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Graphene-Cement Composites: The next generation of construction materials?

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ABSTRACT

Reinforcing materials have been widely used to compensate for the quasi-brittle behavior of cement. For decades, steel, polypropylene, glass, and carbon fibres have been used for their compatibility and reinforcing ability, and more recently, graphene and its derivatives have been gaining attention. Graphene is a one atomic thick two-dimensional carbon-based nanomaterial with exceptional mechanical, electrical, and thermal properties. Its discovery in 2004 led to the 2010 Nobel Prize and the emergence of a new class of 2D materials. Graphene can be functionalized at a molecular level and applied to a wide range of multifunctional applications, including infrastructure, aerospace, transportation, and energy systems. This presentation highlights the (i) characterization of various forms of graphene derivatives, (ii) review of the state-of-the-art, and (iii) exploratory, experimental research on the microstructure of the graphene-cement based composite. The paper highlights challenges and directions for further investigation with potential application to nuclear infrastructure.

INTRODUCTION

There is interest in the multifunctionality of concrete, namely, having improved strength, durability, longer service life, and smart properties. Graphene derivatives, in that aspect, open the door to modifying traditional cement-based concrete at a nano-microscale, which can make concrete multifunctional. Fig. 1 shows the concept of developing a graphene cement-based composite system with multifunctionality. The extraordinary properties of graphene and its derivatives, such as 2D nanoscale size, high strength, functional groups, electrical conductivity, Qureshi & Panesar (2020), can be utilized to modify the cement-based composites to develop specific functionality. These functionalities of graphene could enhance the composite's mechanical properties, durability performance, and service life, as well as smart properties such as self-sensing, heat energy transmission and storage, electromagnetic interference shielding, and radiation shielding. Smaller proportions of graphene nano additives (0.02 -0.1 wt% of cement) can exhibit similar mechanical properties and durability of concrete and composites compared to materials without graphene, Krishna et al., (2021), Qureshi & Panesar (2017). Additionally, graphene's electrical conductivity, Talga, (2018), high impermeability, Lin & Du, (2020) and shielding performance, Sun et al., (2017) allow designing smart construction composite systems for advanced infrastructure development. This includes prospects for nuclear.

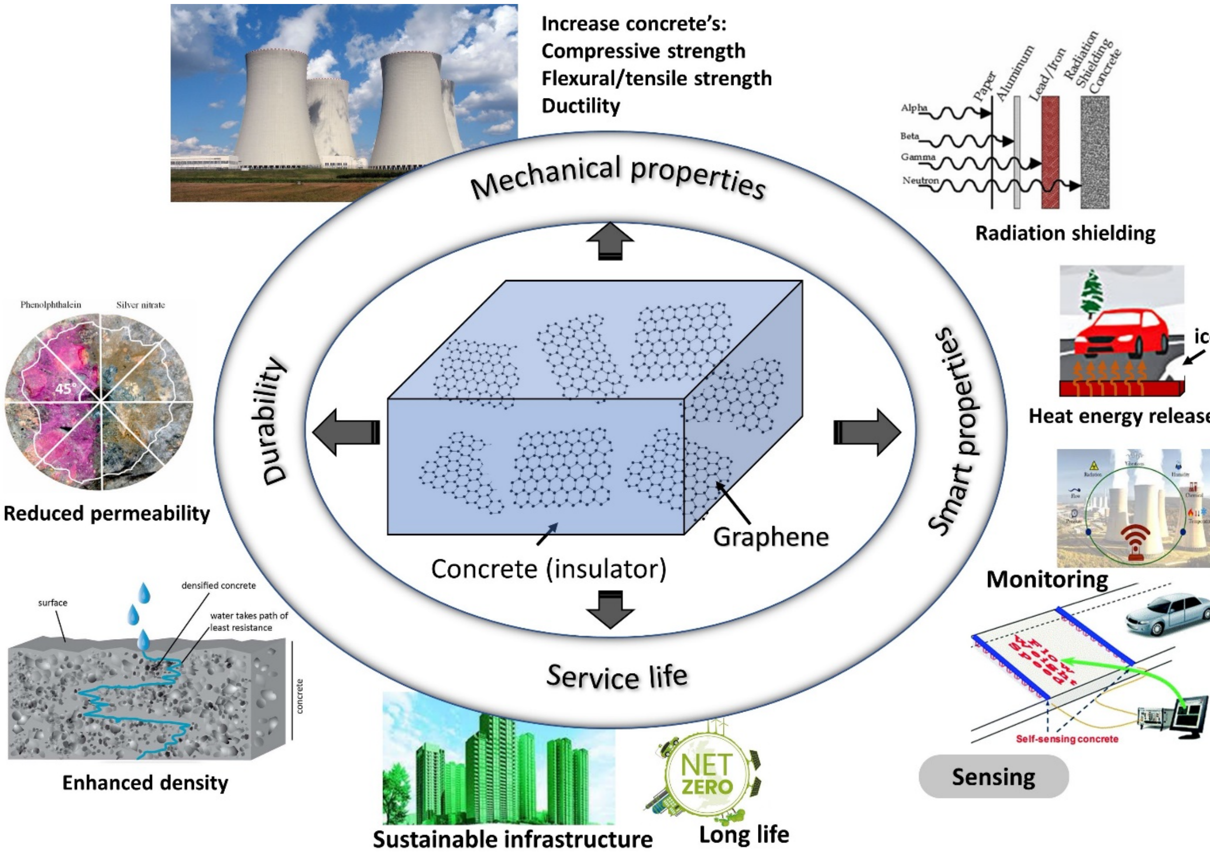


Figure 1. Multifunctional concrete with graphene-based materials.

