Improving the mechanical properties of cementitious composites with graphite nano/micro platelets addition

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Abstract. Applications of nanotechnology in construction material industry have attracted the attention of researchers due to their exceptional mechanical properties and high potential to be used as reinforcement within cement matrix. Among all the nano materials, use of carbon based nano materials (CNM’s) is one of the most important areas of research in the field of nanotechnology in cementitious systems. In this study, nano/micro platelets of raw graphite were introduced in the cement composite to investigate its effects on the mechanical properties of resulting matrix. Graphite nano/micro platelets (GNMP’s) were added in 0.05 and 0.1 % by weight of cement. The results were quite encouraging and even with a very small addition of Graphite nano/micro platelets, considerable improvement in compressive strength was observed. Effect of added content of GNMPs on flexural strength of cement composite was also investigated using three-point bending test and a significant improvement in flexural strength of cementitious matrix was achieved.

1. Introduction:

Cement based composite materials are most widely used materials for building and construction work due to high availability, low manufacturing cost and low maintenance cost [1]. Despite of various advantages, low tensile strength and low fracture energy make cementitious materials susceptible to cracking [2]. This cracking process starts with remote nano-cracks, which then conjoin to shape micro-cracks and in turn form macro-cracks within the matrix of cement. To arrest these cracks to propagate to higher degrees, concrete is reinforced initially with fibres of micro sizes. These micro fibres do not restrict the cracks to produce at micro level but minimize their propagation to macro level [3]. If the concrete is reinforced with nano fibres, the propagation of nano cracks to micro-cracks can be impeded to a large extent [4].

Due to an ultrafine size, nano particles present several distinct advantages as potentially effective microstructural reinforcements for high strength and high performance cementitious composites [5, 6]. Having super mechanical properties and smart potentials, these nano-particles have engendered notable interest amongst the world’s research community and have been applied in many fields to fabricate new smart materials with novel functions [7, 8]. Among all conventional nano-materials, the carbon based nano materials are the most abstracting. When carbonaceous nano-particles are assimilated with traditional cementitious materials, the resulting composites possess smart multifunction properties that can be utilized for the development of super high-rise, high strength and intelligent civil infrastructure systems [9-11].

Numerous types of carbon nano particles such as graphene oxide (GO), multi wall carbon nanotubes (MWCNT) and graphene nano platelets (GNP) are utilized by the researchers to enhance the mechanical and smart properties of carbonaceous materials [12-15]. Babak et.al observed 48% increase in tensile strength by addition of 1.5 wt.% GO content [4]. Gong et.al found that intruding
0.03 wt.% GO sheets into cement paste can increase the compressive and tensile strength of cement composites by 46% and 25%, respectively, due to a reduction of pore size in cement matrix [16]. Wang et al. incorporated multiwall carbon nanotube (MWCNT) in Portland cement paste and observed 50% enhancement in compressive strength and the flexural strength of the modified paste was increased by only 10% [17]. Konsta-Gdoutous et al. observed that the addition of 0.08% of MWCNTs to cement paste resulted in 35% increase in flexural strength [18, 19]. Recently, Mokhtar observed that with the addition of 0.02% graphene oxide nano platelets (GONPs), compressive strength has increased by about 13%. While 0.03 wt% of GONPs increase the flexural strength by 41% at than that of the control paste [20].

Graphite nano/micro platelets (GNMP’s) are a type of carbon-based nano-particles that is derived from flakes of natural graphite. Natural graphite is a layered compound embodying a series of stacked, parallel, flat-structured layers of graphene. These are bi-dimensional (2D) carbon nanomaterials with nano/micro scale thickness and several micrometers diameter, and have one more dimension than carbon nanotube and carbon nanofiber [21], as shown in figure 1.

![Layered structure of graphite showing the Sp² hybridized carbon atoms tightly bonded in hexagonal rings](image)

So far, however, little attention has been paid to explore the tremendous beneficial impacts of GNMP’s in cementitious composites. In this paper, the impact of homogenous suspension of GNMPs on the compressive and flexural strength of cement-based composites was explored. Furthermore, the microstructure of the modified composites was studied and compared with the microstructure of control specimen. To study the morphology and the microstructure of the cement-based composites, field emission scanning electron microscopy (FE SEM) was used.

2. Materials and experiments:
Locally available ordinary Portland cement (Type1, Grade 53) confirming to ASTM C150 (standard specification for Portland cement) was used as binding material in mortar. Lawrencepur sand with fineness modulus of 2.3 was used to prepare mortar specimens. Graphite nano/micro platelets (GNMPs), prepared by the planetary ball milling of natural graphite flakes having mean particle size of 6.02 μm were utilized as nano/micro reinforcement. Acacia gum (AG) was used for effective dispersion of GNMPs into water.

