**STUDY OF GRAPHENE NANO PLATELETS IN CONCRETE**

1. **Introduction**

Concrete is the most used construction material which has gone under many evolutions but still due to its huge requirement many modifications are to be made, so it becomes more advanced composite material which helps in increasing the concrete strength[1]. The many uses of high performance concrete are limited, however, by the cement-based materials' low tensile strength, extreme brittleness, and ease of crazing. Cement composites have been suggested to have their flexural strength, toughness, and microcrack reduction enhanced by the addition of common components such as steel, natural, glass, carbon, and synthetic fibers. Although fibers may greatly enhance the flexural toughness of cement composites by postponing the emergence of macro-cracks, they are unable to prevent the creation of micro-cracks [4]. An increasing amount of nanoengineering research in the last few years has concentrated on its possible use in concrete. Because of their exceptional physical and chemical characteristics, nanoparticles added to concrete mixtures may greatly enhance their microstructure [1]. It has been found that nano-particles can fill the spaces in cement paste matrix, resulting in reduced porosity, increased strength, and improved durability. However, it should be mentioned that not all the beneficial effects of nano-particles may be realized unless they are evenly distributed throughout the matrix [2]. Nanomaterials, such as nano-kaolinite clay, nano-silica, nano-TiO2, nano alumina, and graphene, have attracted a lot of interest from researchers in the last 10 years. Research suggests that these nanoparticles, when added to cementitious materials, might increase their mechanical properties and durability[3] .

Nanomaterials come in many forms, such as carbon nanotubes (CNTs), graphene oxide (GO), reduced graphene oxide (RGO), and graphene nanoplatelets (GNPs), also known as multi-layer graphene. Among these nanomaterials, carbon nanotubes (CNTs) have been extensively used to improve the material characteristics of cementitious composites. Graphene is a single-layer sp2-bonded carbon sheet, and carbon nanotubes (CNTs) are tubes of this material on a molecular scale. Graphene and carbon nanotubes (CNTs) both have exceptional mechanical characteristics. In contrast to carbon nanotubes (CNTs), which have a Young's modulus of around 0.3 to 0.9 TPa and a tensile strength of 130 GPa, graphene has a Young's modulus of approximately 1 TPa. Carbon nanotubes may have one or more walls, depending on their structure. Prices for SWNTs and MWCNTs vary widely depending on quality and type; however, when compared to other types of carbon-based nanomaterials, GNPs stand out as a potential candidate for the creation of nano-reinforced cementitious composites due to their two-dimensional structure, large specific surface area, and high surface-to-volume ratio [9]. Additionally, GNPs may be mass-produced to meet industrial demand; their price per kilogram can be anywhere from $65 to $400 [9]. Researchers looked at how GNP affected the bond tension in HPC. The bond tension, caused by its bridging activity, was shown to be significantly reduced with the addition of GNP. In addition, there was a 73% increase in failure strain and a 30% increase in loading capacity for 0.03% GNP. Energy absorption capacity increased by 187%, flexural strength by 276%, tensile strength by 40%, and toughness by 59% when 0.3% GNP was added [1,5,9,6,10].

1. **Effect of production of graphene nano platelets on environment**

Ioanna Papanikolaou[7] found out that during manufacture of GNP, the graphite is mixed with water and heated. Exfoliation and expansion of the mixture is done using electricity. Water consumption is very less, so it has no effect on nature and toxicity produced while mining and transporting can be reduced through optimization and producing according to requirement. Most harm is done to nature while using electricity in the production of GNPs. By producing electricity through renewable energy production like wind energy, solar energy etc...we can produce graphene without harming nature or eco system. An output of 0.86 kgCO₂ is associated with 1 kg CEM I. Were as GNPs produces 0.17 kg co2 equivalent. So, we can say that the production of GNP is environmentally friendly if used as a supplement [7].

2.1 Selection of GNP product

There are a variety of GNP products available in the market, with different sizes, physical properties, and manufacturing method. All types of GNP are used to enhance the quality of the concrete material but selecting the GNP which provides better concrete strength should be our priority. Below are some of the qualities of GNP which effects the enhancement of cementitious material.

1) Graphene-based materials acts as barriers to inhibit the flow of ions due to their intrinsically impermeable character.

2) Cement hydration and microstructure densification will be accelerated by the nanoscale thickness of GNP.

3) The pore systems will be refined by blocking the linked pores using GNP's layered morphology.

**3) Types of dispersion**

The GNP particles always remains agglomerates in the water. It means that there will not be any homogeneous mixture between concrete and GNP. So, in order to get benefits from the nano materials it needs to be dispersed [8]. There are different ways to disperse GNP in concrete which will affect concrete in different ways. And they are listed below

1. By adding GNP with respect to ratio of cement normally mixed in 10% water with polycarboxylate based superplasticizer and mixed with high shear mixing for 30,60,90 minutes [9].
2. Adding the GNP with 10% water and superplasticizer and sonicating it and mixing it after sonication of 30min in high shear mixing [1,5,9,6,10].
3. Aqueous solutions of ethanol include an equivalent amount of the graphene suspension. [3].
4. A certain amount of CO890 was dissolved in water using mechanical stirring, then the GNPs powders were added into aqueous CO890 solutions, followed by ultra-sonication for 30 min in a probe sonicator [4].

