimen so that the load was applied evenly over the entire length. Concrete mixing was performed 5–6 times on various days depending on the mixing ratio.

Usually, a compressometer is used to check the stress-strain curve in concrete. However, since the concrete used in this study is high-strength concrete, a compressometer cannot be used, so strain gauges are attached to the upper, middle, and lower positions to confirm the concrete stress-strain relationship.

To check the horizontal strain and Poisson's ratio, the horizontal strain was attached together. The material test photos for mortar and concrete are shown in Fig. 3.

Table 5
Mix proportion of cement mortar and concrete.

	Mix ID	Type of aqueous solution	W/C	W (kg/m^3)	C (kg/m^3)	S (kg/m^3)	A (kg/m^3)	CNT (wt%)	NS (wt%)	GO (wt%)	Remark
Mortar	M-OPC	–	0.3	251 (0.54)*	836 (1.8)*	1257 (2.7)*	–	–	–	–	Water: DI water
	M-0.02GCS-N	NC	0.3	251 (0.54)*	836 (1.8)*	1257 (2.7)*		0.01 (0.00018)*	0.1 (0.018)*	0.02 (0.00036)*	Sand type: Standard sand
	M-0.04GCS-N									0.04 (0.00072)*	
	M-0.06GCS-N									0.06 (0.00108)*	
	M-0.02GCS-C	C	0.3	251 (1.08)*	836 (3.6)*	1257 (5.4)*		0.01 (0.00036)*	0.1 (0.036)	0.02 (0.00072)*	
	M-0.04GCS-C									0.04 (0.00144)*	
	M-0.06GCS-C									0.06 (0.00216)*	
Concrete	C-OPC	–	0.22	159	335	930	895	–	–	–	Water:
	C-0GCS	C		(8.64)*	(38.64)*	(32.33)*	(50.21) *	0.01 (0.00386)*	0.1 (0.386)*	–	tap water Sand type:
	C-0.04GCS							0.01 (0.00386)*	0.1 (0.386)*	0.04 (15.456)*	fine aggregate

W: water, C: cement, S: fine aggregate, A: coarse aggregate
*actual mixing amount (unit: kg)

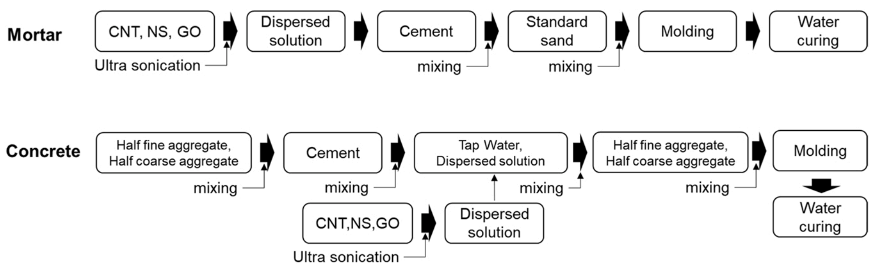


Fig. 2. Mortar and concrete mixing procedure.

4. Results and discussion

4.1. Effect of dispersion method

The absorbance of the sonicated solution for the entire aqueous solution and the sonicated solution for the concentrated solution is compared and shown in Fig. 4. Dispersion was compared in two aqueous solutions. One is mixed with DI water and the second is $Ca(OH)_2$ aqueous solution. In $Ca(OH)_2$ aqueous solution, the reaction of the GCS composite can be simulated in high alkali state due to the hydration reaction of cement [36].

As a result of dispersion evaluation, when diluted in DI water, 0.06GCS, containing the most GO, showed the greatest dispersion, but when diluted in $Ca(OH)_2$ aqueous solution, 0.04GCS was confirmed to be the largest. In the concentrated solution, it was also confirmed that the largest dispersion was shown at 0.04GCS. In the case of comparing the concentrated solution and the general sonicated solution, it was confirmed that the dispersion of the two solutions was similar, so the amount of the sonication of the aqueous solution was increased and the time was shortened compared to the amount of the solution. It was confirmed that the difference was not significant, and it was confirmed that the largest dispersion was observed in the amount of specific GO (0.04GCS), as in the previous study [26].

