Morphed graphene as reinforcement for oil-well class G cement composites

Materials Letters 404 (2026) 139656

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Morphed graphene as reinforcement for oil-well class G cement composites

Luca Lavagna [a,*], Mattia Bartoli [b], Matteo Pavese [a], Maria C. Beldouque Correa [d], Alberto Tagliaferro [a,c], Francisco Robles Hernandez [d]

[a] Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24,10129 Turin, Italy
[b] Center for Sustainable Future Technologies @POLITO, Istituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy
[c] Faculty of Science, Ontario Tech University, Simcoe Street North, Oshawa, ON L1G 0C5, Canada
[d] College of Engineering, Division of Technology, University of Houston, Houston, TX 77204-4020, USA

A R T I C L E I N F O

Keywords:
Morphed graphene
Cement
Reinforced materials

A B S T R A C T

Morphed graphene (MG) has only recently been put forward as the perfect reinforcement composite material for structure composites due to its unique mechanical properties. This article addresses the possibility of applying MG as a toughener phase in composites of cement for oil-well. MG was synthesized from petroleum coke through control milling and incorporated into cement with varying concentrations (0.1–1 %). The mechanical behavior of MG-reinforced cement demonstrated significant improvements, including enhanced fracture energy, flexural strength, and compression strength. Electron microscopy morphological analysis confirmed that MG effectively reduced porosity and improved particle cohesion.

1. Introduction

Studies have demonstrated that nano- and micro-scale reinforcement can enhance the fracture resistance of cement-based materials by reducing the formation and growth of cracks. This improvement has valuable potential for addressing issues such as seismic activity, pressure-related stresses, or structural flaws [1]. The addition of a very small amount of carbon-based nano-reinforcement can lead to significant enhancement in both compressive and flexural strength. This improvement is attributed to the combined effects of enhanced nucleation of cement hydration products and the inhibition of crack propagation [2]. Toughening of cement composites is a field of great interest [3] due to their intrinsic brittleness and great solicitations that are exposed to [4]. Different studies shown that the addition of a very low dosage of graphene the compressive strength increases due to a more regular structure of C-S-H that reduce the inner pores in cement [5]. Recently, a new carbon allotrope named MG was described [6–8]. MG is composed of distorted covalently cross-linked graphene layers bonded with a sp^2 hybridization but a sp^3 like arrangement. Among its phases, morphed graphene RH-II phase is rippled structure emerging when graphene sheets undergo mechanical deformation induced by compressive strain promoted by ball milling [6]. MG has shown surprising properties as reinforcement agent for a wide range of matrices in concentrations from 1 % to 5 % [9,10]. In this work, we are exploring the use of MG as toughening agent in oil-well cement showing an improvement in all the properties by using concentration of MG ranging from 0.1 % up to 1 %. The results underscore the promise of MG as an economical reinforcement material for high-performance cement composites, opening the door to advanced structural applications.

2. Materials and methods

The MG is manufactured from soots, in this case we used PetCoke that is an oil-and-gas by product and very abundant. The PetCoke is grind in a Nutribullet® for periods of 1 min at a time until fine powder (−150 mesh) is produced. The fines are collected and milled in Spex. The Spex procedure was previously reported in [6,7]. The cement used for this study is an American Petroleum Institute oil-well cement Class G. The MG nanoparticles were used to prepare cement-based composites, containing 0.1; 0.5 and 1 % bwoc (by weight of cement). The percentage was chosen according to preliminary studies in the literature on the use of graphene-like materials cement composites [11]. The procedure to prepare cement consists in the dispersion of MG in water with an ultrasonic tip for 15 min at 100 W power. The suspension of MG and water was mechanically stirred, and cement powder was gradually added. The mixture with a water-to-cement ratio of 0.45, was then cast into appropriate molds and cured for 24 h at 85 °C in 100 % relative humidity. Prismatic molds of size 20x20x80 mm were used for the cement