So, in general GNP are dispersed using superplasticizer and mixed with concrete so that the lumps of GNP should not create the week points in the concrete. It should homogeneously mix with concrete and reduce the pores in concrete which directly increases the physical property of the concrete. Because of the presence of carboxylate groups and poly ethylene oxide (PEO) side chains in the main carbon chain, a polycarboxylate-based superplasticizer is required in this case. Dissolved in water, the GNPs, water, and PEO side chains form an interface that absorbs the primary carbon chains. This side chains will help in separating the graphene and surround it with the water particles so that the graphene gets dissolved easily this reaction is called as steric hindrance. An important process to incorporate GNP in concrete.

**4) Physical property**

**4.1 water sorptivity of the above concrete cubes**

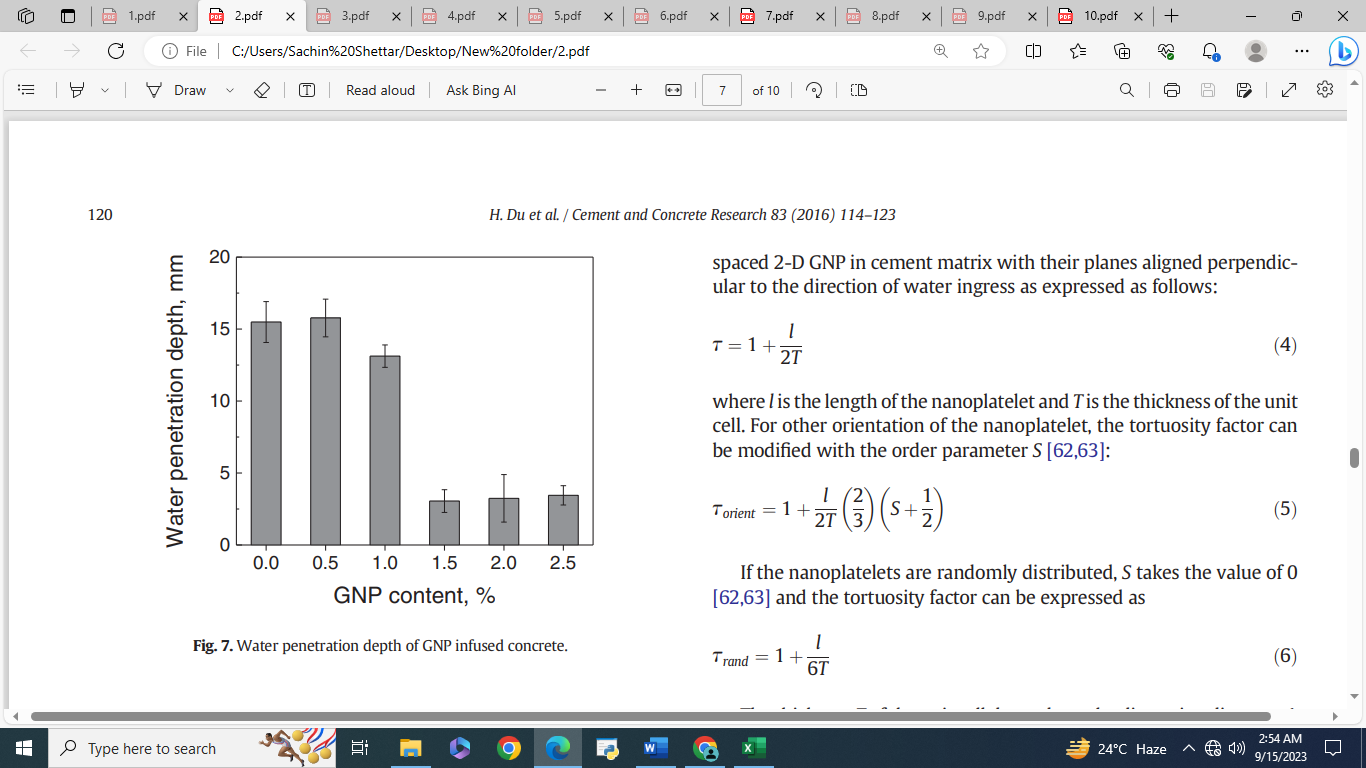
Hongjian Du showed that considering above points a mix proportion of concrete was prepared i.e., in the ratio 1:2.75:0.485 written in the ratio cement: sand: water. And 3 types of GNP were used in this plane cement concrete. Water sorptivity of the above concrete cubes were measured after 28 days using o ASTM C 1585. Results of the experiment showed that GNP having high aspect ratio will enhance the property of the concrete. The three types used in concrete have the property as given in Table 1. [2]

**Table 1 physical property of GNP [2]**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| GNP product | Density, ρ(g/cm3) | Surface area, A (m2 /g) | Diameter, D (μm) | Thickness, t (nm) | Aspect ratio, λ | Purity, % |
| A 3775 | 2.26 | 23.7 | 8.0 | 37 | 215 | 99 |
| M 850 | 2.26 | 13 | 3.6 | 71 | 50 | 99.5 |
| TC 307 | 2.16 | 352 | 2.6 | 3 | 1000 | 99.9 |

In most cases GNP A3775 was selected which enhance the concrete more efficiently. It is selected because it has average aspect ratio and it’s available easily [2].

