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USING GRAPHENE AS A NANOFILLER IN THE CONSTRUCTION INDUSTRY

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Abstract: This research provides a review intended to explore and give an overview about the use of graphene as a nanofiller in the construction industry. The paper starts with providing detailed information concerning the need for adopting micro-fibers in the ordinary Portland cement (OPC) structures. Then the paper explores the limitations of using these micro-fibers compared to using engineered nanomaterials. Furthermore, the paper briefly discusses the effect of using two engineered nanomaterials currently employed in the construction industry, namely the Nano-Silica and Carbon Nanotubes while highlighting their shortcoming. In addition, the paper discusses the graphene and its different forms. Moreover, the advantages of both the graphene nanoplatelets and the graphene oxide are thoroughly investigated to highlight the benefits of their adoption in the composite over the OPC structures. More specifically, this research shows that the incorporation of graphene in the construction industry due to its higher specific surface area and aspect ratio increases the cement hydration making the section in consideration more dense, durable, ductile, more resistant to higher compressive strength and tensile strength, more resistant to thermal cracking and to the phenomenon of freeze and thaw, and also more resistant to fire, impact and blast compared to the OPC structures. Last but not least, limitations and barriers that currently hinder the widespread adoption of the graphene in the construction industry are presented hoping that future research could tackle them because it is expected that the adoption of graphene will revolutionize the construction industry while preserving and sustaining the environment.

1 INTRODUCTION

The construction industry plays a vital role in the development of the nations, contributing to up to 9% of gross domestic product (GDP) of the developed countries (Chitkara, 1998). Since concrete is the most used material worldwide, it is the subject of increased research to enhance its different properties. Concrete is basically composed of coarse and fine (sand) aggregates, cement and water. Unfortunately, 5% of the CO2 global emission is caused by the production of concrete. This is due to the chemical reaction of the production of one if its main constituents, which is ordinary Portland cement (Crow, 2016). Consequently, research has been focused on producing a more durable and less permeable concrete mix which can not only withstand higher compressive and tensile stresses, but also a matrix that is more economical and environmentally friendly. In this regard, construction professionals explored the use of micro-fibres (to control crack propagation) and supplementary cementitious materials (SCM) (such as waste/by-products like fly ash, silica fume, slag cement) into the concrete mix which helped achieve higher mechanical properties resulting in reduced concrete section dimensions and hence saving the environment (less CO2 gas emissions).

2 COMPARING MICRO-FIBERS TO ENGINEERED NANOMATERIALS

2.1 The Presence of Macro-Cracks

Lab analysis showed that the presence of relatively large voids (pores) in the Ordinary Portland Cement (OPC) paste can initiate macro-cracks in concrete which weakens its tensile strength and this is why it is considered a brittle material.

2.2 The Incorporation of Micro-Fibers and their Shortcomings

In order to enhance the mechanical properties of the concrete, different types of micro-fibers including glass, steel, synthetic material and carbon, are used to control the cracking that occurs. These randomly oriented micro-fibers, which are closely spaced, fill the voids and hence better control the crack propagation (Gong et al., 2016). The micro-fibers provide a bridging mechanism that improves the toughness and tensile strength of the concrete since they create a dense system of micro-cracks instead of large ones, however, they cannot hinder the initiation of cracks nor they affect the compressive strength of concrete. Therefore, engineered nanomaterials are introduced to provide better modification (reinforcement) at the nanoscale (Chuah et al., 2014).

2.3 The Introduction of Engineered Nanomaterials

There are four principal types (shapes) of engineered nanomaterials: zero-dimensional nanoparticles (mainly spheres and atomic clusters [point particles]), one-dimensional nanofibers (nanofibers in the shape of rods or wires like Carbon Nanotubes [CNT]), two-dimensional Nano sheets (in a form of plates or multilayers like Graphene Oxide [GO]) and three-dimensional nanomaterials (equiaxed nanometer-sized grains) (Ngô & Pan, 2014).

This research briefly discusses the effect of using two engineered nanomaterials currently employed in the construction industry, namely the Nano-Silica and Carbon Nanotubes while highlighting their shortcomings.

Table 1 presents a comparison between some of the nanomaterials and micro-fibers used in the construction industry. As can be interpreted from the table, the addition of the graphene oxide and the Carbon Nanotubes can enhance the durability and strength of the concrete. In addition, figure 1 shows the different particle sizes of concrete constituents together with their specific surface area (Chuah et al., 2014).

