The effect of graphene nanoplatelet addition on the mechanical, durability and self-healing properties of engineered cementitious composites

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Abstract. Nanomaterial usage is an effective method to enhance the mechanical and durability properties of cementitious materials. Graphene Nanoplatelets (GNPs) are cost-efficient graphene-based nanomaterials that can exhibit graphene-like features. Although GNPs have been found to improve mechanical and durability properties, their effect on the self-healing behavior of cementitious materials, particularly Engineered Cementitious Composites (ECC), has not been examined in the literature studies. Therefore, this study aims to investigate the effects of GNP addition on mechanical, durability and self-healing behavior of ECC. During the study, the mechanical, durability, and self-healing characteristics of ECC with and without GNP were observed by using various mechanical and non-destructive test methods. Compression test, four-point bending test, resonance frequency test, ultrasonic pulse velocity test, sorptivity test, electrical impedance test and microscopic inspection were conducted. According to the test results, 0.05% GNP addition increased the compressive strength of ECC specimens. With the effect of GNP, first cracking strength, ultimate flexural strength and deformation values increased both for virgin and preloaded ECC specimens. The preloaded specimens with GNP performed similarly to virgin specimens under bending. The cracks of preloaded GNP specimens were either closed completely or extensively compared to control specimens. The crack numbers of GNP specimens after failure were also greater than that of control specimens. Accordingly, the flexural and self-healing behavior of the specimens improved with GNP addition. The effect of improvement by GNP addition was also evident in nondestructive tests. A considerable increment occurred in electrical resistance with GNP addition.

1 Introduction

There is a consistent increase in the demand for high performance construction materials due to the requirement to build structures with more resilience and sustainability. To meet this demand, the primary goal of material research is usually to improve the mechanical and durability properties of cement-based materials. The use of fibers as reinforcement is an efficient way of improving the ductility and tensile properties of cementitious materials. For instance, ultra-high performance fiber reinforced cementitious composites (UHPFRCC) are able to exhibit high tensile ductility. Engineered cementitious composites (ECC), a distinct type of UHPFRCC, include polyvinyl alcohol (PVA) fibers and present a high tensile strain capacity of up to 3 or 5%, that is hundreds of times greater compared to conventional concrete [1, 2].

Along with fibers, the nanomaterial inclusion is another effective way of enhancing the mechanical and durability characteristics of cementitious materials. Nano-silica (nano-SiO2), nano-alumina (NA), carbon-nanotubes (CNT), carbon-nanofibers (CNF), titanium dioxide nanoparticles (nano-TiO2), and graphene-based materials such as graphene, graphene oxide (GO), graphene nanoplatelets (GNP), and graphene oxide nanoplatelets (GONP) are among the nanomaterials that can be incorporated in cementitious materials [3, 4]. GNPs and GONPs, are cost-effective alternatives compared to other graphene-based nanomaterials. Because GNPs and GONPs are made up of graphene stacks, the main characteristics of graphene are often inherited by these materials. They have two-dimensional sheets with a thickness of less than 10 nanometers in their structure [5, 6]. GNPs are a viable option for the production of nano-reinforced cementitious composites due to their low cost, 2D structure, large specific surface area, and high surface-to-volume ratio. When incorporated, GNPs become attached to CSH gels and can increase the gel strength. A finer and denser microstructure is formed as a result of the reduction in weak cement hydration products by using GNPs. As the porosity decreases, the mechanical characteristics of the material improve as well [7, 8]. According to literature, since GNPs are hydrophobic, they tend to agglomerate in water. For that reason, GNPs should be evenly dispersed and stabilized before being used. GNPs are distributed into the cementitious matrix via a dry or wet dispersion technique. The GNPs are directly mixed with cement in dry dispersion using mechanical stirring [7].

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Ultrasonic treatment combined with mechanical stirring and surfactant usage has been the most commonly used method for dispersing and stabilizing GNP in cement [8]. The stability and dispersion of GNRs in water can be effectively achieved by using a polycarboxylate-based superplasticizer as a surfactant. GNPs have been seen to improve the mechanical and durability properties of cementitious materials when they are uniformly dispersed. In literature studies, it was observed that GNPs can decrease porosity and permeability against water and aggressive ion intrusion, increase compressional and flexural strength, slow down chemical attack, improve corrosion and freezing-thawing resistance [4, 5, 6, 9, 10, 11, 12, 13].

The impact of graphene nanoplatelets (GNPs) on the mechanical and durability characteristics of cementitious composites has been the subject of several studies, but the effect of GNPs on self-healing behavior, particularly for Engineered Cementitious Composites, has not been investigated. Therefore, the aim of this study is to investigate the effects of 0.05% GNP addition on the mechanical, durability, and self-healing behavior of ECC specimens.

