

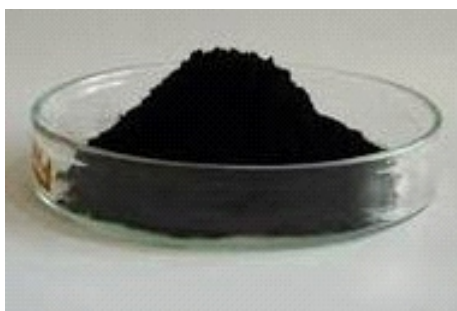
Minimizing Carbon Footprint

Nanocomposite of Cement and Graphene Oxide: Impact on Strength Properties and Carbon Footprint

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Graphene oxide used in preparation
M30 concrete

ABSTRACT

In the present now, need for the high performance of cement-based materials and the call for energy conservation and environmental protection has attracted immense scientific attention. Graphene oxide based nanomaterial is promising candidate by virtue of large specific surface area, excellent physical properties. This paper explores the key role played by graphene oxide (GO) in the cement concrete at different concentrations of 0.025, 0.05, 0.075 weight% GO of cement respectively. Compressive strength results have proved, a small quantity of GO is good enough to obtain substantial increase in strength properties of concrete. The usage of tiny quantity of GO offers a silver lining to reduce the carbon foot print associated with cement consumption. Graphene oxide based nanocomposite cement has potentially important role to play to achieve India's ambitious target to reach net-zero emissions by 2070 declared at COP 26 (26th UN Climate Change Conference of the Parties (COP26) at Glasgow, United Kingdom.

KEYWORDS: Graphene Oxide (GO), Carbon nanotube (CNT), Cement hydration, Cement hydration products

Introduction

Cement is an extensively used construction material due to the low cost and high compressive strength. The principal hydration products of cement are made up of nanocrystalline regions with the atomic structure resembling tobermorite and/or jennite[1]. This provides an opportunity to apply nano-materials and nano-technology in cement-based materials to modify their structures at the nano-scale and finally improve their macro-scale properties. The large specific surface area of the nano-materials can provide nucleation sites for hydration products. Moreover, the nano-materials can occupy the pores within cement matrix to provide a dense microstructure. Out of different options, carbon based nano-materials have gained importance to be incorporated in cement matrix due to their low density, high strength and high corrosion resistance. Carbon nanotube (CNT), a one-dimensional tubular structure with high aspect ratio, has unique crack-bridging effect to slowdown the crack propagation within cement composites[2]. Graphene oxide (GO) is a derivative of graphene[3], which can be viewed as a layer of graphene with grafted oxygen functional groups. The active functional groups promote chemical or physical interactions with cement, which can improve the interfacial bonding with the host materials.

Why Graphene Oxide (GO)? Why not Carbon Nanotube (CNT) for Cement Composite?

Many researchers found that the addition of CNTs to cement composite resulted in negligible change in strength or even a reduction in strength of the composite in some cases[4,5]. The explanation is by and large associated to the poor dispersion of CNTs and weak bonding between the CNTs and the cement matrix. Due to strong vander Waal's attractive

forces between particles, CNTs tend to form agglomerates or bundles which may become defect sites in the composites. The lack of interfacial areas between CNTs and the cement matrix reduces CNT's reinforcing efficiency, even though CNTs exhibit excellent mechanical properties. On the other hand GO being functionalized with oxygen, can easily make bonds with cement matrix[6]. The greater exposed surface area of graphene oxide sheets generates more potential sites for advantageous chemical or physical interactions, which in turn improve bonding between graphene sheets and host cement material.

Potential of Graphene Oxide to Reduce Carbon Footprint

Studies have shown on addition of relatively small amounts of graphene oxide enhances the strength of standard concrete; appreciably less cement could be needed to realize corresponding structural performance, therefore, reducing the carbon footprint. The additional strength might also reduce the need for steel reinforcement to enable further reductions in CO₂ emissions. University of Cambridge study indicates that if the addition of graphene oxide results in a 5% reduction of the Portland cement, the effect on global warming could reduce by 21%[7] another study from the University of Exeter, estimated that 125g of graphene oxide can decrease the total volume of cement down to 148kg per cubic metre of concrete (>50 wt% reduction of cement required for the original strength). With reference to environmental perspective, that would translate to total decrease of 446 kg/tonne emissions of CO₂[8].