Table 1: Material Properties of Typical Fillers (Chuah et al., 2014)

Material	Elastic Modulus (GPa)	Tensile Strength (GPa)	Elongation at break (%)	Density (kg/m^3)	Diameter/ Thickness (nm)	Surface Area (m^2/g)	Aspect Ratio
Graphene	1000	≈130	0.8	2200	≈0.08	2600	6000-600,000
GO	23-42	≈0.13	0.6	1800	≈0.67	700-1500	1500-45,000
CNTs	950	11-63	12	1330	15-40	70-400	1000-10,000
Carbon Fiber	7-400	0.4-5	1.7	1770	6000-20,000	0.134	100-1000
Polymeric Fiber (Polypropylene and Nylon)	3-5	0.3-0.9	18	900	18,000-30,000	0.225	160-1000
Glass Fiber	72	3.45	4.8	2540	5000-10,000	0.3	600-1500
Steel Fiber	200	1.50	3.2	7800	50,000-900,000	0.02	45-80

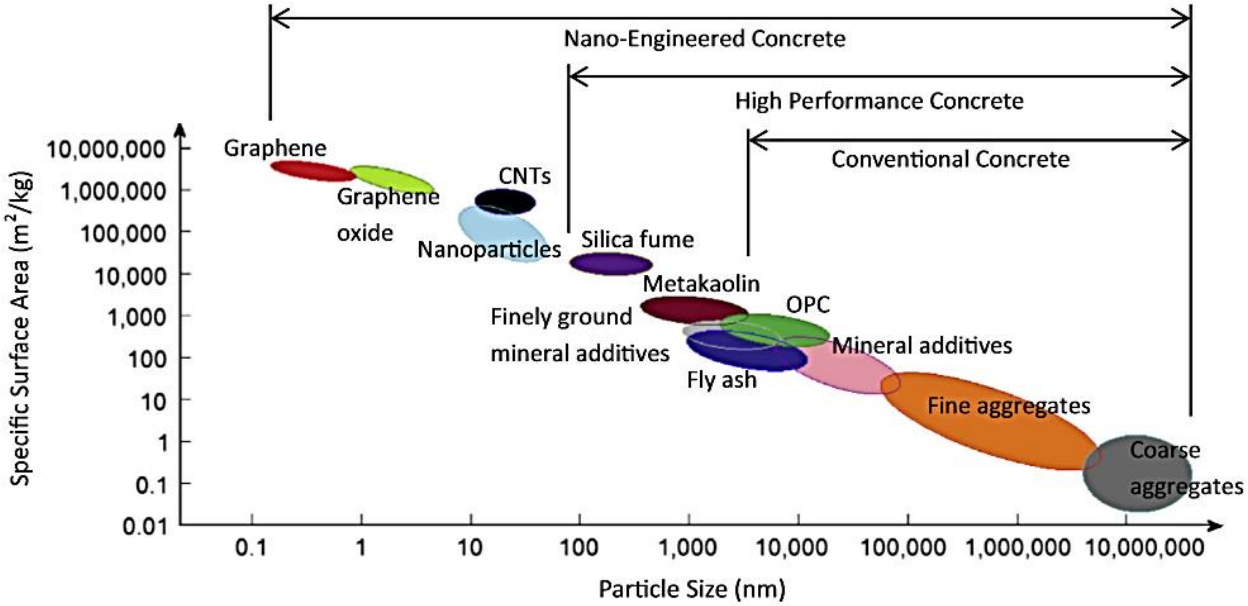

Figure 1: Comparison of the different particle sizes of concrete constituents together with their specific surface area (Chuah et al., 2014)

2.4 Current Advances Regarding Carbon Nanotubes and Nano-Silica

Carbon Nanotubes (CNT) and Nano-Silica are more efficient than micro-fibers/fillers (Fly ash and Silica Fume) since they control the initiation of cracks at the Nano level before these cracks propagate to be micro-cracks (Pan et al., 2013).

In the case of Nano-Silica, the reason is that the relatively large specific surface area of Nano-Silica (300m^2/g) promotes the hydration of cement given that the Nano-Silica promotes the accelerated silicate initial polymerization since it accelerates the Ca_3iO_5 (C_3S) dissolution phase hence accelerating the formation of the C-S-H (Calcium-Silicate-Hydrate). However, given that the Nano-Silica has a low aspect ratio – a spherical shape with less than 30 nm diameter – it cannot stop the micro-cracks that stem from the Nano cracks (Björnströma et al., 2004; Sikora et al., 2015).