* Corresponding authors.
E-mail address: luca.lavagna@polito.it (L. Lavagna).

https://doi.org/10.1016/j.matlet.2025.139656
Received 13 August 2025; Accepted 12 October 2025
Available online 13 October 2025

composites. The transmission electron microscopy (TEM) analysis on MG was carried under low dose conditions in the TEAM 05 microscope at the Molecular Foundry-Lawrence Berkeley National Laboratory operated at 80 keV. Raman spectroscopy was performed using a Renishaw inVia equipped with a green laser line (514 nm) with a 50× objective. Raman spectrum was fitted by using the methodology proposed by Tagliaferro et al. [12]. The morphology of both MG and cement composite were investigated using a Field Emission Scanning Electrical microscope (FE-SEM) Zeis SupraTM 25. The mechanical behavior of the cement composites was evaluated using a three-point bending test, with crack mouth opening displacement (CMOD) control according to the JCI-S-001-2003 standard. Testing was conducted using a ZwickLine z050 single-column mechanical testing machine following the procedure described in literature [11].

3. Results

The MG structure shown in Fig. 1b-d is not the typical graphene structure as this material has an intermediate plane that expands the planes from 0.33 nm to 0.36–0.38 nm and this is a new and a unique phase known as morphed graphene [6,7]. The arrows in Fig. 1d identify the intermediate plane seen un morphed graphene. Morphed graphene demonstrated to have unique characteristics for composites such as outstanding elasticity with an average particles size of up around 40 nm [9]. What is important about this phase is its ability to be preserved through manufacturing and permits improvements.

As reported in Fig. 1a, the Raman spectrum of MG showed sharp D and G peaks formed respectively by one component (named D) centered at 1343 cm^{-1} and two components centered at 1480 cm^{-1} (G^1) and 1580 cm^{-1}(G^2) and a structured 2D region with three detectable components named 2D (2687 cm^{-1}), D + G (2915 cm^{-1}) and 2D (3163 cm^{-1}). As reported by Shimoidara et al. [13], G^2 peak raised from graphitic domains with a high bond angle order while G^1 originated from amorphous domains with a higher angle disorder. Accordingly, the ration between G^1 and G^2 was proposed as measure of bond angle disorder and MG showed a value of 0.4 inferior to the one observed in non-activated carbon black (around to 0.6) [13] proving a higher angle order. Furthermore, the ration between D and G peak of up to 0.9 suggests a long-range order close to those obtained by thermal annealing of non-graphitizable biomass derived carbon treated temperature higher than 1000 °C. Furthermore, we observed a peak at 863 cm^{-1} reasonably due to iron based traces left by the milling media [14] or other trace materials present in PetCoke such as pure S or S rich compounds.

The mechanical performances of MG used as reinforcement in cement base composites is shown in Fig. 2. Flexural strength showed improvement compared to OPC of 38 % for 0.1 % and up to of 80 % for 0.5 %. Further improvement of MG amount did not significantly change the flexural strength values. By adding up to 0.1 wt% of MG, we observed a toughening effect as shown by both fracture energy and compression strength results that reached up to 2.8 ± 0.5 J and 55.78 ± 1.5 MPa respectively. By increasing the quantity of MG up to 0.5 wt%, we observed an increment in the brittleness of the material with a significant decrement of both fracture energy and compression strength as shown in Fig. 3 b and c. We hypothesized that the decrement of mechanical properties of MG based composites loaded with 1 wt% was due to the poor dispersion or the carbon additions act as stress concentrators in part due to a lack of cohesion. This is translated into the optimization of the requirements in terms of fillers into the composites as we minimize the morphed graphene additions, and we maximize the composite's mechanical properties. The FE-SEM captures reported in Fig. 3