Graphene oxide addition into construction materials does come with its own implications to the carbon footprint. Product Carbon Footprint (PCF) calculations consider the entire life cycle of the product. This means looking into energy requirements of the raw materials that make up graphene, how it is manufactured, transported, used and disposed of.

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Understanding the PCF of graphene will help manufacturers to understand the impact of their product, and enable process optimisations such that climate neutral products can be offered, and strong carbon reduction targets can be set[9]. In most cases, electricity use is the largest contributor to CO₂ emission-switching to decarbonised energy sources will naturally reduce the carbon footprint of the production methods and any resulting products[10]. For high volume construction applications there will ultimately need to be a trade off between cost of graphene oxide production, quality of graphene oxide and contribution to CO₂.

India's ambitious target to achieve net-zero emissions, removing as much carbon dioxide from the atmosphere as is produced by 2070 has been declared at COP 26 at Glasgow, United Kingdom[11]. India's overall cement production accounted for 294.4million tonnes (MT) in FY21 and 329million tonnes (MT) in FY20[12]. Due to the increasing demand in various sectors such as housing, commercial construction and industrial construction, cement industry is expected to reach 550-600 million tonnes per annum (MTPA) by the year 2025[12]. Graphene oxide based concrete has potentially important role to play to achieve COP 26 target.

Synthesis of Graphene Oxide

The synthesis method utilizes highly oxidative ingredients for graphite exfoliation. This route follows a fixed stoichiometry of reactants. The synthesis route is called improved Hummers method[13], a 9:1 mixture of concentrated H₂SO₄ /H₃PO₄ (360:40 ml) is added to a mixture of graphite flakes (3 g). The mixture was stirred continuously with magnetic stirrer. Then KMnO₄ (18 g) is added to acidic slurry, producing a slight exothermic 35–40 °C reaction. The reaction mixture is then heated to 50 °C and stirred for 8 h. The reaction mixture is cooled to room temperature and poured onto ice (~400 ml) with 30% H₂O₂ (5 ml). The slurry is centrifuged (4000 rpm for 4 h), and the supernatant liquid is decanted until decanted water shows neutral pH. The remaining solid material is dried in oven for 12 hours ensuring complete moisture removal. The obtained GO lumps were crushed via mortar pestle and sieved through mesh to obtain as GO fine powder.

Table 1: Design mix concrete (M30) ingredients.

Ingredients	Quantity (kg)
Cement	25
Coarse aggregate (20mm)	34.26
Fine aggregate (10mm)	28
Crushed sand	45
Admixture	0.25
Water	10
Water to Cement ratio	0.39

Table 2: Weight % of GO added to M30 concrete mix.

Weight % of GO in concrete mix
0.025% of cement
0.05% of cement
0.075% of cement

Preparation of GO-Concrete

Design mix concrete (M30) was used to prepare GO based concrete by employing ingredients as listed in Table 1. GO was added to concrete mix via ultrasonication through water component of M30 concrete in following percentages as illustrated in Table 2. Fig.1 shows GO-Concrete nanocomposite preparation flowsheet. All the raw materials including fine aggregate (Fig.2a), coarse aggregate (Fig.2b), crushed sand (Fig.2c), and graphene (Fig.2d). These raw materials are homogeneously mixed using motorised concrete mixer as