FORMS OF GRAPHENE DERIVATIVES AND ITS CHARACTERIZATION

Graphene is one atomic thick layer of carbon atom densely packed in a hexagonal lattice in 2D plains. It is a single layer of graphite commonly exfoliated by a chemical reduction or mechanical process. Graphene in its pristine form has limited use in the modification of construction materials. Alternatively, common forms of graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO), and graphene nanoplatelet (GnP), have been increasingly used to modify cement-based construction materials, Krishna et al., (2021), Qureshi & Panesar (2020), Wu, Qureshi and Wang (2021). GO and rGO are mono to few layers (typically up to 10) of graphene attached with different proportions of oxygen-containing functional groups in its surface. GnP is a few to several layers of graphene (up to 100) without any functional groups.

Fig. 2 presents the characterization of graphene materials using advanced microscopic techniques such as scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX), atomic force microscopy (AFM), x-ray diffraction (XRD), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR) at the University of Toronto. SEM images show a thin plane formation pattern by GO (Fig. 2a), rGO (Fig. 2b) and G (Fig. 2c) with the plane size of 2±1 µm, 4±2 µm, and 3±1 µm, and the C and O contents from EDX 62-65% and 35-38%, 77-87% and 13-22%, and 99% and 0%, respectively. Fig. 2d-f show few-layer (1-5 layers) GO, rGO, and GnP. However, all three graphene derivatives show agglomeration behaviour after dispersion in water, a challenge commonly tackled during composite production process. Fig. 2g shows the XRD pattern diffraction peak at 2θ ~10.12° for GO, and a 2θ wide band around ~24.90° and 43.18° for rGO and GnP, respectively. The interlayer (***d*** spacing) for GO, rGO, and GnP calculated using the Bragg's equation are 0.85, 0.35, and 0.33 nm, respectively. The calculation procedure can be found in, Qureshi, Panesar, Sidhureddy, Chen, and Wood (2019). Typical D and G Raman bands of graphene are located at ~1350 cm^{-1} and ~1583 cm^{-1} (Fig. 2h). The ratio between D and G Raman bands intensity, I_D/I_G, is an efficient indicator for determining the level of functional groups present in graphene, which is 0.83, 096 and 0.25 for GO, rGO and GnP, respectively. The I_D/I_G ratio increases from GO to rGO due to the removal of functional groups and the formation of defects in the graphene plane, Chen, Long, Xia, Zhang, and Cai (2012), Qureshi and Panesar (2019a). Then again, the I_D/I_G ratio is low (~0.25) for GnP since no defects/functional groups are present. The indicative functional groups for graphene materials are determined using FTIR, as shown in Fig. 2i. The bond stretching peaks of GO for hydroxyl (-O-H at ~3220 cm^{-1}), carbonyl (C=O at 1730 cm^{-1}), aromatic (C=C at 1620 cm^{-1}), carboxy (C-O at 1415 cm^{-1}), epoxy (C-O-C at 1228 cm^{-1}), hydroxyl (C-OH at 1070 cm^{-1}). rGO demonstrated substantial losses of oxygen functional groups, and no other peak was found in the GnP due to the absence of functional groups. This is similarly reported in, Gholampour, Valizadeh Kiamahalleh, Tran, Ozbakkaloglu, and Losic (2017), Qureshi and Panesar (2019b). Fig. 2 presents an example of how graphene materials are characterized. This is important for developing a specific understanding of the graphene derivatives and how they may impact the composite.