The 0.05% GNP amount was used as a starting/reference point in this study. Because in studies with GNP usage, there were solid contributions of GNP behavior. Compressive strength test [14], four-point bending test, resonance frequency test (RF) [15], ultrasonic pulse velocity test (UPV) [16], sorptivity test [17], electrical impedance test (EI) [18], and microscopic inspection were the test methods applied in the study.

### 2 Experimental Method

#### 2.1 Materials

The primary goal of this research is to find out how Graphene Nanoplatelets (GNP) affect the mechanical, durability, and self-healing characteristics of ECC specimens. For this reason, the study was achieved through ECC production with and without Graphene Nanoplatelets.

CEM I 42.5 Portland Cement (PC), Class C fly ash (FA), fine silica sand (S) with an average grain size of 200 m, graphene nanoplatelets, water (W), polycarboxylate-ether based high range water reducing admixture (HRWRA), and polyvinyl alcohol (PVA) fibers were the materials used in the production of ECC. The mix design of ECC can be found in Table 1. The amount of GNP was the 0.05% of the total cementitious material amount and the PVA amount was 2% by volume.

#### Table 1. The mix design of ECC.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Proportions (kg/m³)</th>
<th>Ratio Name</th>
<th>Ratio Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>555</td>
<td>GNP/CM*</td>
<td>0.05%</td>
</tr>
<tr>
<td>FA</td>
<td>666</td>
<td>FA/PC</td>
<td>1.2</td>
</tr>
<tr>
<td>W</td>
<td>333</td>
<td>W/CM*</td>
<td>0.27</td>
</tr>
<tr>
<td>S</td>
<td>438</td>
<td>S/CM*</td>
<td>0.36</td>
</tr>
<tr>
<td>HRWRA</td>
<td>7.4</td>
<td>HRWRA/PC</td>
<td>1.3%</td>
</tr>
<tr>
<td>PVA</td>
<td>26</td>
<td>PVA Volume</td>
<td>2%</td>
</tr>
</tbody>
</table>

CM: Cementitious Materials

#### 2.2 Mixing

For control (CTRL) mixture, Portland cement, fly ash and sand were mixed until they were uniformly combined by using a planetary mixer. Then water and HRWRA was added to solid mix. The flow value was found as 40 cm with slump flow test. As a final step, PVA fibers were added and mixed until they were evenly distributed in the matrix. When slump flow test was applied after fiber addition, it was seen that flow value decreased to 10 cm. Once the mixing was completed, control mixture was placed into the molds in order to prepare the ECC specimens with desired dimensions. For GNP mixture, Portland cement, fly ash and sand were mixed in the planetary mixer until they were uniformly blended. GNP was added into the mixing water with polycarboxylate-ether based HRWRA and stirred. An ultrasonic bath was used to apply ultrasonic treatment on the GNP suspension. By applying ultrasonic treatment and using HRWRA as surfactant, the stability and dispersion of GNP in water were accomplished. Based on research from the literature, it was decided to use the GNP amount as 0.05% of the total cementitious materials, schedule the ultrasonic bath treatment [5, 6] with duration of 45 minutes [8, 21], and use the amount of polycarboxylate-ether-based HRWRA as about 10 times of GNP content [20, 21, 22]. Figure 1 shows the ultrasonic treatment via ultrasonic bath and dispersion & stability results of GNP suspensions with and without 45 minute-ultrasonic treatment. From Figure 1, it can be understood that ultrasonic treatment was effective on the dispersion and the stability of GNP particles.

![Fig. 1. Ultrasonic treatment via ultrasonic bath - the dispersion and stability status of GNP suspensions with and without 45 minute-ultrasonic treatment.](image-url)
Dry constituents were combined and mixed with ultrasonically treated GNP suspension and remaining HRWRA. Fibers were finally added and mixed until they were evenly distributed in the GNP mixture. The flow value which was around 41 cm before fiber addition was found to be 10 cm after fiber addition. After the mixing, the fresh GNP mix was placed into the molds for the preparation of ECC specimens. Figure 2 shows mixed status and flow of GNP mixture.

For both mixtures, all specimens made from the same batch were kept in molds for 24 hours after placing. After 24 hours, all specimens were taken out of the molds and placed inside of plastic bags to keep the moisture for autogenous curing until the age of testing. At the testing age, specimens were removed from plastic bags and related tests were conducted.