**4.2 Porosity**  
The pore size distribution for different samples were taken after 28 days curing in the sample without GNP large pores more than 1000 mm and capillary force 1000 mm to 100 mm are detected. But in presence of GNP the pores were negligible but in case of small holes addition of GNP increase the number of pores [4]. But these are not harmful so, the decrease in the large pores and increase in the small pores will ultimately affect the compressive and tensile strength positively the porosity for different GNP is given in below bar graph.[6] The superplasticizer used induced as the dispersed also affect the porosity of the structure for example use of PS,NS,MS decrease the porosity by 12.9%, 15.2%, 16.3%[10].

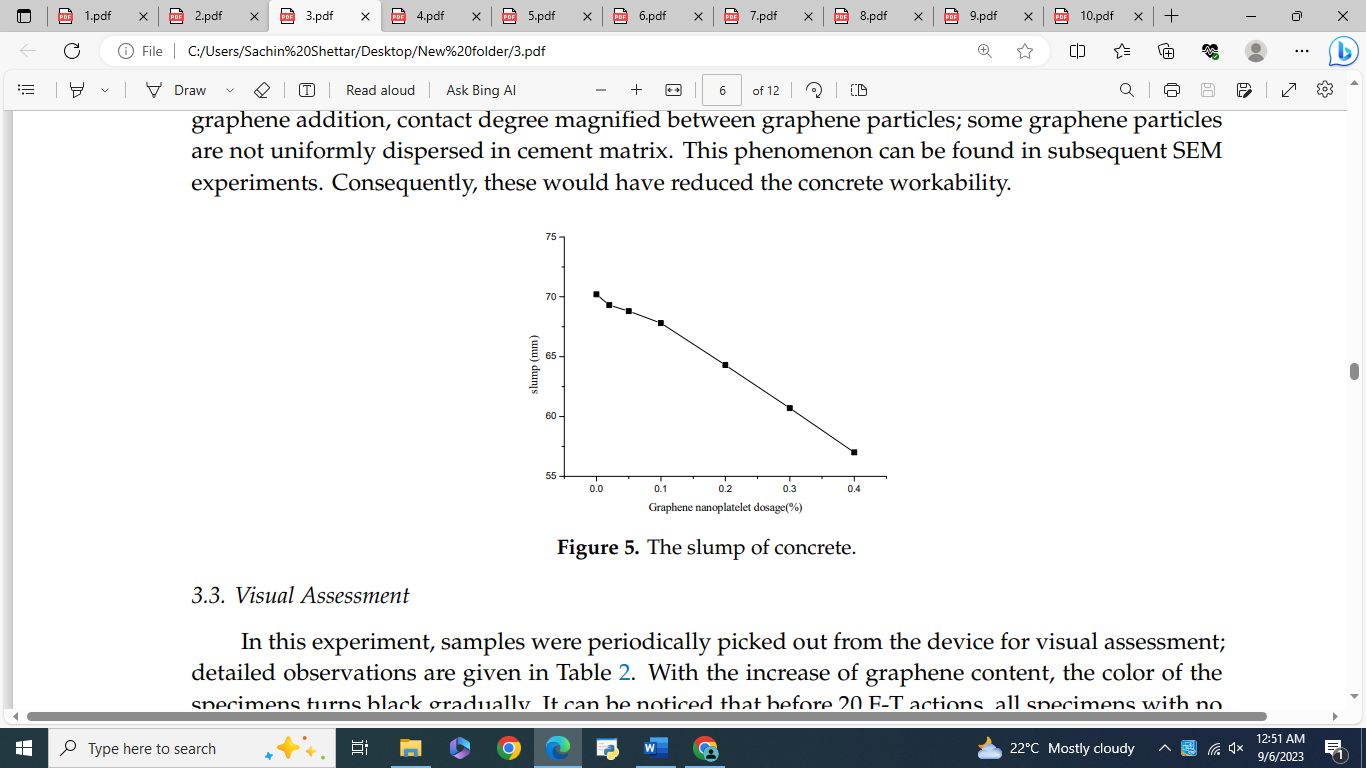


**Figure 1 Water penetration depth of GNP infused concrete [2]**

**4.3 Workability**

There is linear relationship between GNP content and slope. As we already discussed that surface to volume ratio is very large and large area absorbs more water on its surface for the concrete having water cement ratio remains constant. The workability will decrease and also with increase in GNP the particle may not be uniformly distributed. This is found through SEM analysis this will decrease the workability of the concrete [3].

we can use different superplasticizer as the dispersant like poly carboxylate, naphthalene, melamine super plasticizer when its use to display 0.06 weight percent of GNP and used in concrete it decreases its workability. But super pesticides promoted electrostatic repulsion and static repulsion among particles so by adding for practices then not only this first the GNP but also contract the negative effect of GNP so, reduction in workability of concrete for constant super plasticizer [3].