4.2. Strength of cement mortar with triple hybrid nanomaterials

The results of the mortar strength test are shown in Table 6 and Fig. 5. As for the compressive strength of the specimen subjected to sonication on the total mixing water without concentration, the highest compressive strength was shown at 0.04GCS, the same as the dispersion evaluation. The compressive strength increase rate of 0.04GCS compared to OPC is about 11%. These results showed the same pattern as those of the previous study [26], but the increase was not as large as that of the previous study. It was confirmed that the same aspect appeared when compared with the result of mixing using the concentrated aqueous solution. Accordingly, it is

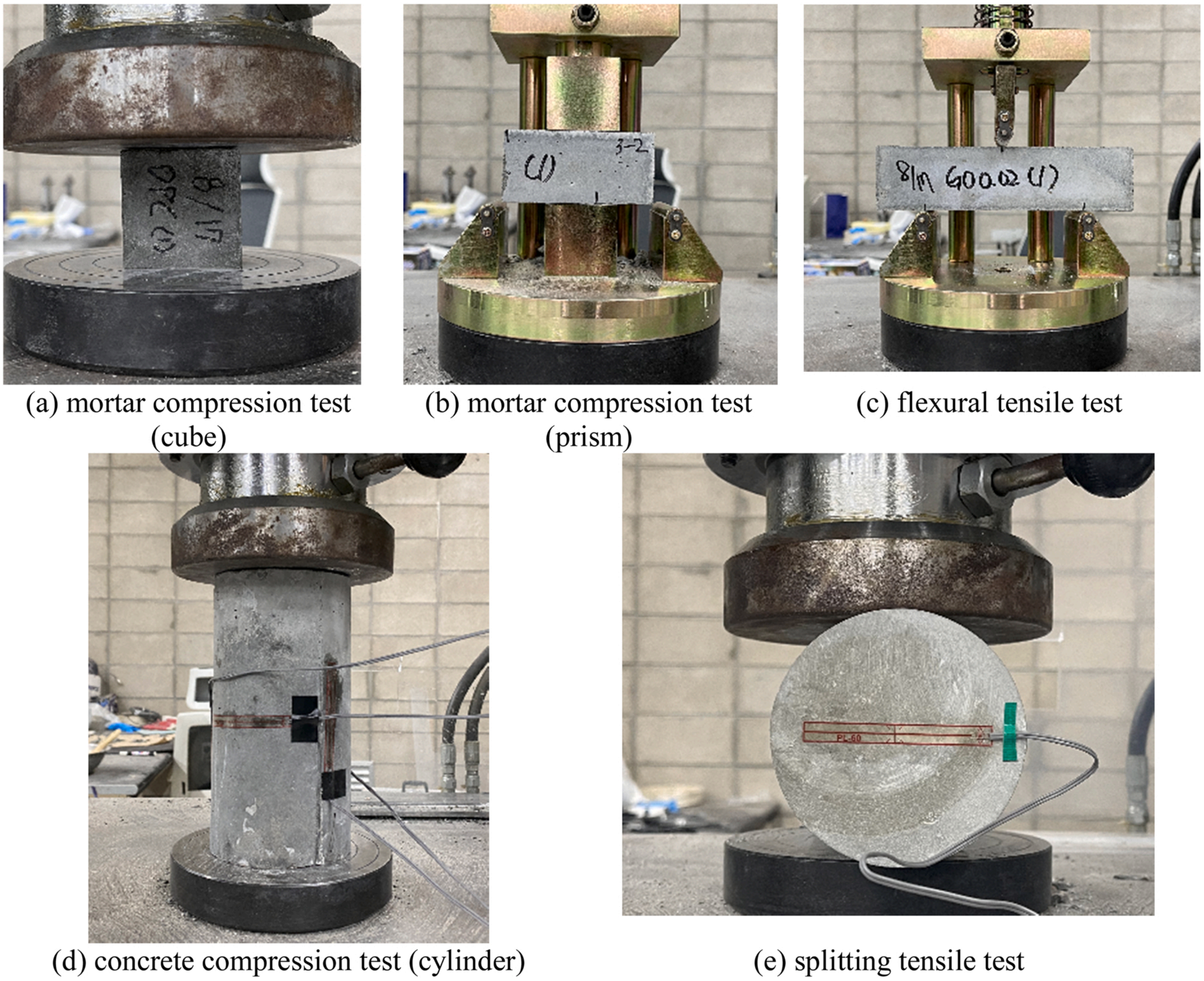


Fig. 3. Mortar and concrete strength test.

expected that the increase in compressive strength by the mixing of the concentrated solution can express more than the same effect as the case of sonicating the entire solution. The coefficient of variation of the data used to evaluate the concentrate is 1.47–3.55% based on the compressive strength at 28 days. In the case of flexural strength, the increase in strength due to the incorporation of nanomaterials had no significant effect. The reason for the lack of significant difference in the increase in tensile strength compared to the increase in compressive strength requires additional analysis.