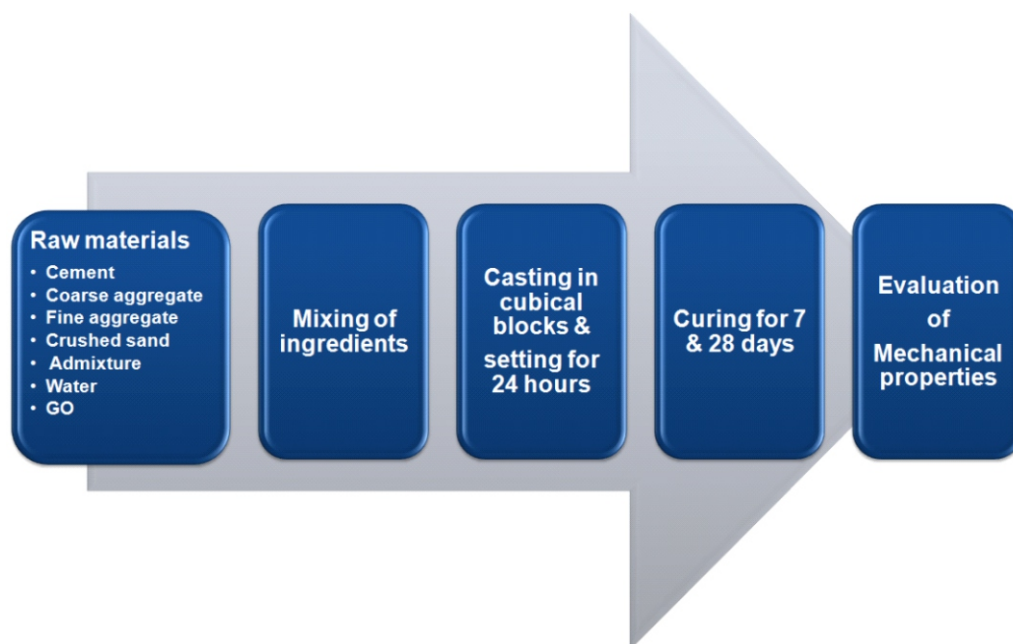


Fig.1: Flow sheet for preparation of GO-Concrete nanocomposite.



Fig.2: a) fine aggregate, b) coarse aggregate, c) crushed sand, and d) Graphene oxide used in preparation M30 concrete.



Fig.3: a) Motorized concrete mixer, b) Concrete moulds, c) Test specimen concrete cubes (15 X 15 X 15cm), d) Compressive strength testing unit.

depicted in Fig.3a. The Fig.3b reveals casting moulds to obtain concrete cubes (Fig.3c.) of size (15 X 15 X 15 cm), these concrete blocks are cured by immersing in water for 7 and 28 days respectively and are eventually used to evaluate the compressive strength using testing unit as shown in Fig.3d.

Results and Discussion

Cement strength is based on reactions between H_2O and the several successive cementitious phases that occur during hydration. Hydration is what causes cement to set and then harden; degree of hardening is function of time and relates to amount of hydration products. Hydration kinetics plays an

important role on the microstructural development and the final properties of hardened cement composites. Cement is a mixture of solid phases that can react with water to produce complex products, including CH, C-S-H gels and ettringite (AFt) as shown in Table 3[14]. The degree of hardening, hydrations kinetics of concrete is indicative of gain in compressive strength. Small amount of GO is making sizable gain in compressive strength properties as illustrated in Fig.4. GO nanosheets act as the nucleation sites for hydration products to speed up cement hydration as portrayed in Fig.5. The highest compressive strength is observed at 0.05 weight% of GO concentration (Fig.4), at 0.025GO concentration the compressive strength is lowered probably due inadequate nucleation sites for cement hydration products, leading to porous microstructure. However, at 0.075GO concentration, agglomeration of GO occurs thereby GO nanosheets are not participating as the nucleation sites for hydration products to speed up cement hydration kinetics.