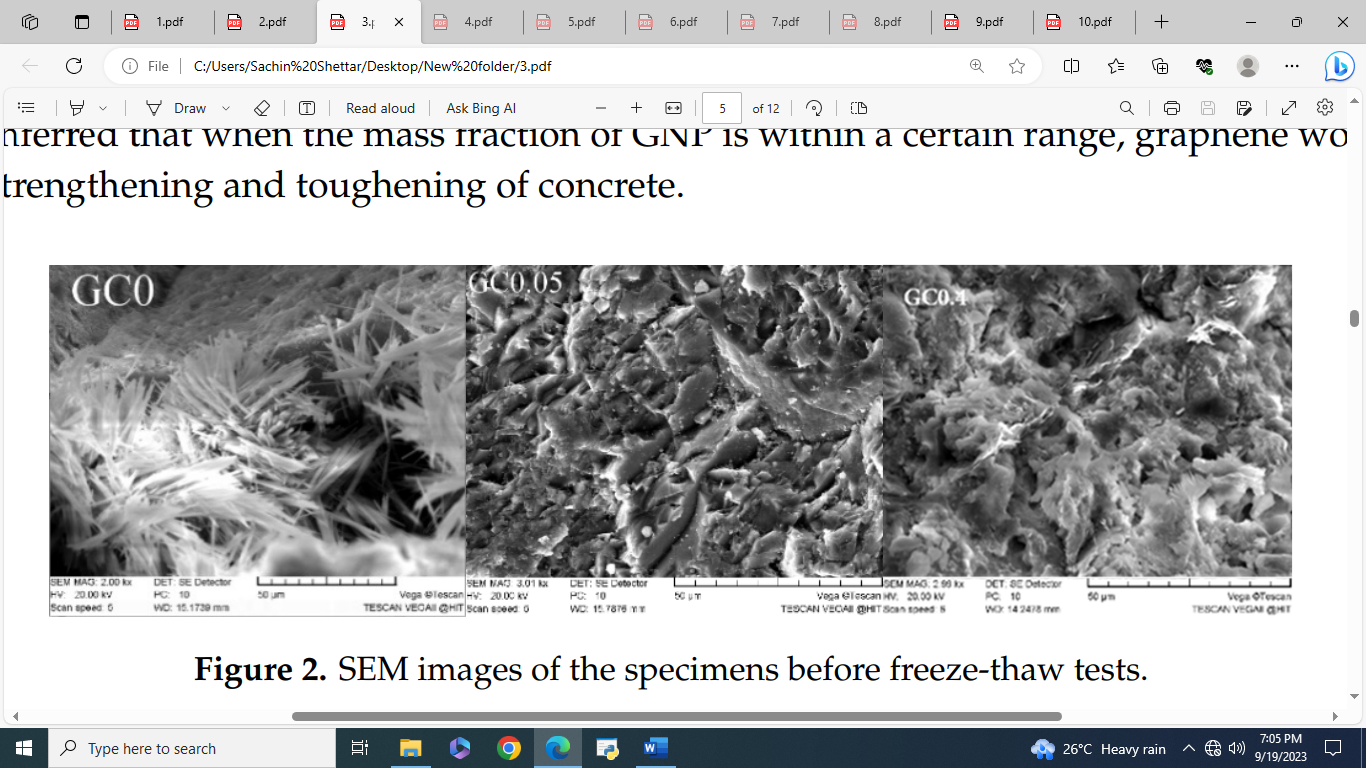
So, in conclusion the workability of the concrete decreases but since we use super plasticizer the effect of GNP on the concrete shows no effect on concretes workability.