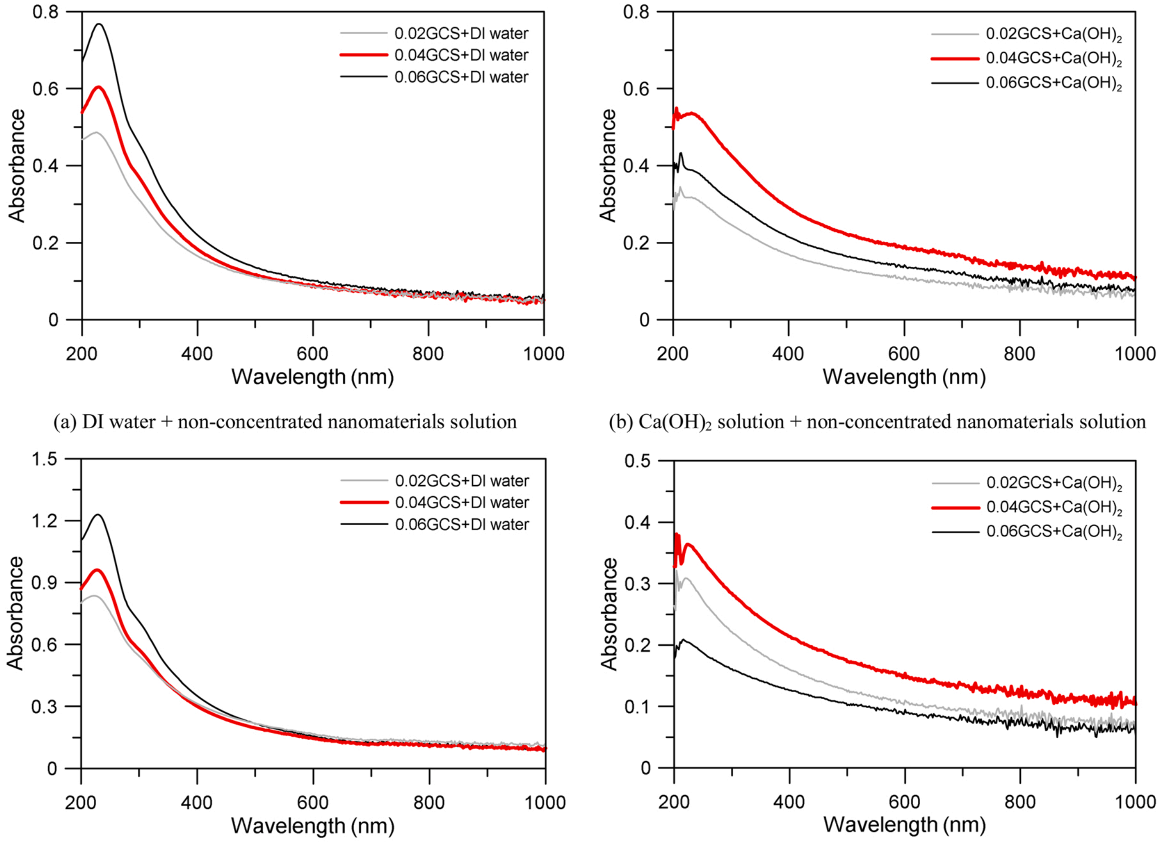
4.3. Mechanical properties of concrete with triple hybrid nanomaterials

4.3.1. Compressive sand tensile strength

Concrete mixing was conducted with the amount of GO as a variable in order to evaluate the mechanical properties according to the degree of dispersion and the compressive strength test. The number of compressive strength specimens for OPC, 0GCS, and 0.04GCS were 46, 36, and 40, respectively, and the number of split tensile strength specimens was 34, 32, and 43, respectively. A summary of the strength test results is shown in Table 7.

As a result of the concrete strength test, it can be confirmed that the improvement in compressive strength is not significant. The NS nanomaterial has the greatest effect on improving the compressive strength of concrete. In the previous study [37,38], the compressive strength of high-strength concrete mixed with coarse aggregate did not significantly increase the compressive strength by about 3–8% due to the influence of coarse aggregate, and this test showed the same results as the previous study. The modulus of elasticity of concrete was calculated as the slope from $0.4f_c^{'}$ to the origin [39]. The modulus of elasticity of the concrete increased by about 10% and the splitting tensile strength increased by about 23%. Since the modulus of elasticity increases with the incorporation of nanomaterials, the ε_0 reaching the maximum compressive strength was small.

To evaluate the mixing control results for nanomaterials, Fig. 6 shows the frequency distribution and probability density function