2.1. Physical and Chemical properties of materials
Chemical composition and physical properties of Portland cement used in this research are shown in table 1. GNMPs have layered structure and the surface texture is abrasive that helps in physical bonding with cementitious matrix. Physical properties of the GNMPs, AG and sand used for this research are listed in table 2.
Table 1: Physical and chemical properties of Cement.

| Chemical composition | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO  | SrO  | K₂O  |
|----------------------|------|------|-------|-------|------|------|------|
| Content (%)          | 68.12| 15.65| 8.63  | 3.68  | 1.32 | 0.76 | 0.6  |

| Physical property    | Insoluble residue mass% | Specific gravity (g/cm³) | Specific surface area (m²/g) | Particle size (d₅₀) (µm) | Loss on ignition Mass% |
|----------------------|-------------------------|--------------------------|------------------------------|--------------------------|------------------------|
| Content              | 0.54 %                  | 3.16                     | 0.82                         | 16.40                    | 2.34                   |

Table 2: Physical properties of GNMPs, AG and Sand.

| Property                          | GNMP's Value | AG Property Value | Value | AG Specific Gravity | Sand Property Value | Value |
|-----------------------------------|--------------|-------------------|-------|---------------------|---------------------|-------|
| Surface Area (m²/g)               | 154          | Surface area (cm²/g) | 36.10 | Specific Gravity    | 1.41                |       |
| Specific Gravity                  | 1.62         | Specific Gravity   | 1.41  |                      |                     |       |
| D₅₀ (µm)                          | 6.78         | D₅₀ (µm)           | 4     |                      |                     |       |
| D₅₀ (mm)                          |              | D₅₀ (mm)           | 0.53  |                      |                     |       |

To visualize the morphology and structure of graphite nano/micro platelets field emission electron microscopy (FE SEM) was performed. FE SEM images of GNMPs shown in figure 2 have endorsed the varying particles sizes ranging from nano to micro scale. The morphology and abrasive surface texture can also be visualized in figure 2.

Figure 2: Scanning electron micrograph of a) Raw graphite. b) Milled GNMPs.

2.2. Preparation of GNMPs modified mortar specimen:

The homogenized suspensions of GNMPs were used to prepare mortar specimens. Water to cement ratio of 0.5 was fixed for all the formulations and cement to sand ratio of 1:2.75 was employed. The total mixing time including dry mixing was about 210 minutes. The detailed mixing regime is provided in Table 3.
Table 3: Mixing Regime of formulations.

| Mixing phase                              | Duration               |
|-------------------------------------------|------------------------|
| Dry Mixing                                | 30 secs (slow mix)     |
| Dry mix + Dispersed GNMPs                 | 60 secs (slow mix)     |
| Dry mix + Dispersed GNMPs                 | 120 (fast mix)         |
| Total Time                                | 210 secs               |

After mixing, prisms were casted using moulds having standard size of 40x40x160 mm³ for each formulation shown in Table 4. After dry curing of specimen in moulds for 24 hrs at 25 ± 1 °C temperature, samples were cured in curing tank for 28 days.

Table 4: Composition of mortar samples

| Denotations  | GNMP's (%) (by mass of cement) |
|--------------|--------------------------------|
| 0GNMPs       | 0                              |
| 0P05GNMPs    | 0.05                           |
| 0P1GNMPs     | 0.1                            |

*For each mix 500g of cement, 1150g of sand and 250ml of water was used

3. Results and discussion
3.1. Compressive strength.

As per ASTM-C-109, load controlled compressing testing was performed on the standard cubes having size of 40mm x 40mm at the rate of 0.25 MPA/sec after curing the specimens for 28 days. The test assembly is shown in figure 3. The results shown in figure 4 indicate a trend of increase in compressive strength of mortar with addition of GNMP’s. This enhancement in strength is directly proportion to the intruded content of GNMP’s.

Figure 3: Compression test assembly

The enhancement in strength can be attributed towards the high elastic modulus of GNMP’s as compared to cement and due to effective bonding between graphitic platelets and hydrated cement. When the load is applied to specimen, the interface between the hydration products of cement and carbon particles take more load than the interface between hydrated cement and aggregates and hence contribute to higher compressive strength of GNMP’s modified mortar.
3.2. Flexural Strength.

To determine the flexural strength, three point bending test was performed on load controlled universal testing machine (UTM) conforming to ASTM C348. The specimen size for this test was 40x40x160mm. The samples were dry cured for one day in the mold and then pond curing was done for 28 day before testing. The assembly for three point bending test in flashed in figure 5.

![Three point bending test assembly](image)

**Figure 5:** Three point bending test assembly

The test results shown in figure 6 elucidated that flexural strength has also increased with the intrusion of GNMP’s as compared to the specimen with no GNMP’s. This increase is also proportional to the added content of GNMP’s due to the ductility provided by the carbon particles. When the %age enhancement in flexural strength was observed, it can clearly be noticed that the maximum enhancement of 125% was achieved with 0.1% inclusion of GNMPs.
3.3. Microstructural analysis.

To investigate the microstructure of plain mortar and GNMP’s modified mortar, field emission scanning electron microscopy (FE SEM) was carried out. It revealed that the mechanism that is participating in strengthening and toughing of the cementitious media is crack contouring and crack branching as shown in FE SEM images. In addition, the presence of the carbon particles also limits the cracking so that the cracks do not propagate to larger sizes as in the case of conventional concrete.

Figure 7 shows microstructure of control sample, elucidating that in case of plain mortar, the crack is following straight trajectory. But in FE SEM images of modified matrix (figure 8), it is evident that the GNMPs platelet is forcing crack to change its straight path and follow a contour resulting in absorption of more energy and delaying the crack propagation.

4. Conclusions:

From the present study, it may be concluded that a remarkable improvement in the mechanical properties of concrete can be achieved with the inclusion of small fractions of GNMP’s in cement mortar.

1. Intrusion of GNMPs by 0.05 and 0.1% enhance the residual compressive strength of the hardened mortar by 165% and 216% respectively.
2. Three point bending test elucidated that flexural strength of the composites modified with 0.05 and 0.1 wt% of GNMPs increases by 62% and 125% respectively as compared to the plain cement mortar.

3. Microstructural analysis through FESEM micrograph confirmed that GNMPs act as bridges between hydrates and compel the cracks to diversify their trajectory inhibiting the crack propagation to some extent.

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