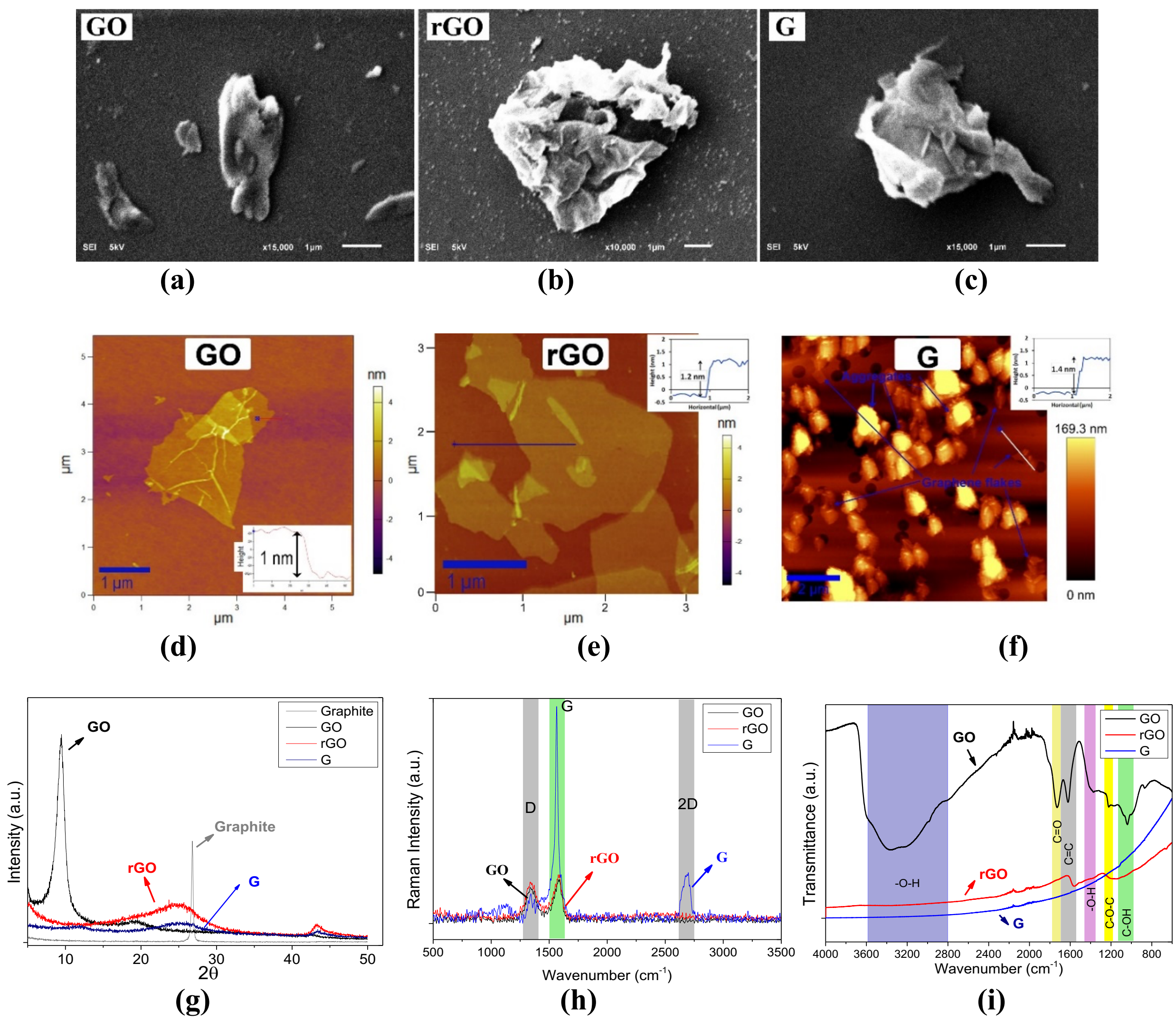


Figure 2. Characterisation of graphene materials; SEM images: (a) GO, (b) rGO, and (c) GnP; typical AFM images in water dispersion: (d) GO, (e) rGO, and (f) GnP; (g) XRD pattern, (h) Raman spectroscopy, and (i) FTIR graph, Qureshi and Panesar (2020).

STATE-OF-THE ART LITERATURE

Researchers have studied a wide range of properties and performance, including hydration, plastic properties (workability, and rheology), mechanical properties (compressive, tensile and flexural strength), and transport properties, Lin and Du (2020), Shamsaei et al. (2018), Xu et al. (2018). There is a general consensus that the workability is adversely affected, and mechanical, and transport properties are enhanced for mixes containing graphene nanomaterials compared to the corresponding control mix (without any form of graphene). What is, however, more critical than the generalized observations, is that the variability of the results is very high. Part of the high variability can be attributed to the fact that researchers are studying G, or GO, or rGO, or GnP, all of which have a different molecular structure, geometry, affinity for water, physical properties and therefore affect properties and dispersibility differently. In addition, there is no unified approach or evaluation of dispersion techniques of the nanomaterial, which consequently yields varying degrees of agglomeration. This presentation carefully dissects the effect of GO vs. rGO vs. GnP on the reported material performance. In addition, the corresponding mechanisms for the enhancement or detriment of the composite properties are discussed.

Mechanical properties enhancement

Mechanical properties of graphene cement-based composite improved with different graphene derivatives. GO being the most studied graphene derivative reported to enhance mechanical properties. Few-layer graphene, GnP and rGO were also used in various studies and reported to increase mechanical properties as well. The optimum range of graphene derivatives, GnP, GO, rGO was reported mostly within 0.02 to 0.1 wt% of cement, resulting in enhancement of cement-based composites (paste, mortar, concrete), compressive strength 30 to 120%, tensile strength 30 to 70%, and flexural strength 30 to 175%, respectively, compared to the cement-based system without any nanomaterials, Chintalapudi and Pannem (2020), Lin and Du (2020), Qureshi and Panesar (2017), Qureshi and Panesar (2019a), Qureshi and Panesar (2019b), Qureshi and Panesar (2020), Qureshi, Panesar and Peterson (2019), Qureshi et al. (2019). The wide variation in the mechanical performance enhancement is owing to different types of graphene materials such as GnP, GO, and rGO, as well as variation in their characteristics, such as functionalization state, physical properties, size, thickness, and dispersion state in cement, Qureshi and Panesar (2020). In the case of low functionalized graphene, such as GnP and rGO, their physical strength, size and stack thickness after dispersion in cement matrix is a major influencing factor. The functional groups are vital in composite strength enhancement for functionalized graphene, such as GO.

