Experimental Test and Analytical Modeling of Mechanical Properties of Graphene-Oxide Cement Composites

Zhongcheng Duan^{1,2}, Li Zhang³, Zhiyuan Lin², Ding Fan², Mohamed Saafi⁴, João Castro Gomes⁵ and Shangtong Yang^{2,*}

¹ School of Architecture and Design, China University of Mining and Technology, Xuzhou, 221116, China

² Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, G1 1XJ, United Kingdom

³ Department of Architecture and Building Environment, the University of Nottingham, Nottingham, NG7 2RD, United Kingdom

⁴ Department of Engineering, Lancaster University, Lancaster, LA1 4YW, United Kingdom

⁵ Department of Civil Engineering and Architecture, University of Beira Interior, Covilha, 6201-001, Portugal

ABSTRACT

Graphene oxide (GO) has recently been considered as an ideal candidate for enhancing the mechanical properties of the cement due to its good dispersion property and high surface area. Much of work has been done on experimentally investigating the mechanical properties of GO-cementitious composites; but there are currently no models for accurate estimation of their mechanical properties, making proper analysis and design of GO-cement based materials a major challenge. This paper attempts to develop a novel multi-scale analytical model for predicting the elastic modulus of GO-cement taking into account the GO/cement ratio, porosity and mechanical properties of different phases. This model employs Eshelby tensor and Mori-Tanaka solution in the process of upscaling the elastic properties of GO-cement through different length scales. In-situ micro bending tests were conducted to elucidate the behavior of the GO-cement composites and verify the proposed model. The obtained results showed that the addition of GO can change the morphology and enhance the mechanical properties of the cement. The developed model can be used as a tool to determine the elastic properties of GO-cement through different length scales.

KEYWORDS: Multi-scale modelling; Graphene–Oxide; Elastic properties; Cementitious materials; Upscaling; In-situ SEM test.

* Corresponding authors: shangtong.yang@strath.ac.uk (s.yang).

29 1. INTRODUCTION

30 Nanomaterials have recently attracted considerable attention for their application to cementitious
31 composites, for improving the properties of cement/concrete. A wide range of nanomaterials such as
32 metal oxide or silica ¹, nanofibers ², nanotubes ³ and graphene ⁴ have been added into cementitious
33 materials to improve their compressive and flexural strength, Young's modulus and other
34 microstructure properties. Graphene is a single atom thick sheet of hexagonally arranged carbon
35 atoms with a carbon-carbon distance of 0.142 nm ⁵. It is about more than 100 times stronger than
36 steel by weight, conducting heat and electricity efficiently and nearly transparent ⁵. However, there
37 is an issue of dispersion when mixing with cementitious materials. Graphene oxide (GO), a product
38 of chemical exfoliation of graphene, can be an excellent nano reinforcement for cementitious
39 nanocomposites, due to its good dispersability in water, high aspect geometric ratio and excellent
40 mechanical properties.

41
42 Previous studies have revealed that GO shows better adhesion bonding properties to the matrix than
43 graphene, as a result of its oxygen functional groups provided ^{6,7}. Moreover, GO is hydrophilic due
44 to the carbonyl, epoxide, carboxyl and hydroxyl groups on its surface thus making it highly
45 dispersible in water as a result ⁸. Because of these functional groups, GO can react with cement and
46 provide strong stress transfer capacity which enables higher stress transfer between the matrix and
47 the GO, thereby increasing the stiffness of the plain matrix ⁹. Literature review suggests that GO
48 can increase the 28-day compressive and flexural strength of cement by as much as 72.7% and
49 67.1%, respectively at a GO concentration of 0.06 wt% and 0.04 wt%, respectively ⁹. Saafi et al. ⁴
50 investigated the material and mechanical properties of grapheme/fly ash geopolymetric composite
51 cement and experimentally quantified the enhancement in these properties.

52
53 GO can influence the hydration process of cement and alter the microstructure of cement paste. The

54 hydration rate of cement has been found to increase as the GO content increases, due to nucleation
55 effect ¹⁰. However, GO agglomeration can affect the increase of hydration rate of cement ¹¹. GO can
56 also densify cement paste, leading to less porosity and more hydration products; in particular, GO
57 can promote the production of rod-like and needle-like hydration products and their further
58 assembly into regular flower-like or polyhedron-like products, resulting in final formation of a
59 denser microstructure ⁹. Moreover, the workability of GO-cement can be improved by 21% with the
60 addition of 0.03 wt% GO ¹¹. Further, the electrical resistivity of GO-cement can be affected by GO
61 but it varies for different hydration stages and GO dosages ¹⁰.

62
63 Research activities on modeling of GO/cement composites are scarce and to date, most of the
64 models were developed for GO/polymer and carbon nanotube/polymer (CNTRP) composites. A
65 multi-scale modeling approach to extract mechanical properties of CNTRP was developed. ^{12, 13} The
66 model considered effective parameters associated with meso- and micro-scale, non-uniform
67 dispersion of CNTs and non-perfect bounding provided by van der Waals interaction. Both
68 agglomerated and fully dispersed CNTs were formulated in the model. Moreover, the influences of
69 carbon nanotube waviness on the stiffness reduction of CNTRP composites were investigated ¹⁴.
70 The structural and mechanical properties of the graphene/GO based polymer composites were
71 investigated through molecular dynamics simulations ¹⁵. It was found that the interlayer spacing and
72 the layer–matrix interactions control the large scale properties of these composites, thereby
73 affecting the elastic modulus of the composites. Moreover, the chemical composition of individual
74 GO sheets also affects the mechanical properties and the elastic moduli of individual GO sheets
75 decrease with a higher density of oxygen-containing groups. To the authors' knowledge, there is no
76 model for the prediction of the mechanical properties of GO-cement. As a result, proper analysis
77 and design of GO-cement based materials remain a major challenge and hinders the application of
78 GO cementitious composites in civil engineering.