### 2.3 Specimens and Testing

Different mechanical (destructive) and non-destructive testing methods were performed on cubical, prismatic and cylindrical ECC specimens with and without GNP addition. The compression test was applied on 5x5x5 cm cubic ECC specimens. The compressive strengths of three specimens were determined at 7 and 28 days for both CTRL and GNP mixtures. Four-point bending test was applied on 18x7.5x2 cm CTRL and GNP beam specimens to determine flexural properties as well as to assess self-healing. For each mix, mechanical bending tests were performed at the 7 and 28 days. The virgin specimens were first loaded up to failure with the four-point bending test device. At the age of 7 days, the PL specimens were then preloaded to a loading level corresponding to 70% of the ultimate flexure load endured by virgin specimens. After the specimens were preloaded, the specimens were placed into a water bath at 23±2 °C to allow for self-healing to take place and hydration reactions to continue for another 14 days to evaluate self-healing. In addition to mechanical tests, virgin and preloaded beam specimens of CTRL and GNP mixes were subjected to non-destructive tests. Once PL specimens were preloaded at the ages of 7 days, the virgin and preloaded beam specimens were non-destructively tested with RF and UPV test devices and microscopic inspection was conducted on PL specimens weekly.

Cylindrical specimens were also used for non-destructive testing. By using a water cooled diamond saw, Ø10 x 5 cm puck specimens were cut from Ø10 x 20 cm cylindrical specimens. The PL puck specimens were preloaded with splitting tensile test method at the age of 7 days. After preloading, the virgin and preloaded puck specimens were tested with sorptivity and EI non-destructive tests. For all NDT methods, the specimens were placed back in water bath after the first application of NDTs. This was necessary to provide the occurrence of self-healing and the continuation of hydration reactions.

### 3 Results and Discussion

#### 3.1 Compression Test

The compression test was applied on cubic specimens according to ASTM C 109 [14] and following results in Table 2 were obtained.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>7 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTRL</td>
<td>52,47</td>
<td>67,16</td>
</tr>
<tr>
<td>GNP</td>
<td>52,61</td>
<td>72,96</td>
</tr>
</tbody>
</table>

The results of the compression test in Table 2 show that the addition of GNP had almost no impact on 7-days compressive strength values. It is evident that there is not a noticeable increase when the average compressive strength values of the 7-days-old CTRL and GNP specimens are compared.

However, the effect becomes more obvious in the 28-days results. The compressive strength value increased by 8.64% with the addition of GNP [5, 6, 9, 10, 11]. The increase in 28-day values can be attributed to the filling and nucleation effects of GNP [7, 8]. It should be noted that the margin of error for all specimens were around 1MPa.

#### 3.2 Four-Point Bending Test

Fig. 3. Four-point bending test results.
The four-point bending test was carried out on beam specimens and following graphs in Figure 3 and values in Table 3 were obtained. Figure 3 and Table 3 shows the four-point bending test results of CTRL and GNP specimens. The addition of GNP increased the first cracking strength, ultimate flexural strength, and deformation values for both virgin and preloaded specimens [9, 10]. Under bending, the preloaded GNP specimens performed similarly to the virgin specimens, better than all other CTRL specimens. This suggests that GNP addition had an improving effect on the self-healing behavior of the preloaded GNP specimens. With GNP addition, self-healing behavior of PL specimens was enhanced and specimens were able to show a better performance under bending. For both ages, it can be seen that GNP specimens presented a better flexural behavior compared to CTRL specimens of the same age.

**Table 3.** The specific values of four-point bending test.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Ult. Str. (MPa)</th>
<th>Def. at ult. Str. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTRL_7d_V</td>
<td>8,20</td>
<td>1,72</td>
</tr>
<tr>
<td>CTRL_7+14d_PL_UF*</td>
<td>8,35</td>
<td>2,11</td>
</tr>
<tr>
<td>CTRL_7+14d_V**</td>
<td>9,35</td>
<td>2,18</td>
</tr>
<tr>
<td>CTRL_28d_V</td>
<td>9,25</td>
<td>2,55</td>
</tr>
<tr>
<td>GNP_7d_V</td>
<td>11,05</td>
<td>2,30</td>
</tr>
<tr>
<td>GNP_7+14d_PL_UF*</td>
<td>11,05</td>
<td>2,56</td>
</tr>
<tr>
<td>GNP_7+14d_V**</td>
<td>13,6</td>
<td>3,76</td>
</tr>
</tbody>
</table>

*7+14d PL UF: Preloaded specimens that are used for mechanical self-healing evaluation and then loaded up to failure. **7+14d V: Virgin specimens that are used for mechanical self-healing evaluation and then loaded up to failure.