Microstructure

Graphene derivatives improve the microstructure of the cement-based composite. The impact of graphene on the cement microstructure is investigated using different common observation and analysis processes, such as porosity measurement, XRD, TGA, and SEM-EDX (Fig. 3). Functional groups of GO and rGO is reported to react with cement hydration products and form bonding (Fig. 3a), Pan et al. (2015). Graphene nano plane sheet acts as a nucleation site during the cement hydration process, enhancing the hydration products and densifying the composite matrix. This is evident while microstructural quantification using TGA (Fig. 3b) and XRD (Fig. 3c) show graphene derivatives increases cement hydration products ($Ca(OH)_2$ and C-S-H) in the composite matrix, Qureshi & Panesar (2019b). The SEM images correspondently show micropore filling, bonding and toughening effects (Fig. 3 d-f), Qureshi and Panesar (2019b). Overall, graphene is reported to impact the microstructure through the chemical bonding of functional groups with cement hydration products, nucleation effect, pore filling effect, composite interfacial zone bonding effect, and toughening of the matrix. As a result, the composite microstructure improves, which causes enhancement in density, mechanical properties and durability performance of the composite.

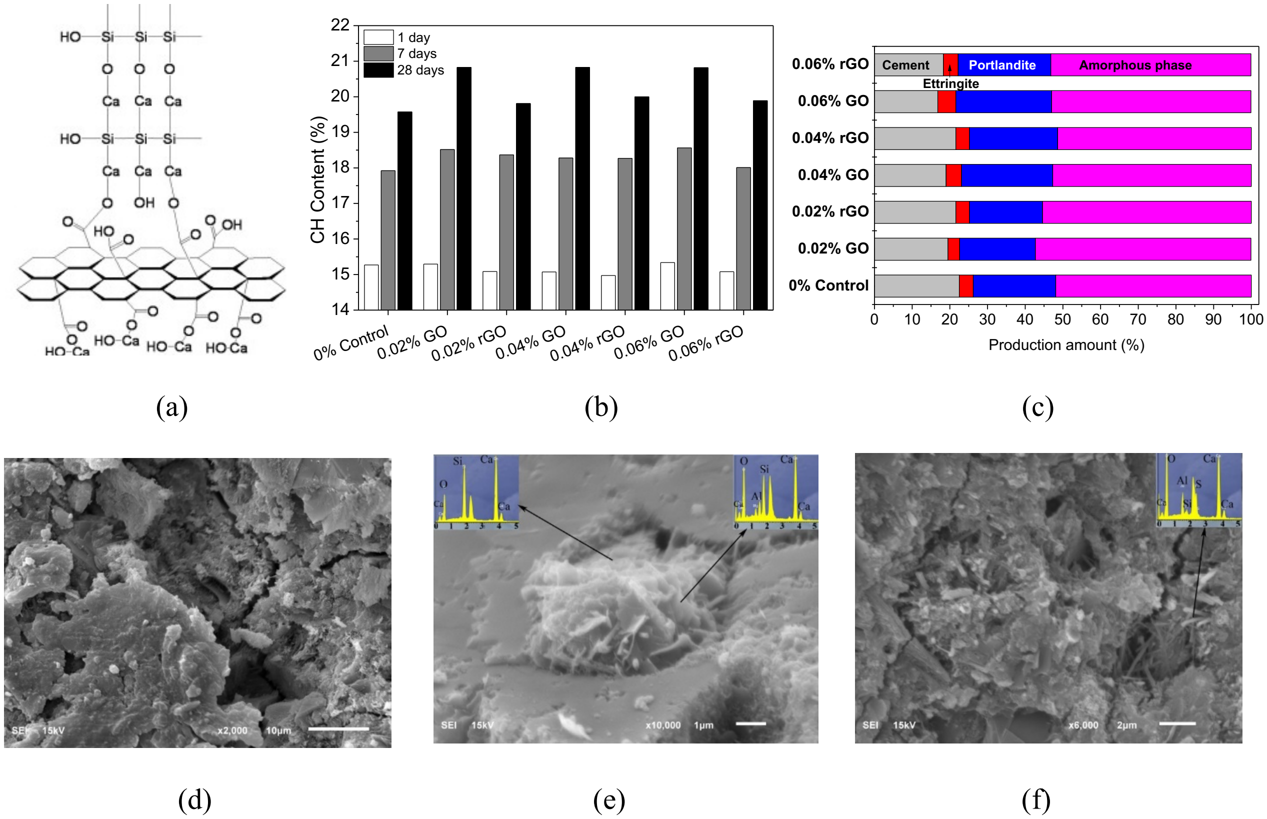
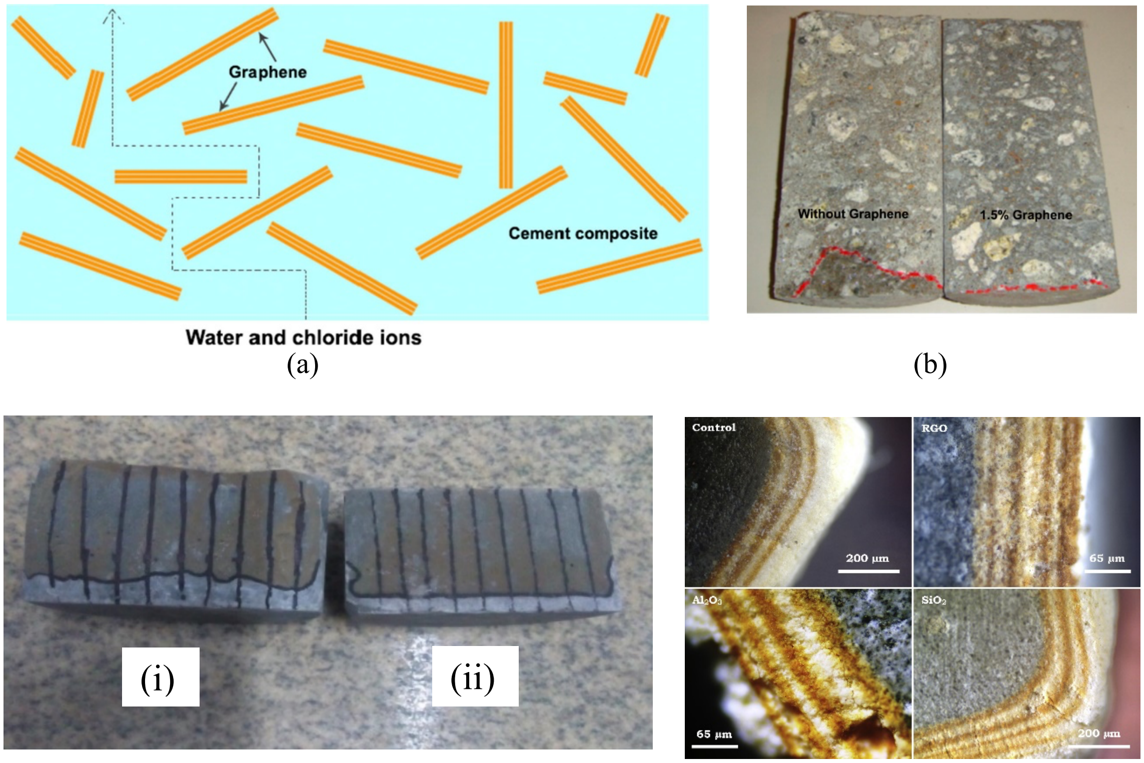