The surface of GO has many oxygen functional groups main included of -OH, -COOH and -SO₃H as shown in Fig.5. The C₃S, C₂S and C₃A attach with functional groups preferentially and form the enlargement points of the hydration products[15]. The growth points and growth pattern of the hydration products are both controlled by GO, which is called a template effect[15]. Scanning electron microscopy (SEM) analysis further corroborates function of GO in enhancing concrete strength properties. Interconnect between the layers of concrete (Fig.6a) is almost non-existent due to zero GO concentration resulting in lower compressive strength. At 0.025% GO concentration, initiation of inter layer bonding is observed (Fig.6b), at 0.05% GO concentration, enhanced inter layer bonding is observed (Fig.6c) confirming the role of GO nanosheets acting as the nucleation sites promoting the growth of hydration products to increase strength properties. When GO concentration exceeds certain threshold value,

Table 3: Abbreviated cementitious compounds.

Compound	Abbreviated formula	Actual formula
Calcium Hydroxide	CH	2(Ca).OH
Calcium Silicate Hydrate	C-S-H	CaO.SiO ₂ .H ₂ O
Tri - Calcium Aluminate	C ₃ A	3CaO.Al ₂ O ₃
Di - Calcium Silicate	C ₂ S	2CaO.SiO ₂
Tri - Calcium Silicate	C ₃ S	3CaO.SiO ₂
Calcium Tri Sulfoaluminate hydrate (Ettringite)	AFt	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ .26H ₂ O

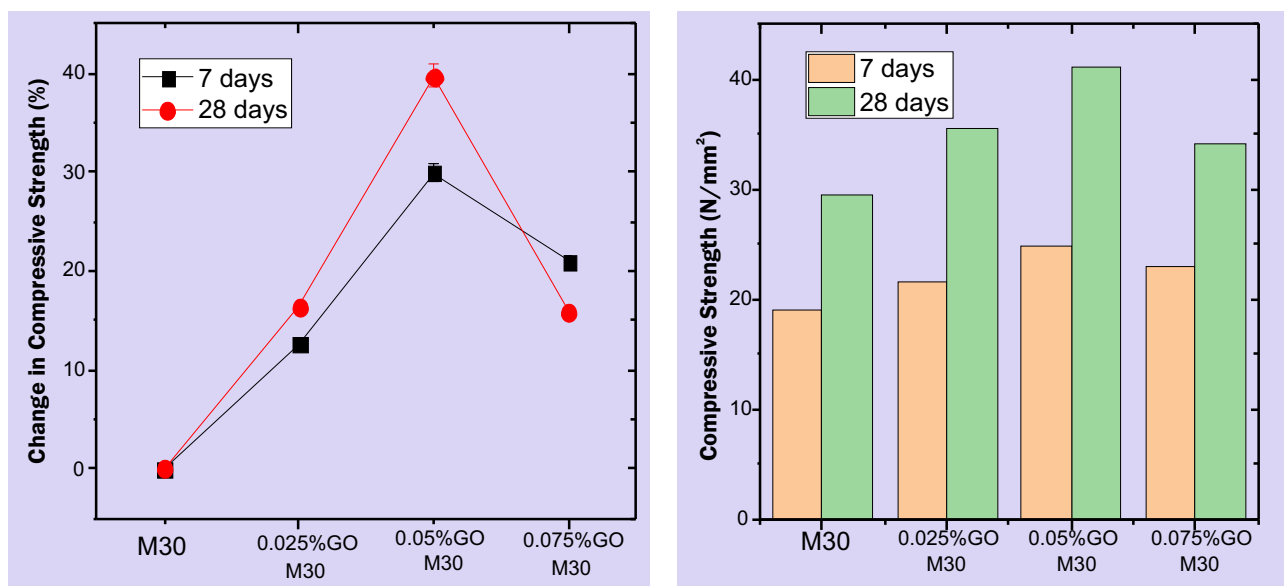


Fig.4: Compressive strength of concrete without GO and GO-Concrete at 0.025, 0.050, and 0.075 weight% GO, respectively.