(a) DI water + non-concentrated nanomaterials solution

(b) $Ca(OH)_2$ solution + non-concentrated nanomaterials solution

(c) DI water + concentrated nanomaterials solution

(d) $Ca(OH)_2$ solution + concentrated nanomaterials solution

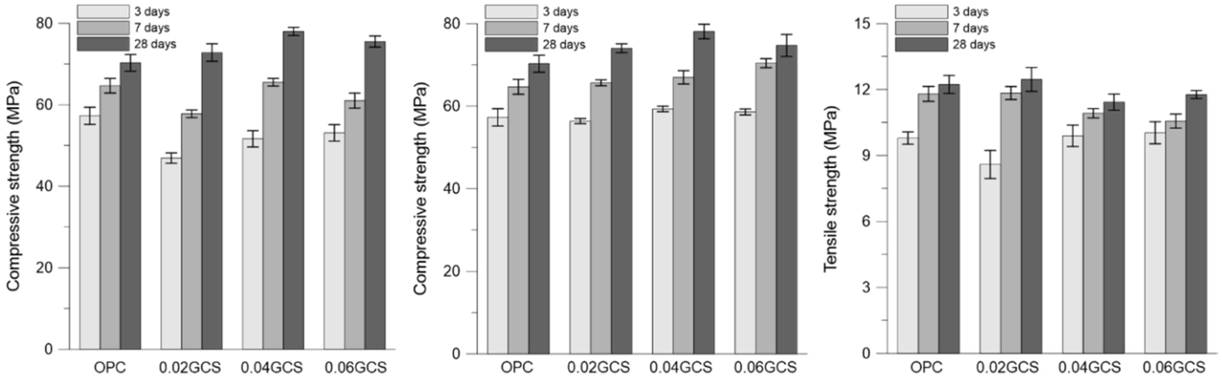
Fig. 4. UV-Vis results for the triple nanomaterials.

Table 6
Cement mortar strength test results.

Mix ID	3-Day Compressive strength (MPa)	7-Day Compressive strength (MPa)	28-Day Compressive strength (MPa)	3-Day Flexural strength (MPa)	7-Day Flexural strength (MPa)	28-Day Flexural strength (MPa)
M-OPC	57.28 (3.65)*	64.68 (2.79)*	70.28 (2.92)*	9.79 (2.88)*	11.80 (2.88)*	12.23 (3.33)*
M-0.02 GCS-N	46.9 (2.73)*	57.77 (1.63)*	72.83 (2.96)*	–	–	–
M-0.04 GCS-N	51.63 (3.91)*	65.52 (1.43)*	78.01 (1.29)*	–	–	–
M-0.06 GCS-N	53.08 (3.82)*	61.01 (3.00)*	75.51 (1.81)*	–	–	–
M-0.02 GCS-C	56.37 (1.11)*	65.66 (1.09)*	74.03 (1.47)*	10.78 (1.70)*	11.52 (2.07)*	12.79 (0.88)*
M-0.04 GCS-C	59.32 (1.12)*	66.97 (2.41)*	78.10 (2.26)*	11.09 (2.13)*	11.68 (1.88)*	11.48 (3.04)*
M-0.06 GCS-C	58.58 (1.21)*	70.40 (1.57)*	74.69 (3.55)*	10.36 (8.54)*	11.66 (4.67)*	11.04 (3.27)*

* coefficient of variation (unit: %)

(PDF) for the test results. The ACI committee 214 [40] classifies the results of mixing control as the coefficient of variation for the results of the concrete strength test. A coefficient of variation of 15 % is defined as the average control, less than 10% as excellent control, and greater than 20 % as poor control. As a result of statistical analysis of the compressive strength data, it was confirmed that all coefficients of variation for compressive strength were within 10 %. In the case of splitting tensile strength, unlike other formulations, the 0GCS formulation had the largest coefficient of variation of 14.71 %. This can be judged that the nanomaterial mixing control is not as good as compared to 0.04GCS due to agglomeration when it is mixed using a concentrated aqueous nanomaterial



(a) compressive strength of non-concentrated solution (b) compressive strength of concentrated solution (c) tensile strength of concentrated solution

Fig. 5. Strength of cement mortar.

Table 7
Concrete strength test results.

Mix ID	f_c' (MPa)	ε_0	E_c (MPa)	f_{sp} (MPa)
C-OPC	82.78 (6.20)*	0.00268 (7.93)*	32302 (9.86)*	4.25 (10.84)*
C-0GCS	83.90 (6.65)*	0.00254 (13.14) *	33989 (12.87)*	5.14 (14.71)*
C-0.04GCS	83.43 (6.10)*	0.0026 (11.53)*	34980 (11.36)*	5.21 (9.10)*

f_c': concrete compressive strength, ε_0: strain at peak stress, E_c: modulus of elasticity, f_{sp}: splitting tensile strength
*coefficient of variation (unit: %)

solution without GO in the actual formulation. This corresponds to the TEM results of the previous study [26] in which the NS was more agglomerated in 0GCS. Such agglomeration is more pronounced in the concentrate, which can be interpreted as a high variation.