Figure 3. Microstructure of graphene cement composite: (a) interaction of GO's carboxylic acid function groups with $Ca(OH)_2$ and C-S-H of cement paste, Pan et al. (2015), (b) percentage mass loss for CH phase between 400 ºC to 500 ºC over time in thermogravimetric analysis, (c) theoretical volume estimated by Rietveld method quantifying from XRD at 28-day hydrated samples, (d) SEM image of Control (pure cement paste), (e) SEM image of a small pore of 0.04% GO cement composite and (f) SEM image of 0.06% rGO cement composite, (Figure 3b to 3f reproduced from Qureshi and Panesar (2019b)).

Durability performance enhancement

Graphene derivatives were reported to have increased the durability performance of the cement-based system in most of the studies (Fig.4). This is due to the modification of the composite microstructure by graphene. Concrete's penetration resistance against aggressive element enhanced due to the increase of tortuosity path (Fig. 4a) by graphene in the composite matrix, Lin and Du (2020). A permeability study of concrete with 0.05 to 2.5 wt% (of cement) graphene suggests that 1.5 wt% graphene concrete exhibits optimum performance reducing 80% water penetration and chloride diffusion coefficient (Fig. 4b) Du, Gao and Pang, 2016). In another similar study, 0.02% GO performed improved resistance against chloride penetration (Fig. 3c-i) compared to control concrete without GO (Fig. 3c-ii), Wang and Zhao (2018). The use of 0.06% GO in concrete also enhanced the freeze-thaw resistance of concrete through 50% weight loss reduction compared to the reference sample during the test, Mohammed, Sanjayan, Duan, and Nazari (2016). Fig. 3d shows mortar durability performance in an acid (HNO_3) environment. rGO in the cement composite system decreases 46% capillary porosity compared to that of reference cement paste (without any rGO); as a result, the relative durability performance of rGO modified composite results in overall least thickness of degradation compared to the Al_2O_3, SiO_2 containing composites and the reference cement paste mix (Fig. 3d), Muthu and Santhanam (2018). Overall, the durability performance of concrete improved due to the modification of concrete microstructural properties, density and tortuosity path by graphene derivatives.



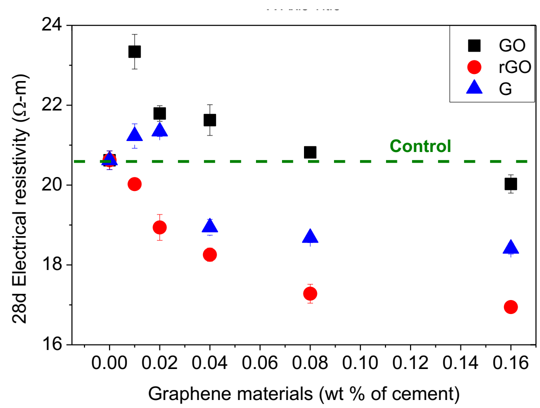
(c) (d)