In the case of Carbon Nanotubes, they have higher aspect ratio compared to the Nano-Silica since their diameters ranges from 1 to 3 nm or 5 to 50nm, single and multiwalled CNTs whereas their lengths could reach centimeters (more than 1000). Also, the CNTs have better mechanical properties since their modulus of elasticity around one Tera Pascal and their tensile strength around one Giga Pascal. Consequently, the higher mechanical properties and higher aspect ratio enhance the strength and toughness of the concrete mix. However, one problem with CNTs is that agglomeration and bundles of CNT may form in the mix due to the strong attractive Van der Waal's forces of the particles. This issue negatively affects the mix since the CNTs become poorly dispersed and consequently weakens the mix. Another problem is that it is difficult to achieve a strong bonding between the Carbon Nanotubes and the concrete mix. This is due to the fact that the CNTs are originally sheets of graphene rolled in a form of a tube. So, there is lower interfacial contact/interaction area between the cement matrix and the CNTs since the outer shell is only in contact (ignoring the internal surface area of the graphene layer) and hence this deteriorates the reinforcing efficiency of the CNTs under tensile stresses (easily pulled) (Pan et al., 2013).

2.5 Problem Identification

As already discussed above, it is crucial environmentally and economically to find the most optimum concrete matrix which will allow the reduction of the concrete section while maintaining appropriate mechanical properties that could be sustained throughout the life cycle of the building section. Previous studies illustrated above show the benefits of the engineered nanomaterials over the micro-fibers. However, there are serious problems with each of these solutions as discussed in details above. This is why, there is a new trend in the construction industry to introduce the so called “the miracle material: The Graphene” as a filler in the concrete mix in order to overcome the above listed problems.

3 THE MIRACLE MATERIAL: THE GRAPHENE

Graphene is a “one-atom thick planar sheet of sp^2-bonded carbon atoms densely packed in a hexagonal lattice" (Schlüter et al., 2012). It is a single layer of graphite. The graphite is a natural crystalline form of the carbon. The Van der Waals attractive forces stack multiple layers of graphene together and this creates the Graphite. Graphene is “the thinnest and strongest of all known materials” (Schlüter et al., 2012) exhibiting exceptionally high modulus of elasticity around 1 TPa, tensile strength of 130 GPa together with a surface area of 2600 m^2/g. Compared to traditional micro-fibers, graphene has superior electrical conductivity and thermal properties, higher stiffness and strength, smaller spacing, and higher aspect ratio (much more than the CNTs) which allow it to hinder and stop the propagation of Nano cracks (Gong et al., 2015). The graphene’s planner/flat structure and higher surface area increase its contact with the material in consideration since its upper and lower surface are in full contact which provides better bonding (Pan et al., 2013).

4 DIFFERENT FORMS OF GRAPHENE AND ITS ADVANTAGES

Graphene can be present under different forms, namely, as a pristine graphene with no defects, or as a monolayer of graphene which contains few defects, or as oxidized graphene or as graphene nanoplatelets. A thorough description of the graphene platelets and graphene oxide are presented in this research together with their advantages given their usage in the construction industry.

4.1 Graphene Nanoplatelets

4.1.1 Description

Graphene nanoplatelets are formed by combining several layers of graphene which is different than the monolayer graphene. Hence, they are less susceptible to entanglement and agglomeration due to their relative thickness which can attain 100nm (Ranjbar et al., 2015).

4.1.2 Advantages

A. The incorporation of graphene nanoplatelets improves significantly the thermal diffusivity of the concrete composite during hydration and consequently reduces the occurrence of thermal cracking of large structure which improves the durability of the concrete composite (Sedaghat et al., 2014).

B. Graphene nanoplatelets (GNP) can also be used as an additive to the fly ash based geopolymers. The geopolymers are currently considered as replacement for the cement given their rapid strength development, their chemical stability, cost efficiency, low shrinkage rate, and high resistance to freeze and thaw. However, the geopolymers are quasi brittle ceramic like material, that can abruptly fail due to their low flexural/tensile strength. Consequently, improving the mechanical properties by the introduction of the graphene nanoplatelets is crucial. Laboratory results showed that the introduction of graphene nanoplatelets with just 1% of the weight of the geopolymer section increased its compressive strength by 44% and its flexural/tensile strength by 216%. This increase is due to uniform stress distribution through the composite in addition to the different enhancement mechanisms which include crack deflection, crack bridging, crack branching and pull out. Figure 2 shows the uniform stress distribution mechanism of the graphene nanoplatelets fly ash based geopolymers when exposed to a compressive load.