The splitting tensile strength according to the concrete compressive strength is shown in Fig. 7. The relationship between compressive strength and splitting tensile strength was compared with the average of each batch of concrete mixed five times. ACI 363R-10 [39] and Hueste et al. [41] report that the splitting tensile strength is proportional to the square root of the compressive strength. Mokhtarzadeh et al. [34] report that the index is proportional to the power function rather than 0.5, and in a recent study, an index other than 0.5 fits the data better for high-strength concrete [39]. Dewar et al. [42] stated that the splitting tensile strength compared to the compressive strength decreased as the high strength concrete. However, as the relationship between the splitting tensile strength of high-strength concrete has not yet been defined, this study evaluated the relationship of the splitting tensile strength to the square root of the compressive strength ($f_{sp}/\sqrt{f_c'}$). The $f_{sp}/\sqrt{f_c'}$ of OPC was 0.485 on average. 0GCS and 0.04GCS had an average of 0.55, which was about 14% larger. Although it was all smaller than the 0.56 coefficient suggested by ACI 318–19 [39], the tensile strength of splitting increased according to the incorporation of nanomaterials, and it is expected that the GCS composite can improve the tensile strength of OPC regardless of dispersion due to bridging effect of f-CNTs.

4.3.2. *Modulus of elasticity*

In Section 4.3.1 above, the modulus of elasticity according to the incorporation of nanomaterials was calculated. In order to analyze this in detail, the distribution of modulus of elasticity according to the concrete compressive strength for each specimen was analyzed (Fig. 8). As for the modulus of elasticity, the square root of ACI 318–19 [39] is proportional to the compressive strength, but Eurocode2 [43] is proportional to the 0.3 square of the compressive strength, and fib Model Code 2010 [44] and KDS 14 20 10 [45] are defined as proportional to $\sqrt[3]{f_c'}$ In this study, the coefficient was compared with respect to the cube root of the compressive strength ($E_c/\sqrt[3]{f_c'}$).

The $E_c/\sqrt[3]{f_c'}$ of OPC is 7656, and 0GCS and 0.04GCS are 8204, and it can be confirmed that the coefficients increase by about 3% and 7%, respectively. In all mix proportions, it was slightly smaller than the modulus of 8500 suggested by KDS 14 20 10 [45], but the GCS composite can also improve the modulus of elasticity of OPC like the previous splitting tensile strength results.

4.3.3. *Compressive stress-strain relationship*

Shah et al. [46] report that the Poisson's ratio of concrete and the time of increase of the volumetric strain of concrete change according to the size of the aggregate and the condition of the interface treatment of the aggregate. This phenomenon is due to the