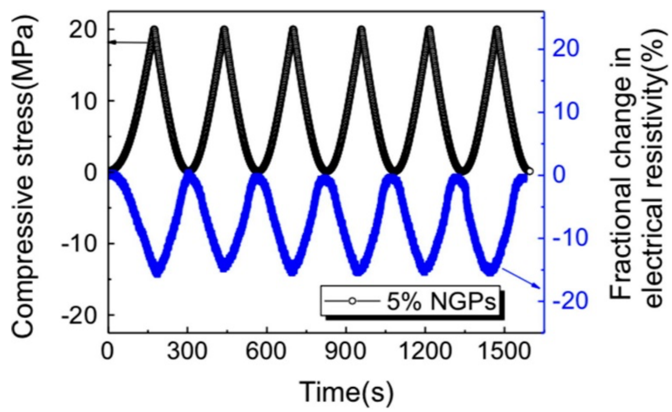
Figure 4. Durability performance of graphene cement-based composite: (a) Influence of randomly oriented graphene on the tortuous path, Lin and Du (2020), (b) Enhancement on-resistance of concrete against water penetration with 1.5% graphene, Du et al. (2016), (c) Split specimens with spraying 0.1 mol/L AgNO3 solution: (i) reference; (ii) specimen with 0.02 wt% GO Nanosheets, Wang and Zhao (2018), and (d) Optical micrographs revealing the formation of the brown rings in the four pastes subjected to nitric acid attack, Muthu and Santhanam, (2018).

Smart properties and multifunctionality

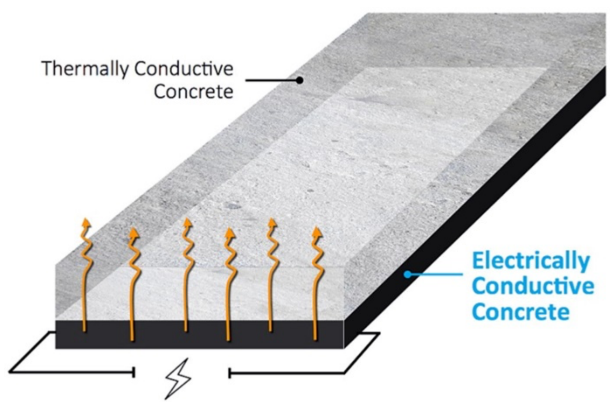
Graphene shows prospects for developing smart properties and multifunctionality in cement-based composite. Fig. 5 presents smart properties development by graphene in the cement-based composite. The electrical resistivity of cement composite decreases up to 18% with the increasing proportions of GnP and rGO up to 0.16 wt% in the composite due to their high electrical conductivity property (Fig. 5a), Qureshi and Panesar (2020). However, this is not the case for GO in the composite due to its no conductive properties. Cement composite with a higher proportion of graphene (0 to 10 vol% of cement) shows piezoresistive behaviour, and the percolation threshold of graphene was 2%, showing up to 15.6% fractional change electrical resistivity under 10 MPa compressive stress (Fig. 5b), Sun et al. (2017). Another interesting smart property that graphene can influence in the cement-based composite is to modify its thermal conductivity. This is owing to the fact that well-dispersed graphene in the composite develops a continuous heat transfer channel within the matrix, enhancing the thermal conductivity. The combined effect of electrical and thermal conductivity property of graphene cement-based composite shows prospects for smart road infrastructure development application, which will not require de-icing salt application in the future as the concept depicted in Fig. 5c, Talga (2018). Graphene's electromagnetic interference (EMI) shielding capacity may enhance the EMI shielding of cement-based composites. Sun et al. (2017) have shown that 10 vol% graphene in the cement-based composite can reach 104 dB EMI shielding, which is

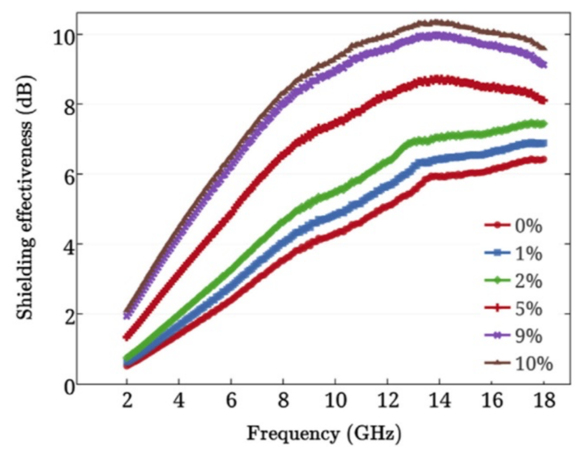
1.6 times compared to the corresponding plain cement composite (without graphene) (Fig. 5d), Sun et al., (2017). Combining one or more of those smart properties and the enhancement of mechanical properties and durability performance of graphene cement-based composite opens the prospects for developing multifunctional composite for future generation smart infrastructure.