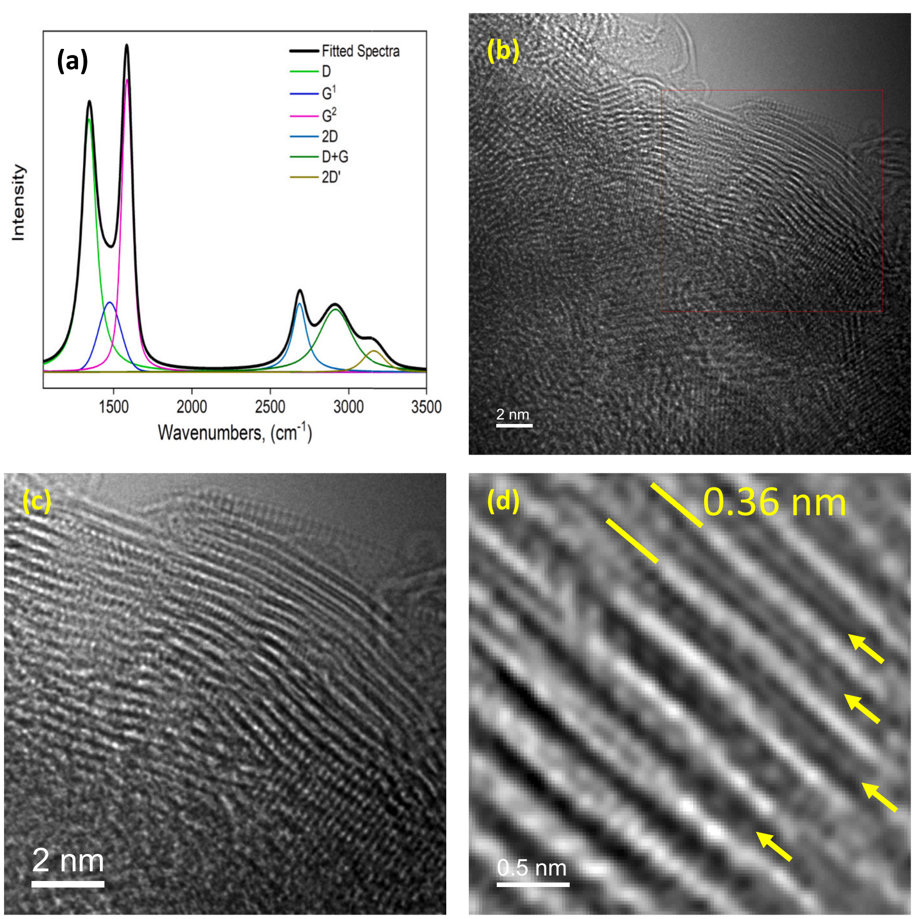

Fig. 1. Characterization of morphed graphene: a) Raman spectra of MG and b-d) TEM microscopy.

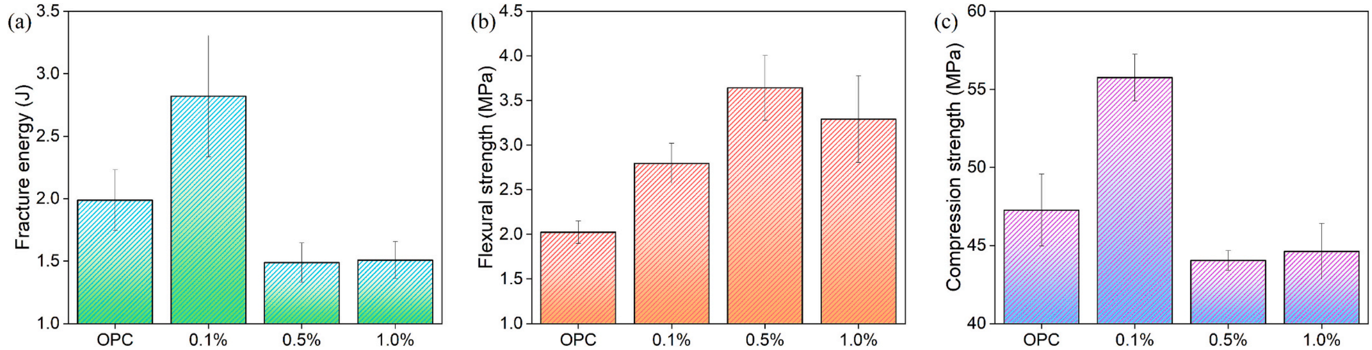

Fig. 2. Mechanical results: a) fracture energy, b) flexural strength and c) compression strength.