**5) Chemical property**

**5.1 SEM and TEM analysis**

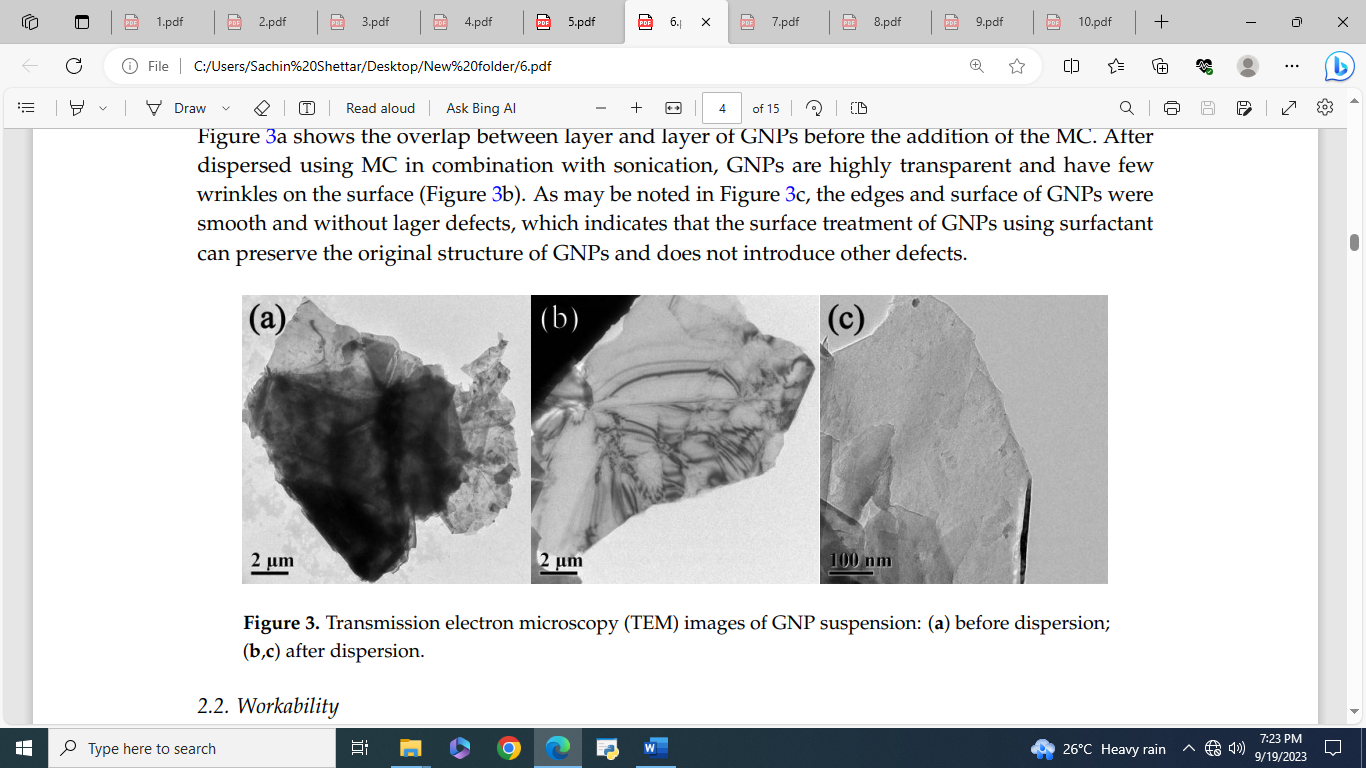
Guofang Chen[3], observed that Without GNP, the sample has more volume porosity and is rich in acicular and rod cement hydration products including AFt, AFm, Ca(OH)2, and C-S-H gel, as pointed out by Guofang Chen [3]. Reportedly, when combined with cement and graphene, nano-particles of graphene might alter the size and structure of hydration crystals while without altering their type; they could also fill gaps and speed up the development of hydration products. Figure 2 shows that specimens treated with GNP have more compact hydration products and a more uniform microstructure than regular concrete specimens. The presence of intersecting microcrystals significantly improves the mechanical characteristics of the concrete [3,4].

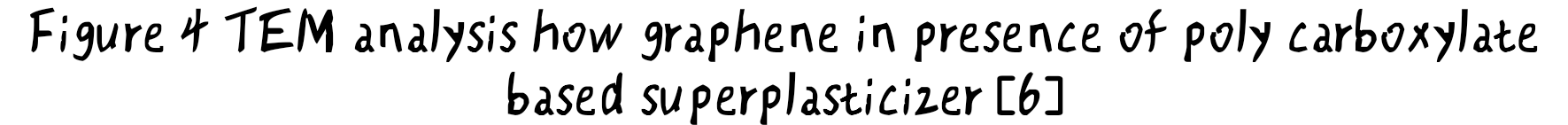
In the below pictures GC represents the presence of GNP and the number represent the percentage of GNP in the concrete.



But as we can see the increase in nanoparticles would cause the graphene to concentrate at a point and that concentrated region is weakest point of the concrete. So, the GNP should be within the limits so that it can be homogeneously mixed with the concrete. [3,4]