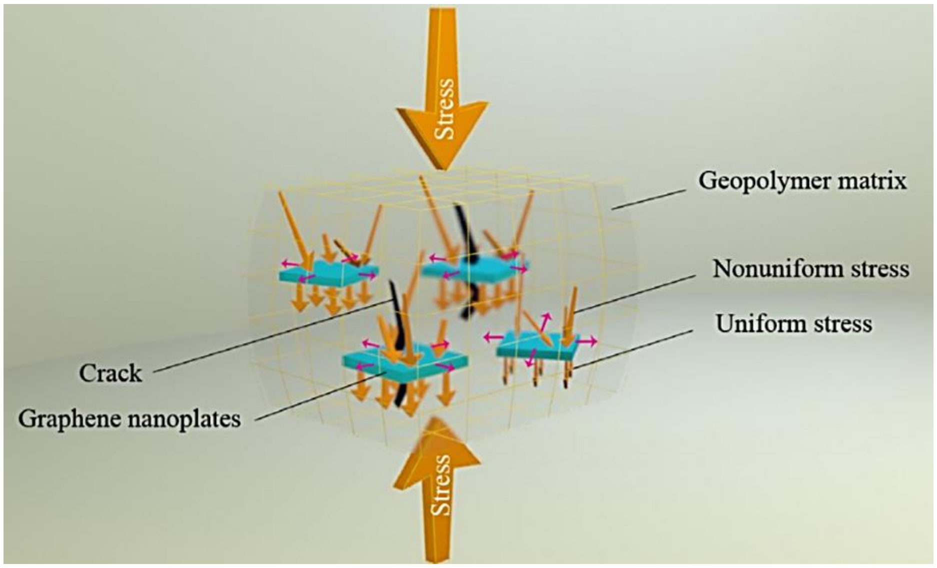

Figure 2: Scheme of GNP Fly ash geopolymer composites under compression load (Ranjbar et al., 2015)

Under compression, the vertical stresses are resisted by the ultrahigh modulus of elasticity of the graphene nanoplatelets which provides higher resistance to failure for the geopolymers since the nanoplatelets transfer the stress uniformly across the mix (consequently, a larger area carries the induced stress). The reason is that the cracks fail to propagate since the cracks fail to pass through the graphene nanoplatelets/ Nano Sheets. Consequently, passing through the sheets requires higher energy to penetrate and ultimately this increases the compressive strength of the geopolymer (Ranjbar et al., 2015).

C. Other results reported in the literature showed that the introduction of graphene nanoplatelets with a weight of only 0.125% increased the fracture energy of pristine epoxy by 115% and its fracture toughness by 65%. To reach the same results but using CNTs, double the weight percentage was required. Also, the epoxy crack propagation was reduced 25 times thanks to the 2-D planar structure of graphene that deflected the cracks more effectively that the CNTs that are 1-D with lower in its aspect ratio. This can be illustrated in figure 3 (Rafiee et al., 2010).