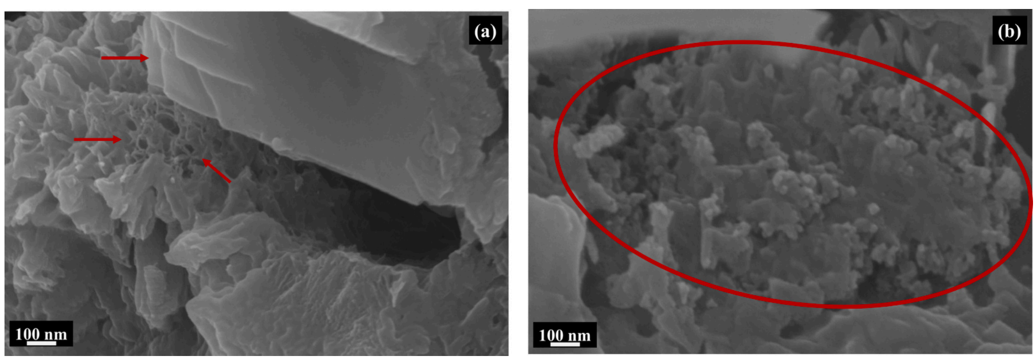

Fig. 3. FESEM pictures of a) oil-well cement and b) MG based oil-well cement composites.

provided an intriguing point of view of the differences between the fracture section of oil-well cement. As shown in Fig. 3a, the oil-well cement showed fracture section characterized by lamellae tighter with porous network (indicated by the red arrows) with large hole left behind after the material failure. The MG based oil-well cement composites showed the presence of round shape particles embedded into the cement matrix (Fig. 3b, red circle) due to the presence of MG that reduced the local porosity of the materials. This could be accountable for the improved mechanical properties observed. In other words, morphed graphene fills the gaps within the cement particles creating reinforcement sites. The nano-reinforcement and nano-bridging between the graphene nanoparticles and C-S-H phase typically happens due to the nucleation effects. These mechanisms subsequently increase the toughening of final cement composites [11].

4. Conclusions

This work reported the use of MG as toughening agent for cement-based composites. The empirical evidence proved the toughening effectiveness induced by the addition of up to 0.5 % of MG reaching an improvement of both fracture energy and compression strength results of up to 42 % and 18 % compared with OPC. The presence of morphed graphene (MG), which fills gaps and strengthens the cement matrix through nano-reinforcement and nucleation effects, leading to improved mechanical properties. This study was a first attempt on the spread of MG to produce new classes of improved reinforced cement composites for high tech applications.

CRediT authorship contribution statement

Luca Lavagna: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Mattia Bartoli:** Conceptualization, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Matteo Pavese:** Conceptualization, Resources, Supervision, Validation, Writing – review & editing, Funding acquisition. **Maria C. Beldouque Correa:** Formal analysis, Investigation, Methodology, Software, Visualization. **Alberto Tagliaferro:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Francisco Robles Hernandez:** Funding acquisition, Investigation, Resources, Supervision, Validation, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] J.-K. Kim, Y. Mai, High strength, high fracture toughness fibre composites with interface control—a review, Compos. Sci. Technol. 41 (1991) 333–378, https://doi.org/10.1016/0266-3538(91)90072-W.
[2] H. Yang, H. Cui, W. Tang, Z. Li, N. Han, F. Xing, A critical review on research progress of graphene/cement based composites, Compos. Part Appl. Sci. Manuf. 102 (2017) 273–296, https://doi.org/10.1016/j.compositesa.2017.07.019.
[3] V.C. Li, M. Maalej, Toughening in cement based composites. Part I: cement, mortar, and concrete, Cem. Concr. Compos. 18 (1996) 223–237, https://doi.org/10.1016/0958-9465(95)00028-3.
[4] A.T. McQueen, D.M. Long, Greenhouse gas reduction/recovery from portland cement operations - a case study on the solicitation process, system evaluation, funding and status of demonstration, in: IEEE Cem. Ind. Tech. Conf. 2006 Conf. Rec., 2006, p. 10, https://doi.org/10.1109/CITCON.2006.1635708.
[5] C. Benavente, A. Romero, J. Napa, A. Sanabria, Y. Landivar, L. La Borda, P. Pezo, A. Muñiz, M. Muñiz, The influence of graphene oxide on the performance of concrete: a quantitative analysis of mechanical and microstructural properties, Buildings 15 (2025), https://doi.org/10.3390/buildings15071082.