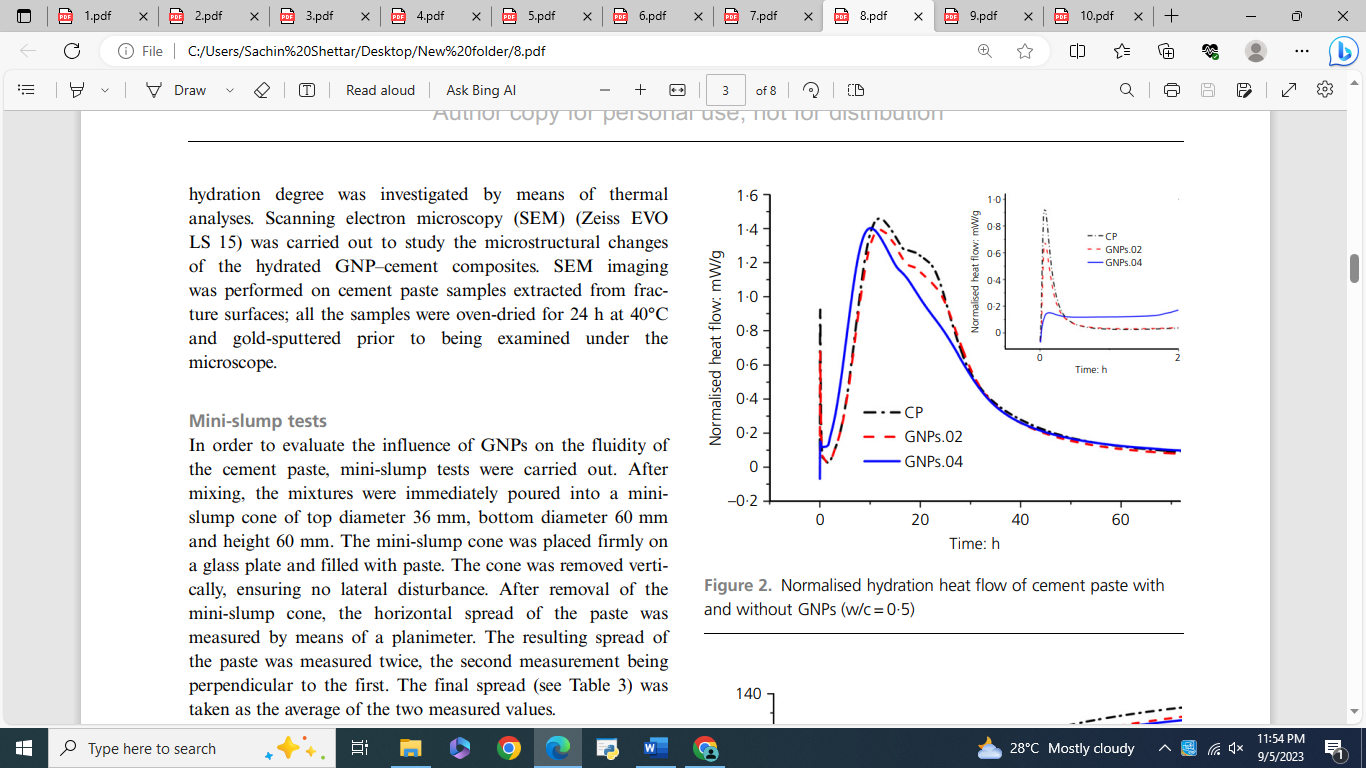
BaominWang[6], found that optimum dispersing status of GNPs in aqueous MC solution was employed using TEM**.** In the 1st figure below the overlap between layer and layer of GNPs. GNPs are highly transparent so, there will be no change in color of concrete and have few wrinkles on the surface. After its mixed with the superplasticizer and sonicated the edges and surface of GNPs were smooth and without lager defects, which indicates that the surface treatment of GNPs using surfactant can preserve the original structure of GNPs and does not introduce other defects.[6]





**5.2 Hydration process**

BaominWang[4] showed that GNPs fill micro pores in the cement matrix by being wrapped by hydration products, creating a network-like structure. There is no alteration in the products of hydration process. In cement-based materials GNP in a concrete will increase hydration reaction of cement material in early stage but when it comes to later stages there is little or no reaction on hydration process. These results are obtained through [4]. GuojianJing[8], says that GNP helps in improving hydration process [8]. Other processes like TG analysis and FTIR analysis also indicate the same results.

To study hydration process thermography Matrix analysis system is used. The samples where heated 25-degree Celsius to 1000 degree Celsius at the rate of 10 degree Celsius per minute by continuous supply of Nitrogen flow 70 ml per minute**.** Degree of hydration was analyzed using thermal analysis.

**Figure 5 Particle size distribution of as-received GNPs [8]**

According to the XRD patterns, the samples' diffraction peak shapes were quite similar to those of regular cement. The addition of GNPs to cement composites did not result in the generation of new phases or modifications to the structure of final hydration products. Table 2 shows that at various hydration ages, the CH crystal particle size in the cement-based mixture containing GNPs was smaller than the control sample. The results show that GNPs have the ability to reduce the size of CH crystal particles. In contrast to the control sample, however, there was no discernible regular pattern in the particle size of AFT crystals in the cement-based mixture including GNPs. Because GNPs are evenly distributed, the data shown above show that they may lower the particle size of CH crystals and speed up the creation of additional crystals in hydration products. Table 2 below shows that melamine super plasticizer, naphthalene, and poly carboxylate are the respective abbreviations. And the numbers 0, 1, 2, 3, and 4 stand for 0.03, 0.06, 0.09, and 0.12% of GNP by weight of cement, respectively.