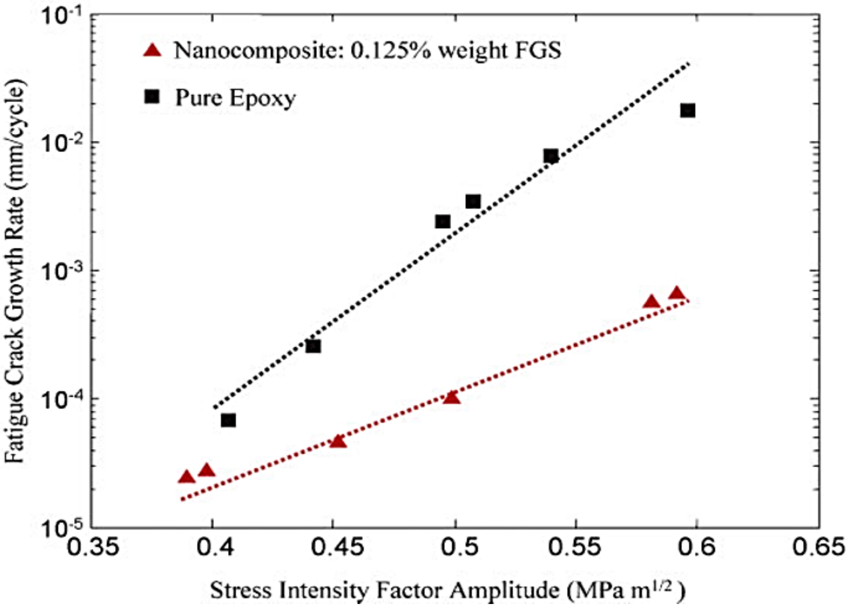

Figure 3: Fatigue crack growth rate vs the stress intensity factor Amplitude (Rafiee et al., 2010)

4.2 Graphene Oxide

4.2.1 Description

Graphene oxide (GO) is a derivative of graphene and it is produced through graphite chemical oxidation process. It is a single (mono) layer of graphene derivatized by a combination of hydroxyl, carboxyl and epoxy functionalities. On the edges and basal planes, the oxygen functional groups alter significantly the Van der Waals attraction forces between the graphene oxide, consequently, the GO sheets become hydrophilic and its dispersion in water improves without the need to add a dispersant, stabilizing agents or surfactant (Pan et al., 2013; Sikora et al., 2015).

4.2.2 Advantages

A. The graphene oxide is a highly reactive nanomaterial since its different functional groups in addition to its 2-D planar high specific surface area and aspect ratio provide a bigger surface area of the calcium-silicate-hydrate nucleation than the CNTs, which provides enhanced degree of graphene oxide cement composite hydration. However, the functionalization of the carbon degrades the graphene's mechanical properties which consequently lowers its modulus of elasticity to be less than 42GPa and its tensile strength to be 130Mpa, yet these properties are still higher than the cement ones (Sikora et al. 2015).

B. Lab results showed that the adoption of graphene oxide with only 0.05% improves the compressive strength of a Portland cement mix from 15% to 33% and its tensile strength from 41% to 59%. Furthermore, a decrease from 32.6% to 28.2% in the total porosity was accomplished which indicates improvement in the pore structure making the section more dense, durable, ductile and more resistant to higher compressive strength as can be illustrated in figure 4 (Duan et al., 2013).

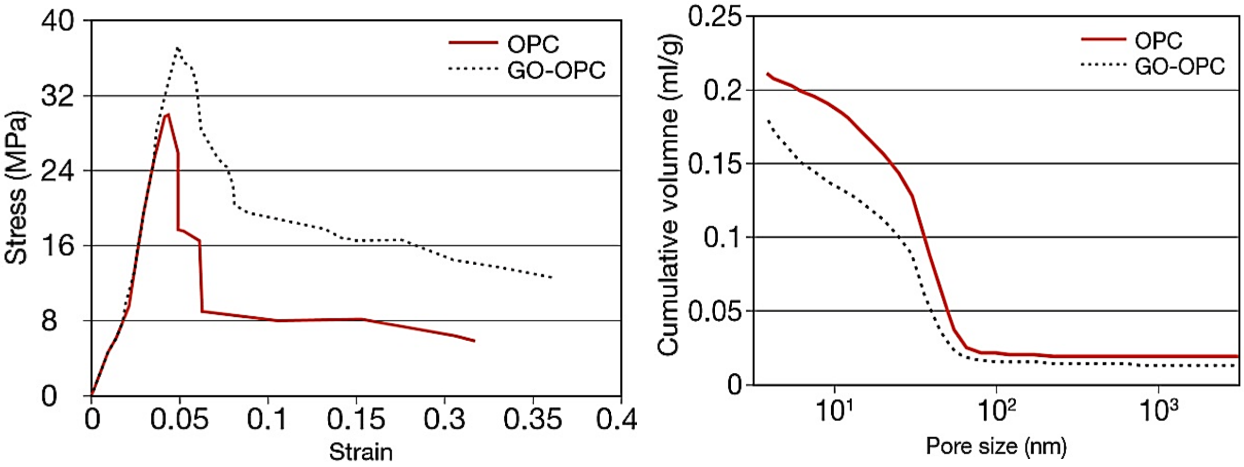

Figure 4: Mechanical properties enhancement given the inclusion of GO sheets in OPC (Duan et al., 2013)

C. Another research showed that the adoption of graphene oxide with only 0.03% improves the compressive strength of a Portland cement mix more than 40%, however, the study reported reduced workability of the concrete (Gong et al., 2015). The reason for this reduced workability is attributed to the graphene oxide bigger specific surface area which requires more water to dissolve.