[6] H.A. Calderon, I. Estrada-Guel, F. Alvarez-Ramírez, V.G. Hadjiev, F.C. Robles Hernandez, Morphed graphene nanostructures: experimental evidence for existence, Carbon 102 (2016) 288–296, https://doi.org/10.1016/j.carbon.2016.02.056.

[7] H.A. Calderon, A. Okonkwo, I. Estrada-Guel, V.G. Hadjiev, F. Alvarez-Ramírez, F. C. Robles Hernández, HRTEM low dose: the unfold of the morphed graphene, from amorphous carbon to morphed graphenes, Adv. Struct. Chem. Imaging 2 (2016) 10, https://doi.org/10.1186/s40679-016-0024-z.

[8] L. Prasittisopin, R. Nganglumpoon, C. Thongchom, J. Panpranot, Systematic review and thematic analysis of the utilization of carbon quantum dots (CQDs) in construction materials, J. Mater. Sci. Mater. Eng. 20 (2025) 53, https://doi.org/10.1186/s40712-025-00258-z.

[9] H.A. Calderon, F. Alvarez Ramirez, D. Barber, V.G. Hadjiev, A. Okonkwo, R. Ordoñez Olivares, I. Estrada Guel, F.C. Robles Hernandez, Enhanced elastic behavior of all-carbon composites reinforced by in-situ synthesized morphed graphene, Carbon 153 (2019) 657–662, https://doi.org/10.1016/j.carbon.2019.07.012.

[10] A. Raghatate, F.D. Cortes Vega, O. Velazquez Meraz, K. Ahmadi, N.M. Chaudhari, D. Solanki, A.B. Puthirath, N. Castaneda, P.M. Ajayan, J.M. Herrera Ramirez, V. Balan, F.C. Robles Hernández, Sustainable biocomposites for structural applications with environmental affinity, ACS Appl. Mater. Interfaces 14 (2022) 17837–17848, https://doi.org/10.1021/acsami.2c02073.

[11] L. Lavagna, A. Santagati, M. Bartoli, D. Suarez-Riera, M. Pavese, Cement-based composites containing oxidized graphene nanoplatelets: effects on the mechanical and electrical properties, Nanomaterials 13 (2023), https://doi.org/10.3390/nano13050901.

[12] A. Tagliaferro, M. Rovere, E. Padovano, M. Bartoli, M. Giorcelli, Introducing the novel mixed gaussian-Lorentzian Lineshape in the analysis of the Raman signal of biochar, Nanomaterials 10 (2020) 1748, https://doi.org/10.3390/nano10091748.

[13] N. Shimodaira, A. Masui, Raman spectroscopic investigations of activated carbon materials, J. Appl. Phys. 92 (2002) 902–909, https://doi.org/10.1063/1.1487434.

[14] C.M. Phillippi, K.S. Mazdiyasni, Infrared and Raman spectra of zirconia polymorphs, J. Am. Ceram. Soc. 54 (1971) 254–258, https://doi.org/10.1111/j.1151-2916.1971.tb12283.x.