(a) **(b)**



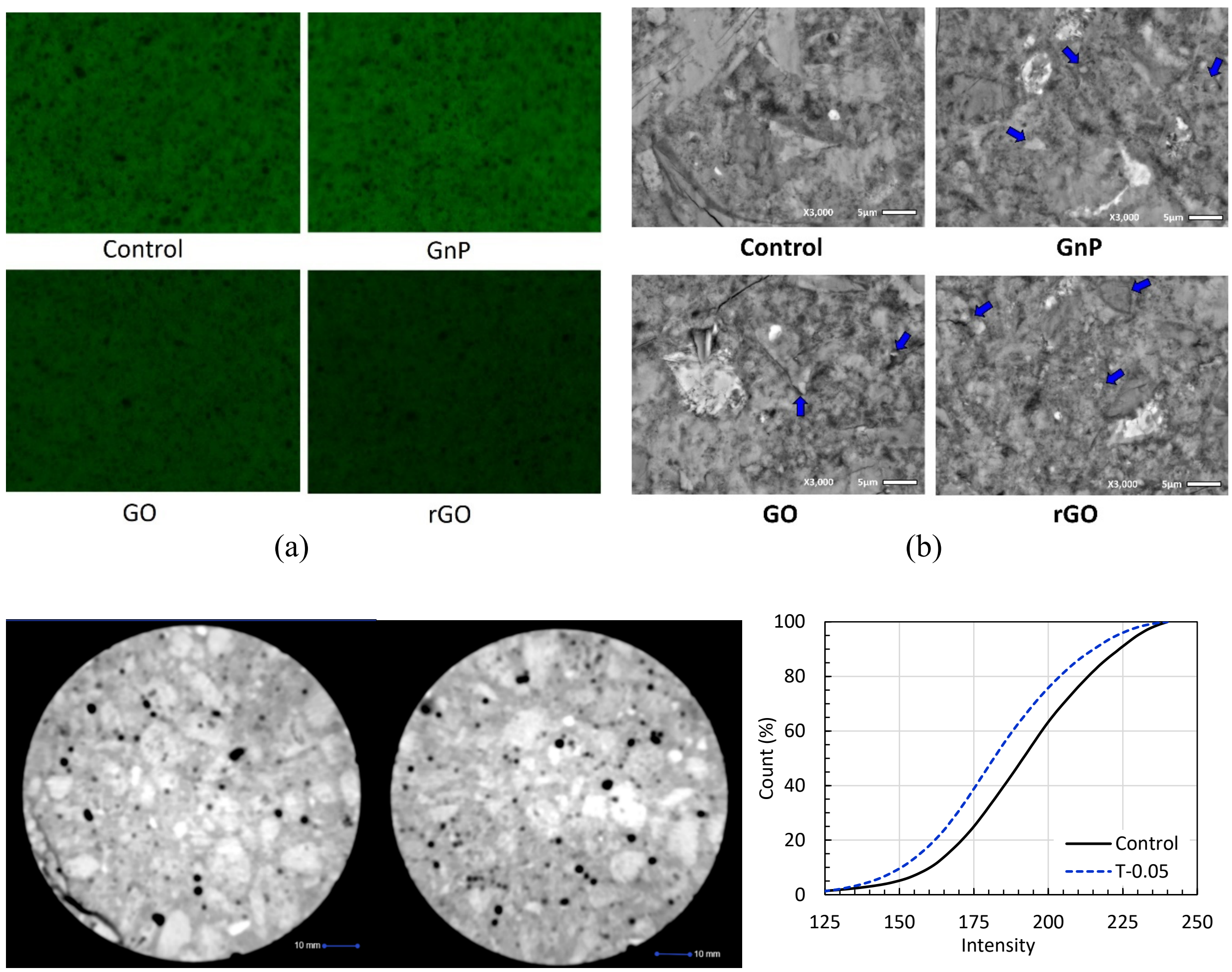


(c) **(d)**

Figure 5. Smart functionality: (a) average electrical resistivity of 28-day GCCs, Qureshi and Panesar (2020), (b) Piezoresistive behavior of cement composites infused with 5% graphene under cyclic loading, Sun et al. (2017), (c) Concept of de-icing application on the graphene reinforced concrete pavement, Talga (2018), and (d) Effectiveness of electromagnetic shielding of the cement composites infused with 0%, 1%, 2%, 5%, 9% and 10% graphene, Sun et al. (2017).

EXPERIMENTAL FINDINGS

The research program at the University of Toronto evaluates the hydration, workability, mechanical properties, microstructure and transport properties of graphene-cement composites (namely using different forms of GO, rGO and GnP). Some preliminary microstructural studies are presented in this section from the ongoing studies to understand how graphene can modify the composite and improve performance, such as barrier mechanism, EMI and nuclear radiation shielding. Fig. 6 presents microstructural image analysis of graphene-cement based paste and concrete. Fluorescence microscopic images show that 0.1 wt% of GnP, GO, and rGO (as characterized in Fig. 2) have densified the cement paste composite and decreased the light transmittance (Fig. 6a). rGO, in that aspect, show promising darkness following GO and GnP. The corresponding SEM images in Fig. 6b suggest that graphene materials have uniformly distributed in the matrix, densified it forming good bonding and filling the micropores. A recently upgraded forms of GnP produced by thermomechanical exfoliation (TME-GnP) by Zentech ltd. was used to produce concrete with 0.05 wt% of cement (T-0.05). Computed tomography (CT) imaging conducted at UWE Bristol suggests that GnP decreases the transmission of X-rays (Fig. 6 c and d). The greyscale threshold intensity of T-0.05 was 156 compared to that of 164 for the subsequent control concrete without GnP. Also, the distribution curve shifting up for corresponding grayscale intensity indicates a denser microstructure and less X-ray transmission. These preliminary results show promise for graphene-cement based composite as an improved radiation shielding construction material.



(c) (d)

Figure 6. Microstructural analysis, graphene-cement paste composite: (a) Fluorescence microscopic image and (b) SEM images, and graphene-cement concrete: (c) CT scan images, and (d) distribution of intensity from CT scan image avoiding coarse aggregate and large pores.