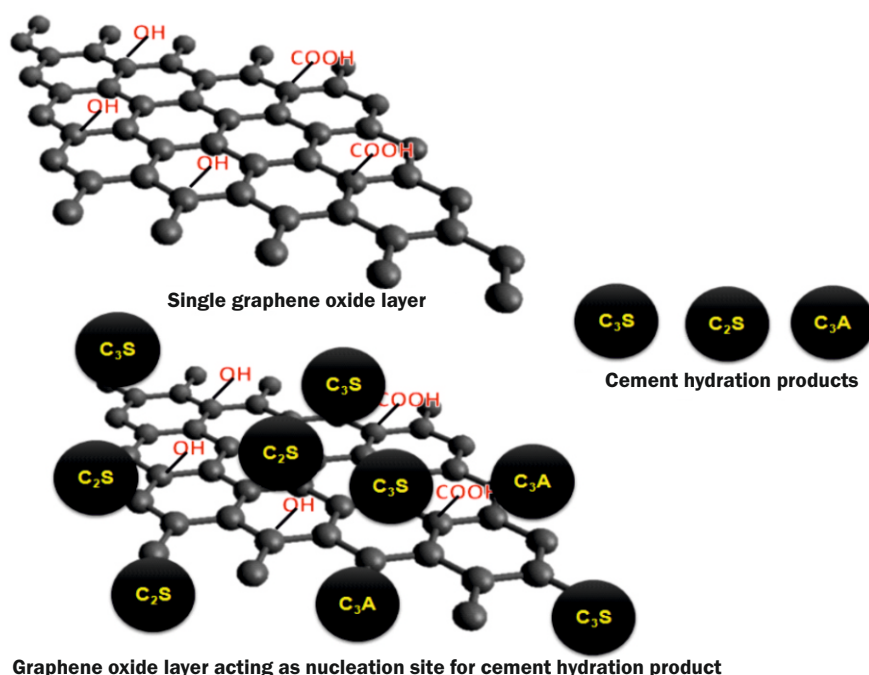


Fig.5: Schematic illustrating the role of GO acting as nucleation sites to cement hydration products.

agglomeration of GO occurs favouring random structure as indicated in Fig.6d, hence GO no longer act as seeding sites for cement densification.

Conclusion

The key role played by graphene oxide (GO) in the cement concrete has been investigated at different concentrations of GO. Compressive strength results have improved, a small quantity of GO is good enough to obtain substantial increase in strength properties of concrete. The usage of tiny quantity of GO offers a silver lining to reduce the carbon foot print associated with cement consumption. Graphene oxide based concrete has potentially important role to play to achieve India's ambitious target to reach net-zero emissions by 2070 declared at COP 26 in Glasgow and mitigate environmental concerns.

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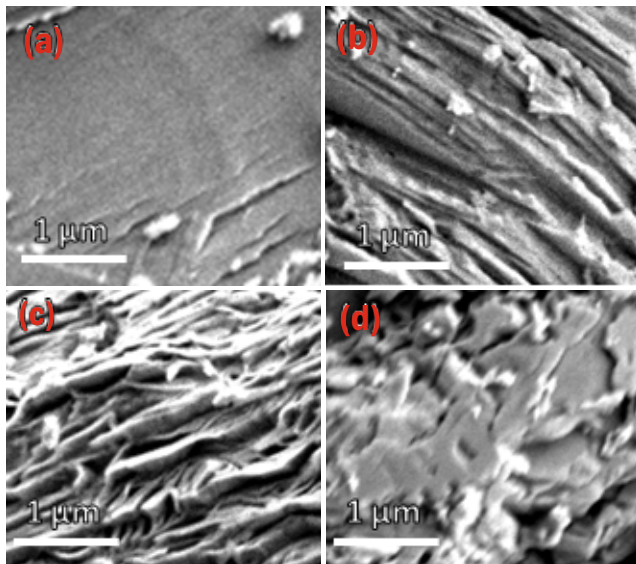


Fig.6: (a) SEM image of plain M30 concrete without GO, (b) GO-Concrete at 0.025 weight% GO, (c) GO-Concrete at 0.05 weight% GO and (d) GO-Concrete at 0.075 weight% GO.

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