### 3.3 Resonance Frequency Test

The resonance frequency test was performed on beam specimens according to ASTM C 215 [15] and following frequency results in Figure 4 were obtained.

Resonance frequency test was conducted at transverse and longitudinal mode weekly after preloading at 7 days. Resonance frequency values were ranged between 1500 Hz to 2500 Hz for transverse and 7000 Hz to 11000 Hz for longitudinal modes. The detrimental effect of preloading was more obvious on the longitudinal mode frequency values. For both type of specimens, GNP addition positively affected the increase of resonance frequency values. In GNP preloaded specimens, the resonance frequency increase percentage were very close to CTRL preloaded specimens’. With the help of GNP addition, the resonance frequency values of virgin and preloaded specimens increased.

### 3.4 Ultrasonic Pulse Velocity Test

The ultrasonic pulse velocity test was also conducted on beam specimens according to ASTM C 597 [16] and following velocity results in Figure 5 were obtained.

In UPV test, the measurements were taken in indirect method for the inclusion of the cracks of PL specimens. The velocity values were changing between 4500 and 6000 m/s. The ultrasonic pulse velocity values were affected in a positive way with the GNP addition. In that way, velocity results presented a similarity to resonance frequency results. It is commented that the filling and nucleation effect of GNP affected the permeability of matrix [7, 8]. With the help of GNP addition, the ultrasonic pulse velocity values of virgin and preloaded specimens increased.

### 3.5 Sorptivity Test

The sorptivity test was applied on cylindrical puck specimens according to ASTM C 1585 [17] and following results in Figure 6 were obtained.

[Sorptivity Test](#)
When the results of the sorptivity test examined, it is seen that the reduction in water absorption with time was higher in sound specimens with GNP in comparison with CTRL specimens of same ages implying a better filling effect of GNP particles and formation of a finer, and denser microstructure.

For preloaded specimens of both mixtures, preloading resulted in an increase in sorptivity, however as self-healing proceed GNP mixtures were able to close their cracks and absorb less water. From this result, it is interpreted that the filling effect of GNP particles became involved and formed the finer, denser microstructure [7, 8]. Therefore, the durability and the self-healing enhancement of GNP specimens were evident.

3.6 Electrical Impedance Test

The electrical impedance test was also applied on cylindrical puck specimens according to ASTM C 1876 [18] and following results in Figure 7 were obtained.

![Electrical Impedance Test](image)

**Fig. 7.** Electrical impedance test results of CTRL and GNP specimens.

In electrical impedance test, the cracks of PL puck specimens were vertically aligned and parallel to the electrical current. When electrical impedance values of the same age CTRL and GNP specimens are compared, it can be observed that electrical impedance increases with GNP addition. This can be attributed to decrease in interconnected pores when GNP is used as electrical resistivity is dependent on the amount, connectivity and the existence of water in the pores.

Even though GNP is a conductive material, the electrical impedance values and the resistance to electrical current increased with GNP addition. At this point, it should be stated that the 0.05% GNP amount is a low concentration. And at low GNP contents, the GNP addition increases electrical resistivity instead of leading to an increment in electrical conductivity [19].

As per the sound specimens, EI values of preloaded specimens were also increased with time. The percentage of total increase in preloaded specimens is higher for GNP specimens when compared to virgin CTRL and GNP specimens. This indicated that the self-healing behavior and related electrical impedance values of the preloaded GNP specimens were definitely affected from GNP addition. Because with the self-healing, the specimens were able to resist the electrical current passing through in uniaxial direction. And this resistance leads to higher values of electrical impedance.

3.7 Microscopic Inspection

Microscopic inspection was performed on beam specimens. According to the inspection, following measurements shown in Figure 8 were taken.

![Microscopic Measurements](image)

**Fig. 8.** Microscopic measurements of preloaded CTRL and GNP beams (1mm scale).

A digital microscope was used to capture and measure the crack widths of preloaded specimens at 20x and 200x magnification. The specimens of GNP mixture preloaded at 7 days self-healed and the cracks closed to a large extent during the course of self-healing according to microscopic inspection results shown in Figure 8. In terms of cracks closure, CTRL specimens exhibit healing with a crack width decrement from 150 µm to approximately 100 µm. When observed it was seen that the cracks of GNP specimens which had originally 150 µm width got extensively closed and the specimens were able to self-heal almost completely within the same amount of time. Therefore, it can be said that the preloaded GNP specimens outperformed the CTRL specimens in terms of self-healing ability under water curing, and that the addition of GNP had a definite improving impact on the self-healing of ECC.