CONCLUSION

Graphene-cement based composite shows prospects for developing multifunctional construction materials for future infrastructure development. Graphene-cement composite consistently shows improved strength, durability, microstructure, piezoresistive properties, and radiation shielding performance. Variability in reported properties and performance of graphene-cement composites can be due to the lack of good characterization of graphene materials, consistency in mix design formulations, dispersion protocols, and the effect of the material system tested (i.e. paste, mortar or concrete). There is a need for further research to (i) optimize and quantify the adequacy of dispersion of the nanomaterials, (ii) examine the material properties of concrete composites containing graphene forms, (iii) investigate long term durability, and (iv) smart properties.

REFERENCES

Chen, C., Long, M., Xia, M., Zhang, C. and Cai, W. (2012). Reduction of graphene oxide by an in-situ photoelectrochemical method in a dye-sensitized solar cell assembly. *Nanoscale Research Letters*, 7(1), 101.

Chintalapudi, K. and Pannem, R. M. R. (2020). An intense review on the performance of Graphene Oxide and reduced Graphene Oxide in an admixed cement system. *Construction and Building Materials*, 259.

Du, H., Gao, H. J. and Pang, S. D. (2016). Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet. *Cement and Concrete Research*, 83, 114–123.

Gholampour, A., Valizadeh Kiamahalleh, M., Tran, D. N. H., Ozbakkaloglu, T. and Losic, D. (2017). From Graphene Oxide to Reduced Graphene Oxide: Impact on the Physiochemical and Mechanical Properties of Graphene–Cement Composites. *ACS Applied Materials & Interfaces*, acsami.7b16736.

Krishna, R. S., Mishra, J., Nanda, B., Patro, S. K., Adetayo, A. and Qureshi, T. S. (2021). The role of graphene and its derivatives in modifying different phases of geopolymer composites: A review. *Construction and Building Materials*, 306, 124774.

Lin, Y. and Du, H. (2020). Graphene reinforced cement composites: A review. *Construction and Building Materials*, 265. Retrieved from https://doi.org/10.1016/j.conbuildmat.2020.120312

Mohammed, A., Sanjayan, J. G., Duan, W. H. and Nazari, A. (2016). Graphene Oxide Impact on Hardened Cement Expressed in Enhanced Freeze–Thaw Resistance. *Journal of Materials in Civil Engineering*, 28(9), 04016072.

Muthu, M. and Santhanam, M. (2018). Effect of reduced graphene oxide, alumina and silica nanoparticles on the deterioration characteristics of Portland cement paste exposed to acidic environment. *Cement and Concrete Composites*, 91, 118–137.

Pan, Z., He, L., Qiu, L., Korayem, A. H., Li, G., Zhu, J. W., … Wang, M. C. (2015). Mechanical properties and microstructure of a graphene oxide–cement composite. *Cement and Concrete Composites*, 58, 140–147.

Qureshi, T. S. and Panesar, D. K. (2017). A review: the effect of graphene oxide on the properties of cement-based composites. In *CSCE Annual Conference* (pp. 642-1 to 642-10). Vancouver, Canada.

Qureshi, T. S. and Panesar, D. K. (2019a). A comparison of graphene oxide, reduced graphene oxide and pure graphene: early age properties of cement composites. In *2nd RILEM Spring Convention & International Conference on Sustainable Materials, Systems and Structures*. Rovinj, Croatia.

Qureshi, T. S. and Panesar, D. K. (2019b). Impact of graphene oxide and highly reduced graphene oxide on cement based composites. *Construction and Building Materials*, 206, 71–83.

Qureshi, T. S. and Panesar, D. K. (2020). Nano reinforced cement paste composite with functionalized graphene and pristine graphene nanoplatelets. *Composites Part B: Engineering*, 197, 108063.

Qureshi, T. S., Panesar, D. K. and Peterson, K. (2019). Thin section microscopy and DVS study to determine the influence of graphene materials on the microstructure of cement based composite. In *17th Euroseminar on Microscopy Applied to Building Materials* (pp. 134–140).

Qureshi, T. S., Panesar, D. K., Sidhureddy, B., Chen, A. and Wood, P. C. (2019). Nano-cement composite with graphene oxide produced from epigenetic graphite deposit. *Composites Part B: Engineering*, 159, 248–258.

Shamsaei, E., de Souza, F. B., Yao, X., Benhelal, E., Akbari, A. and Duan, W. (2018). Graphene-based nanosheets for stronger and more durable concrete: A review. *Construction and Building Materials*, 183, 642–660.

Sun, S., Ding, S., Han, B., Dong, S., Yu, X., Zhou, D. and Ou, J. (2017). Multi-layer graphene-engineered cementitious composites with multifunctionality/intelligence. *Composites Part B: Engineering*, 129, 221–232.

Talga. (2018). Global breakthrough: Graphene-infused concrete conducts electricity. Retrieved from https://www.internationales-verkehrswesen.de/concrete-conducts-electricity/

Wang, B. and Zhao, R. (2018). Effect of graphene nano-sheets on the chloride penetration and microstructure of the cement based composite. *Construction and Building Materials*, 161, 715–722.

Wu, S., Qureshi, T. and Wang, G. (2021). Application of Graphene in Fiber-Reinforced Cementitious Composites: A Review. *Energies 2021, Vol. 14, Page 4614*, 14(15), 4614.

Xu, Y., Zeng, J., Chen, W., Jin, R., Li, B. and Pan, Z. (2018). A holistic review of cement composites reinforced with graphene oxide. *Construction and Building Materials*, 171, 291–302.