**Table 2 particle size of CH crystal in cement-based mixed with GNPs [10]**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Samples | GNP(%)  Concentration | Type of  Superplastisizer | 7d particle size(nm) | | 28d particle size(nm) | |
| CH | AFt | CH | AFt |
| PC-1 | 0.00 | PS | 56.8 | 41.2 | 55.6 | 40.6 |
| PS-2 | 0.06 | PS | 55.3 | 42.0 | 54.8 | 38.7 |
| PC-2 | 0.00 | NS | 65.2 | 38.9 | 55.9 | 36.2 |
| NS-2 | 0.06 | NS | 55.1 | 37.8 | 54.2 | 36.9 |
| PC-3 | 0.00 | MS | 57.4 | 39.6 | 56.1 | 37.9 |
| MS-2 | 0.06 | MS | 56.5 | 39.2 | 55.3 | 36.8 |

1. **Mechanical property**

Mechanical properties are enhanced in a concrete by adding GNP. But it should be optimized using different dispersion techniques and different percentage of GNP gives different mechanical property that includes compressive strength and tensile strength. In general, all the paper shows that there is a small increase in the compressor strength and that is noticeable increase in the tensile strength of the concrete. In samples the early-stage strength of the concrete where high compared to the later stage strength. The factors like dispersion techniques, types of superplasticizer used, percentage of GNP also affect the compressive and tensile strength of the concrete.

The compressive strength and the tensile strength of the concrete for different super plasticizer for different percentage of GNP per weight of cement discussed below [1,5,9,6,10].

**6.1 Compressive and Tensile strength**

Fouad Ismail Ismail [1], showed that with addition of 0.02%, 0.05%, 0.1% of GNP and compressive strength increased by 20.82%, 8.41% and 9.48%. the experiment shows that the best GNP content is best suited when added less than 0.1% below are table representing compressive strength and tensile of the given samples.[1]

**Table 3 compressive strength and tensile strength of concrete [1]**

|  |  |  |
| --- | --- | --- |
| Mix ID | Compressive  strength (MPa) | Direct tensile  strength (MPa) |
| GMC-0.00 | 50.6 | 3.66 |
| GMC-0.02 | 61.14 | 4.76 |
| GMC-0.05 | 54.86 | 3.72 |
| GMC-O.10 | 55.4 | 3.89 |
| GMC-0.30 | 48.94 | 3.09 |
| GMC-0.50 | 49.94 | 3.01 |

Researcher use Chinese standards for the measurement of Mechanical properties. They have taken OPC 42.5. size of coarse and fine aggregates were 5 mm and 20 mm respectively. GNP was suspended in the ethanol aqueous solution. Which consists of graphene layers with thickness of 20nm. 4 types of mix were studied with 0.1%, 0.2%, 0.3% and 0.4% GNP and compressive strength of samples are shown in a below table 4.[3]

**Table 4 compressive strength of the concrete [3]**

|  |  |
| --- | --- |
| GNP in % | Compressive  strength (MPa) |
| 0.0 | 31.7 |
| 0.02 | 37.6 |
| 0.05 | 38.8 |
| 0.1 | 37.97 |
| 0.2 | 34.5 |
| 0.3 | 32.15 |
| 0.4 | 28.53 |

Fouad Ismail Ismail[5], use high performance concrete, silica fumes were used as a replacement for 7% of binding material. Fine aggregate of 4.75 mm of specific gravity 2.65 coarse aggregate 5 mm to 10 mm with specific gravity 2.55. Super plasticizer polycarboxylate Ether material was used 0.02%, 0.05%, 0.1%, 0.3%, and 0.5% of cement weight. The compressive strength and tensile strength of these samples were given in table 5 [5].

**Table 5 compressive strength and tensile strength of concrete [5]**

|  |  |
| --- | --- |
| GNP in % | Compressive strength (MPa) |
| 0.00 | 63.25 |
| 0.02 | 76.42 |
| 0.05 | 66.67 |
| 0.10 | 69.25 |
| 0.30 | 61.17 |
| 0.5 | 61.95 |

BaominWang[10], uses polycarboxylate based superplasticizer is used to disperse GNP. In these test paper different disperse techniques were used and compressive strengths were measured. This can a seen below. In first 4 concrete 0.025%, 0.05%, 0.075% and 0.1% of GNP to the weight of concrete where used and next five samples were using different timing of dispersion like shear mixing and ultrasonic. Result of compressive strength are presented in table 6[10].

**Table 6 compressive strength and tensile strength of concrete [10]**

|  |  |  |  |
| --- | --- | --- | --- |
| Dispersion case | High shear  mixing (in min) | Ultra sonication (min) | Compressive  strength (MPa) |
| control | - | - | 39.3 |
| GC1 | 30 | 0 | 43.8 |
| GC2 | 60 | 0 | 44.8 |
| GC3 | 90 | 0 | 43.8 |
| GC4 | 30 | 15 | 43.2 |
| GC5 | 60 | 15 | 45.3 |
| GC6 | 90 | 15 | 36.3 |

The addition of GNP in the concrete mix using superplasticizer as the dispersant increase the compressive strength and tensile strength of the concrete.Only small amount which is less than 0.3% of GNP to the weight of cement can increase the compressive and tensile strength if we increase the dosage it will adversely affect its strength.[1,3,5,9].

**6.2 Pullout test**

Fouad Ismail Ismail[5], Conducts pullout test using UTM with the capacity of 200 kN. The samples had different content of GNPs with the different diameter is 12, 10 and 16 were used.