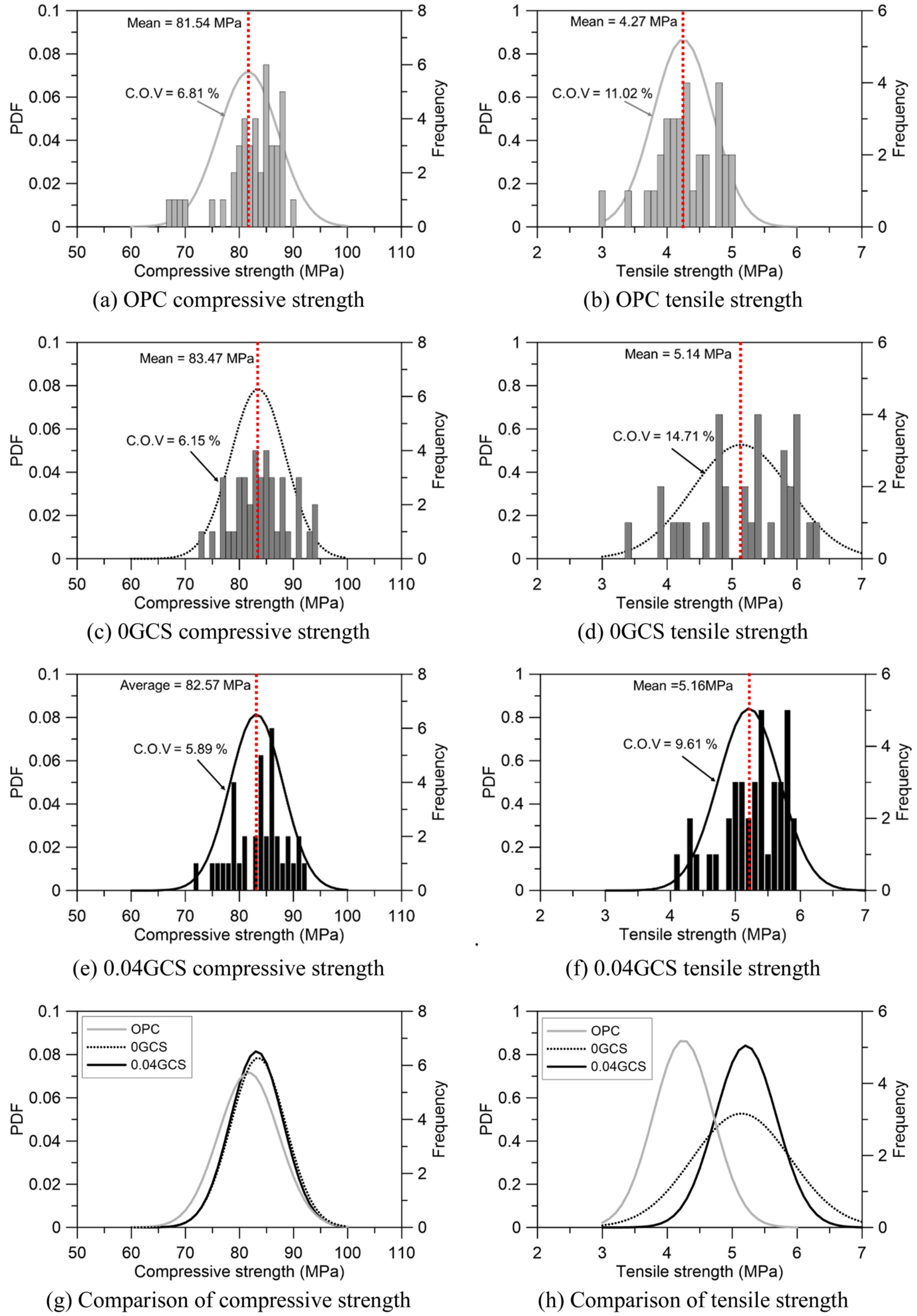


Fig. 6. Strength of concrete.

heterogeneous characteristics of concrete containing both fine and coarse aggregates, unlike cement paste. When the cement paste is compressed, there is no volume expansion, but in concrete, microcracks occur between the aggregate and the cement paste and the volume expands. This volume expansion shows inelastic behavior under uniaxial compression.

In previous studies [10,47], it is reported that dispersion of nanomaterials improves the strength of ITZ and improves the interfacial

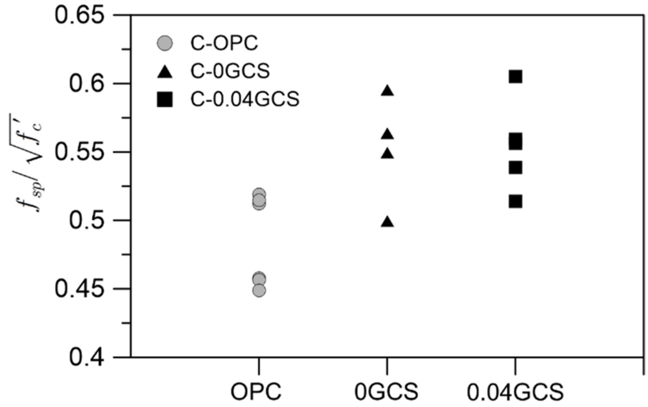


Fig. 7. Relationships between nanomaterials and splitting tensile strength.

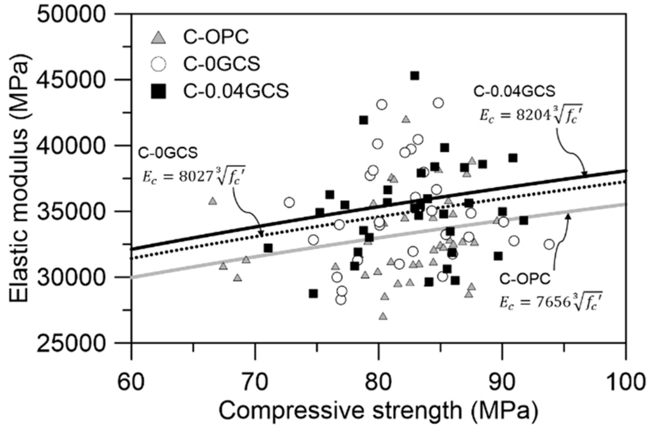


Fig. 8. Relationships between modulus of elasticity and compressive strength.

properties between the aggregate and cement paste. However, since these results have a great influence on the mechanical properties of concrete such as critical stress, Poisson's ratio, and concrete yield point, the effect of mixing of nanomaterials should be analyzed.

To evaluate the critical stress and Poisson's ratio according to the volumetric strain of concrete, gauges were attached as mentioned in the previous experimental plan, and the coordinate system for the gauge attachment details and strain is shown in Fig. 9. In order to measure the average strain of the specimen as it was not possible to use a compressometer in high-strength concrete, vertical gauges (ε_1) were attached to the top, middle, and bottom of the specimens. To measure the horizontal strain ($\varepsilon_2, \varepsilon_3$), a gauge was attached to the side of the specimen in the horizontal direction. Volumetric strain can be calculated as in Eq. (1). where ε_h is the hoop strain and is the gauge value attached in the horizontal direction. The corresponding values are equal to ε_2 and ε_3 (Eq.(2)). Axial strain was measured as the average of three measurements as in Eq. (3).

$$\varepsilon_v = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_1 + 2\varepsilon_h \tag{1}$$

$$\varepsilon_h = \varepsilon_2 = \varepsilon_3 \tag{2}$$

$$\varepsilon_1 = \frac{\varepsilon_{1h} + \varepsilon_{1m} + \varepsilon_{1l}}{3} \tag{3}$$

Critical stress can be obtained from stress-strain curves for axial strain and volumetric strain. As shown in Fig. 10, the stress corresponding to the maximum value of volumetric strain obtained through Eq.(1) is σ_{cr}, and the axial strain at this time is ε_{cr} From this point, the elastic section of concrete can be defined [48], and after that, it can be interpreted that concrete behaves inelastic in uniaxial compression state.