### Table 4. Crack numbers and average widths after failure

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Crack Numbers</th>
<th>Average crack widths after failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTRL 7d V</td>
<td>4</td>
<td>39,95µm</td>
</tr>
<tr>
<td>CTRL 7+14d PL UF</td>
<td>3</td>
<td>58,67µm</td>
</tr>
<tr>
<td>CTRL 7+14d V</td>
<td>5</td>
<td>48,35µm</td>
</tr>
<tr>
<td>CTRL 28d V</td>
<td>5</td>
<td>36,45µm</td>
</tr>
<tr>
<td>GNP 7d V</td>
<td>13</td>
<td>42,92 µm</td>
</tr>
<tr>
<td>GNP 7+14d PL UF</td>
<td>20</td>
<td>37,16µm</td>
</tr>
<tr>
<td>GNP 7+14d V</td>
<td>13</td>
<td>35,92µm</td>
</tr>
<tr>
<td>GNP 28d V</td>
<td>21</td>
<td>40,62µm</td>
</tr>
</tbody>
</table>

When Table 4 is observed, it can clearly be seen that crack numbers of GNP specimens after failure is greater than the crack numbers of CTRL specimens for all ages of four-point bending testing. Compared to CTRL specimens, GNP specimens showed a better multiple cracking behavior. Similarly, energy absorption capacity and tensile ductility of the GNP specimens were considerably higher than that of CTRL specimens. Obviously, self-healing behavior of GNP beam specimens were also positively affected by enhanced flexural performance provided by GNP usage. As for crack opening values after failure, it is observed that specimens with GNP usually showed lower crack opening values than that of CTRL specimens and crack openings remained quite tight after failure. These aspects can be attributed to the bridging effect of GNP which leads to preventing the formation of macrocracks and propagation of the microcracks [8, 9].
3.8 Possible Self-healing Mechanism

According to the four-point bending test results, some of NDT methods and microscopic inspection, it was observed that GNP specimens were able to present a better self-healing behavior than CTRL specimens. The better self-healing performance is thought to result from improving effect of GNP addition on already existing autogenous self-healing of the ECC. The promoting effect can be attributed to the nucleation effect of GNPs. Because GNPs’ large specific surface area and 2D sheet-like structure advance the nucleation effect and enhance the hydration reaction, resulting in more C-S-H gels. The graphene sheets can act as nucleation sites and bond to C-S-H as well [7,8]. It is presumed that all of these aspects of GNP played an important part on promoting the self-healing behavior of ECC specimens through improved secondary hydration and CaCO₃ formation.

4 Conclusion

In this study, the effects of GNP addition on mechanical, durability and self-healing behavior of ECC specimens were investigated. When GNP specimens were being produced, GNPs were ultrasonically treated with additional surfactant usage to provide proper stability and dispersion. During the research, the laboratory performance of ECC specimens were tested with virgin and preloaded control and graphene nanoplatelet specimens via mechanical and non-destructive test methods. Compressive strength test, four-point bending test, resonance frequency test, ultrasonic pulse velocity test, sorptivity test, electrical impedance test, and microscopic inspection were conducted on beam and cylindrical ECC specimens. According to the test results following conclusions were drawn;

1) As GNP was added as 0.05% the content of cementitious materials, an increase in 28-day compressive strength results was observed. Therefore, the positive effect of GNP addition on compressive strength was present. However, any enhancement was not observed in the 7-day compressive strength results.

2) The first cracking strength, ultimate flexural strength and deformation values greatly improved for both virgin and preloaded specimens when GNP was included. Therefore, the energy absorption capacity and tensile ductility of GNP specimens were definitely greater when compared to CTRL specimens.

3) Although preloaded specimens were exposed to the destructive effects of four point bending up to certain limit, the PL specimens with GNP were able to follow virgin GNP specimens in terms of flexural behavior. This suggest that the self-healing behavior of the preloaded GNP specimens got positively affected from GNP addition. The crack numbers of GNP specimens after failure was greater than the crack numbers of CTRL specimens for both ages of four-point bending testing.

4) According to microscopic inspection, the cracks of beam specimens were either completely closed and/or got closed to a large extent within a short time with the help of water curing after specimens were preloaded at 7 days. The preloaded GNP specimens showed a better self-healing performance under water curing when compared to the CTRL specimens in terms of crack closure with the help of enhanced flexural performance. The effect of improved self-healing by GNP addition was also evident in nondestructive tests.

5) As a summary, GNP addition had a definite positive effect on mechanical properties especially on flexural behavior. A considerable increase occurred in electrical resistance with GNP addition. Most importantly, GNP addition improved the self-healing behavior of ECC specimens.

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