The result shows that ultimate bond stress was increased for all 0.02, 0.05, 0.1, 0.3, 0.5 weight percentage of GNP given best results but as we have seen the compression strength decreases after 0.3% of the GNP so adoption of 0.02% of GNP is more economical.

The increase in the ultimate bond stress after 0.3% of GNP and decrease in compressive strength can be explained through adhesiveness. When the dosage increased the adhesion between Steel bars and adjacent Concrete also increased. This increases bond behavior between steel and concrete.

The influence of the diameter of bar on bond strength is remarkable on 16 mm bar compared to 10 mm and 12 mm bars. Thus we can say that as the diameter of the bar increases the bond strength due to higher surface area of steel [5].

1. **Reduction in cement with maintaining performance**

An increase in concrete performance made possible by GNPs suggests that less cement may be used in the final product. Here are the results of a different study that was conducted assuming a 5% decrease in cement content.

With 5% less cement in this improved concrete mix, the impact on global warming is 15.29 kgCO₂ eq. per cubic meter, far lower than the 19.42 kgCO₂ eq. associated with the base scenario. Consequently, the potential for global warming may be reduced by 21% with only a 5% decrease in cement. This emphasizes the value of adding GNPs to concrete and the importance of lowering the cement content without sacrificing service life [7].

**Conclusion**

The use of GNP in the concrete is a sensitive process but it can be used effectively by engineered methods. Graphene is the wonder material after plastic which can have huge development in many industry including construction industry.

* There are many type of GNP in the market. By using trial and error method by many researchers it is suggested that GNP A3775 is the type of GNP which enhance the concrete more efficiently.
* The use of superplasticizer is very essential while incorporation of the GNP in the concrete but the use of poly carboxylate based super plasticizer is necessary. But here we can see the many types of super plasticizer in the market some of them were tested keeping GNP in constant quantity the results were varying dependent upon the superplasticizer used the porosity of the structure after use of PS,NS,MS superplasticizer decreased the porosity by 12.9%, 15.2%, 16.3%.
* The use of GNP will not change the hydration product but will help in increasing the growth of hydration product and fills the pores and gaps in between which intern increase the strength and durability of the concrete.
* The use of GNP is efficient but only when used in the limited and engineered way if the quantity of the GNP increase then the strength will decrease due to adhesiveness. GNP is not basically a cementitious material so when it is concentrated at a point then the effect will be on concrete property generally 0.3% by weight of cement is the limit.
* The use of GNP can lead to achieve the goal of reduction in the production of the cement though it can’t replace cement but the desired strength can be achieved with less cement. It is seen that 5% reduction in cement content can be achieved, reducing cement by only 5% can result in a 21% reduction in the global warming potential.

**Reference**

[1] Ismail, F. I., Shafiq, N., Abbas, Y. M., Bheel, N., Benjeddou, O., Ahmad, M., & Sabri, M. M. (2022). Behavioral assessment of graphene nanoplatelets reinforced concrete beams by experimental, statistical, and analytical methods. *Case Studies in Construction Materials*, *17*, e01676.

[2] Du, H., Gao, H. J., & Dai Pang, S. (2016). Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet. *Cement and Concrete Research*, *83*, 114-123.

[3] Chen, G., Yang, M., Xu, L., Zhang, Y., & Wang, Y. (2019). Graphene nanoplatelets impact on concrete in improving freeze-thaw resistance. *Applied Sciences*, *9*(17), 3582.

[4] Wang, B., & Shuang, D. (2018). Effect of graphene nanoplatelets on the properties, pore structure and microstructure of cement composites. *Materials Express*, *8*(5), 407-416.

[5] Ismail, F. I., Abbas, Y. M., Shafiq, N., Fares, G., Osman, M., Hussain, L. A., & Khan, M. I. (2021). Investigation of the impact of graphene nanoplatelets (GnP) on the bond stress of high-performance concrete using pullout testing. *Materials*, *14*(22), 7054.

[6] Wang, B., Jiang, R., & Wu, Z. (2016). Investigation of the mechanical properties and microstructure of graphene nanoplatelet-cement composite. *Nanomaterials*, *6*(11), 200.

[7] Papanikolaou, I., Arena, N., & Al-Tabbaa, A. (2019). Graphene nanoplatelet reinforced concrete for self-sensing structures–A lifecycle assessment perspective. *Journal of Cleaner Production*, *240*, 118202.

[8] Jing, G., Ye, Z., Lu, X., & Hou, P. (2017). Effect of graphene nanoplatelets on hydration behaviour of Portland cement by thermal analysis. *Advances in Cement Research*, *29*(2), 63-70.

[9] Jiang, Z., Sevim, O., & Ozbulut, O. E. (2021). Mechanical properties of graphene nanoplatelets-reinforced concrete prepared with different dispersion techniques. *Construction and Building Materials*, *303*, 124472.

[10] Wang, B., & Pang, B. (2019). Mechanical property and toughening mechanism of water reducing agents modified graphene nanoplatelets reinforced cement composites. *Construction and Building Materials*, *226*, 699-711.