The experimental results and stress-strain curves are shown in Table 8 and Fig. 11, and the stress-Poisson's ratio curve is shown in Fig. 12. Here, the stress-strain curve is shown based on representative experimental results to confirm the change of volumetric strain according to the dispersion of nanomaterials at the same elastic modulus. And the compressive strength compared to the critical stress (f_{cr}/f_c') was calculated and the elastic ranges were compared. The critical stress of OPC is about 73 % compared to the maximum

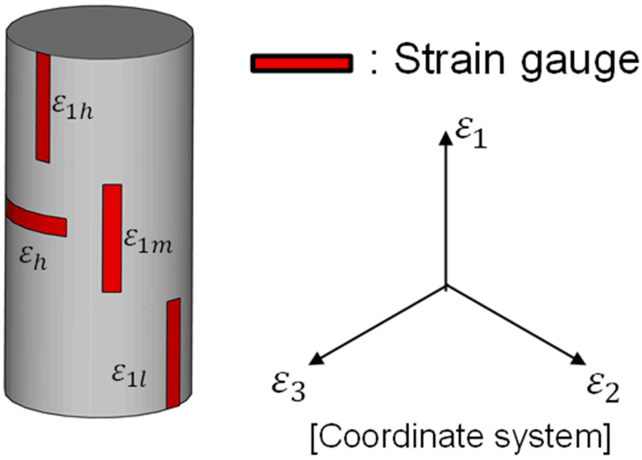


Fig. 9. Strain gauge attachment in concrete uniaxial compression test.

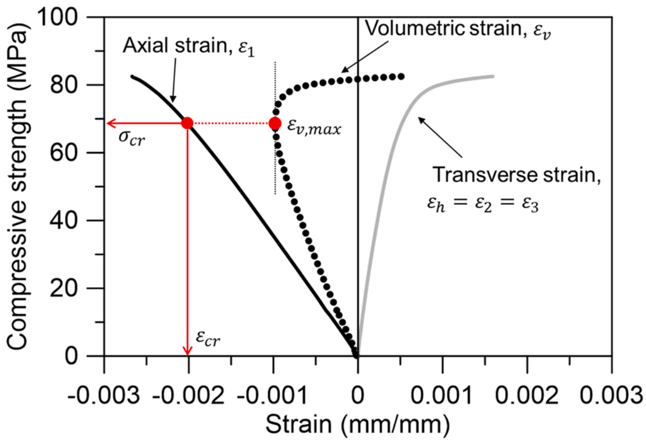


Fig. 10. Schematic drawing of critical stress.

Table 8
Critical stress and Poisson's ratio of concrete.

Mix ID	f_c' (MPa)	f_{cr} (MPa)	f_{cr}/f_c'	ε_{cr}	υ
C-OPC	82.78 (6.20)*	60.09 (11.48)*	0.73	0.0019	0.24 (13.76)*
C-0GCS	83.90 (6.65)*	64.41 (16.45)*	0.77	0.00195	0.25 (22.87)*
C-0.04GCS	83.43 (6.10)*	68.28 (9.81)*	0.82	0.002	0.20 (23.57)*

f_c': concrete compressive strength, ε_0: strain at peak stress, υ: Poisson's ratio, f_{cr}: critical stress, E_c: modulus of elasticity, f_{sp}: splitting tensile strength
*coefficient of variation (unit: %)

compressive stress, 0GCS is 77 %, and 0.04GCS is 83 %, which is about a 4 % and 10 % increase compared to OPC. In addition, it can be seen that the strain at the critical stress point also increased by about 5 %. The Poisson's ratio shown in Table 8 is the value obtained by dividing the horizontal strain by the vertical strain at $0.4f_c'$. It can be observed that the 0.04GCS formulation is about 20 % smaller than the other mix proportions.