D. This means that a higher water to cement ratio shall be incorporated or the inclusion of an admixture is a must to enhance the workability which may affect the compressive strength results reported.

E. The GO inclusion which enhances the durability and strength of OPC could provide further advantages, namely, a reduction in the quantity of steel reinforcement used, and allowing the usage of lighter and thinner concrete structures which could revolutionize the architecture designs - which are always limited by the capabilities of OPC - and also a reduction to consumption of concrete and hence better sustain the environment. Moreover, the increased durability could reduce the need to use anticorrosion steel and hence more savings, in addition to better resistance to freeze and thaw phenomena in cold countries (Pan et al., 2013).

To sum up, the use of graphene nanoplatelets and graphene oxide enhances significantly the properties of an OPC structure. This broaden its construction applications which can range from well cementing, to precast sections and cast in situ marine structures as well as providing better building energy efficiency (Duan, 2013). In addition, the higher durability and smaller pore structures can allow for self-cleaning properties, antimicrobial surfaces properties and higher resistance to fire, impact and blast compared to the OPC structures (Chuah et al., 2014; Duan, 2013).

5 LIMITATIONS, BARRIERS AND DISADVANTAGES OF USING GRAPHENE

The widespread adoption of graphene is limited due to the presence of a number of issues that hinder and endanger its advantages. First, the graphene's high cost of production is considered a major barrier (Pan et al., 2013). Second, difficulties to disperse the graphene due to the attraction forces of Van der Waals causes agglomeration unless graphene is treated as discussed in the above sections. Third, the inclusion of graphene lowers the workability of the concrete mix which requires either to increase the water to cement ratio or to add admixtures, in both cases the laboratory excellent mechanical properties could be compromised (Chuah et al., 2014). Fourth, a research conducted at Brown University has been published highlighting a serious problem that could endanger both the graphene manufacturers' health (while producing graphene, if inhaled) and the end users' health. The problem lies in the capability of the graphene Nano sheets sharp asperity edges to pierce/penetrate human cell membranes, consequently, disrupting the cells normal function (Li et al., 2013).

It is worth to note that scientists and engineers are working around the hour in order to find solution for all these limitations and barriers because tackling them will certainly increase the widespread adoption of graphene and consequently revolutionize the construction industry while preserving and sustaining the environment.

6 CONCLUSIONS

In summary, this research provided detailed review on the use of the miracle material "graphene" under different forms as a nanofiller for the construction industry. The paper first included an overview concerning the need to use micro-fibers in the OPC structures. Then, the advantages of using engineered nanomaterials over the ordinary micro-fibers were highlighted. Furthermore, two engineered nanomaterials "the Nano-Silica" and "the Carbon Nanotubes" were briefly explored to show how they affect the composite in consideration while highlighting their shortcomings. Then, the paper provided detailed information concerning the graphene and its different forms. Moreover, detailed analysis of the graphene nanoplatelets and graphene oxide is provided in this research together with highlighting their numerous advantages over ordinary Portland cement structures. More specifically, this research highlights that the incorporation of graphene in the construction industry due to its higher specific surface area and aspect ratio increases the cement hydration making the section in consideration more dense, durable, ductile, more resistant to higher compressive strength and tensile strength, more resistant to thermal cracking and to the phenomenon of freeze and thaw, and also more resistant to fire, impact and blast compared to the OPC structures. Finally, a set of limitations and barriers against the widespread adoption of the graphene is presented. Tackling all the limitations and barriers will help in the widespread adoption of graphene which will revolutionize to a great extent the construction industry while preserving and sustaining the environment. It is important to stress that the scientist and engineers are working around to hour to keep enhancing the properties of the different nanomaterials used in order to come up with the most optimum composite matrix which provides superior mechanical properties while preserving the environment at the lowest possible cost. A final remark that could be added is that the graphene capabilities are still not fully explored or made advantage of largely in the construction industry. There are lots of technical areas that the graphene can be incorporated in largely which will positively impact its stakeholders, namely, geotechnical engineering piles, hydraulic dam structures, architectural coatings, among other applications to be discovered.

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