As a result of the analysis, the critical stress increased as the dispersion of nanomaterials improved, and the inelastic behavior of concrete was reduced. This phenomenon, which appeared in the mixing using the same aggregate, is more dependent on the mechanical properties between the cement paste and the aggregate than on the effect of the cement paste itself. Accordingly, it is expected that the dispersion of the nanomaterial will increase the bond strength at the interface between the aggregate and the cement paste,

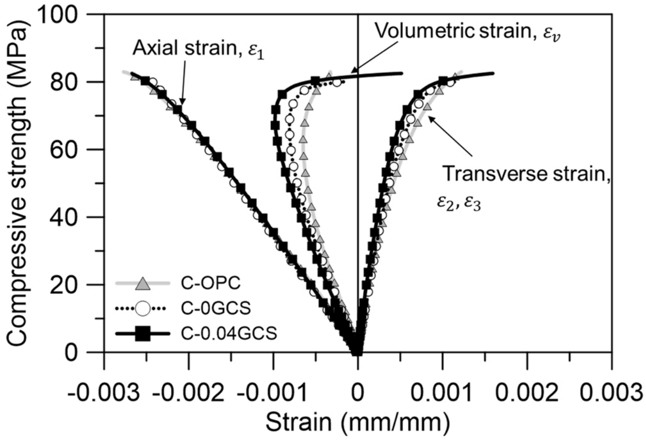


Fig. 11. Stress-strain relationship of concrete.

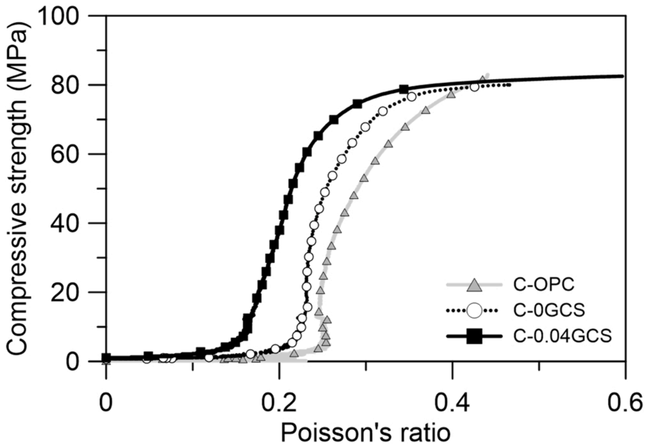


Fig. 12. Stress-Poisson's ratio relationship of concrete.

thereby improving the mechanical properties of concrete. In a future study, the analysis of ITZ between concrete and the interface according to the dispersion of nanomaterials should be examined in detail.

5. Conclusions

In this study, the mechanical properties of concrete were evaluated using a concentrated aqueous solution of nanomaterials for practical application of nanomaterials. Triple nanomaterials (f-CNTs, NS, GO) were used to improve the mechanical properties of concrete by increasing the dispersion of the concentrated aqueous nanomaterial solution without a special pretreatment process. The strength according to the dispersion of the triple nanomaterial was evaluated in the mortar, and material tests were performed on concrete based on the result. The results are as follows:

(1) As a result of confirming the dispersion by the triple nanomaterial, 0.04GCS showed the greatest dispersion in $Ca(OH)_2$ in a high alkali state. In the mortar strength test, 0.04GCS showed the greatest compressive strength as in the dispersion evaluation. These results were the same for the non-concentrated solution and the concentrated solution. Accordingly, it is determined that the concentrated solution exhibits the same effect as the sonication method used in previous methods.

(2) As a result of statistically comparing the compressive strength and tensile strength data of a number of concrete cylinders incorporating nanomaterials, the average and coefficient of variation of the compressive strength did not differ significantly. The splitting tensile strength was similar to that of 0GCS and 0.04GCS containing GO, which is about 1.23 times that of OPC. The 0GCS data showed a relatively large variation, and it is judged that the data is not evenly distributed due to the aggregation of nanomaterials. It was confirmed that the modulus of elasticity of the concrete increased with the mixing of nanomaterials, and 0GCS and 0.04GCS were improved by 3% and 7% compared to OPC, respectively. Therefore, it is shown that the mechanical properties of concrete increase according to the mixing and dispersion of nanomaterials.

(3) A strain gauge was attached to the specimen to evaluate the uniaxial compression behavior of concrete mixed with nanomaterials. It can be seen that the critical stress increased according to the GO incorporation, and it was found to increase by about 10% according to the GO incorporation compared to the maximum stress. In addition, it was confirmed that the Poisson's ratio also decreased by about 20% as the dispersion increased. Due to the effect of nanomaterials, the volume expansion of concrete was reduced, and in particular, the better the dispersion, the greater the range of elastic behavior of concrete. Accordingly, it is judged that the improvement of dispersion according to the mixing of triple nanomaterials enhances the bond strength of the interface between aggregate and cement paste.
(4) In this study, the enhancement of concrete mechanical properties was mainly evaluated, and the cause of this was described assuming the improvement of dispersion. In a future study, it is necessary to quantitatively evaluate the cause of the increase in concrete mechanical properties by analyzing it in detail for ITZ. In addition, the concrete used in this study is a study conducted only for high-strength concrete. Therefore, considering the effect of nanomaterials at various water-cement ratios, it is judged that nanomaterials can be applied more widely to concrete.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that has been used is confidential.

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