80 This paper attempts to experimentally investigate the properties of GO-cement and develop a
81 multi-scale analytical model for the elastic modulus of the GO reinforced cement, which is a key
82 material parameter representing the elasticity of material. Volume fractions and mechanical
83 properties of different phases at various length scales are considered in the formulation of the
84 macroscale Young's modulus. Voids have also been considered in the formulation by assuming zero
85 stiffness of them. In-situ SEM three-point bending tests were carried out to understand the fracture
86 mechanisms of GO-cement composites and verify the derived model by comparing the Young's
87 modulus obtained from both modeling and experimental tests. Mercury Intrusion Porosimetry (MIP)
88 tests are also carried out to find out the effects of adding GO on the porosity of cement. Some key
89 parameters such as the bulk and shear moduli of GO and Calcium Silicate Hydrates (C-S-H) were
90 chosen and their effects on the macroscale Young's modulus have been investigated. The developed
91 model can be used as a useful tool for predicting the Young's modulus of GO-cement with a variety
92 of composition and fractions. Accurate prediction of the mechanical properties of GO-cement will
93 help accelerate the application of GO into civil engineering industries.

94

95 **2. MODEL FORMULATION**

96 In this paper, GO-cement composites are studied at 3 different length scales, as shown in Figure 1.
97 At microscale, there are mainly GO and C-S-H while at mesoscale, calcium hydroxide (CH), voids
98 and some unhydrated cement^{16, 17}. To determine the scales in multi-scale modelling, the structural
99 dimensions need to be significantly larger than the dimensions of the material in homogeneities.
100 Accordingly, Representative Volume Element (RVE) is introduced to represent the basic unit of
101 homogeneity. Eshelby tensor and Mori-Tanaka solution are employed in the process of upscaling
102 the elastic properties of GO-cement through different length scales. There is an argument that the
103 GO is a disk-like material while Mori-Tanaka may not be directly applicable. However, in practice,

104 a few layers of GO always stack together or fold, forming a roughly spherical shape, as shown in
 105 Figure 2. It is almost impossible to have a single layer of disk-like GO sheet in cement and the
 106 application of Mori-Tanaka scheme can therefore be justified. This justification is evident in some
 107 previous work, e.g., Alkhateb et al.¹⁸ and Noh et al.¹⁹. RVE is utilized which is essential to find the
 108 homogenized constitutive response at each smaller scales^{20, 21}. In this paper, an RVE with a size of
 109 50×50μm is chosen for the two-phase matrix-inclusion geometries at the microscale level. At this
 110 level, the RVE is displayed in Figure 3. The average strain of the RVE is equal to the homogenized
 111 strain.

112
 113 At microscale, C-S-H is considered as the matrix and GO as the inclusion. As shown in Figure 3.
 114 The matrix phase has a volume V_m and a volume fraction f_m . The volume for the inclusion phase
 115 is V_i and the volume fraction is f_i . The relationships between these parameters can be expressed as
 116 follows,

$$117 \quad f_m = \frac{V_m}{V_p} \quad (1a)$$

$$118 \quad f_i = \frac{V_i}{V_p} \quad (1b)$$

$$119 \quad f_m + f_i = 1 \quad (1c)$$

120 In order to work out the stress and strain fields in the RVE, the mechanical response of each phase
 121 needs be determined by assuming each constituent phase follows its own constitutive relations. The
 122 continuum mechanism can then be applied to describe the relation between the average stress and
 123 strain in the sub-domains of the RVE, presented as follows,

$$124 \quad \bar{\sigma} = \mathbf{C}_p \bar{\varepsilon} \quad (2)$$

125 where $\mathbf{C}_p$ is the Elasticity tensor and determines the stress-strain relationship for each phase

126 individually.

127

128 To relate the stresses/strains across phases, concentration tensors are introduced. In linear
129 continuum micromechanics, the homogenized strain $\bar{\epsilon}$ can be linked to the individual strain ϵ_r at
130 different phase by means of a linear strain localization condition which can be shown as follows:

131
$$\epsilon_r = \mathbf{A}_r : \bar{\epsilon} \quad (3)$$

132 where $\mathbf{A}_r$ is the fourth-order concentration (localization) tensor.

133 By introducing the fourth-order unit tensor $\mathbf{I} = \frac{\partial \epsilon_{ij}}{\partial \epsilon}$, $\mathbf{A}_r$ can be expressed as follows:

134
$$\langle \mathbf{A}_r \rangle_{V_p} = \mathbf{I} \quad \text{or} \quad f_m \mathbf{A}_m + f_i \mathbf{A}_i = \mathbf{I} \quad (4)$$

135 where $\mathbf{A}_m$ and $\mathbf{A}_i$ are the 4th order localization tensor for matrix and inclusion respectively.

136 Therefore, $\mathbf{A}_m$ can be expressed as follows.

137
$$\mathbf{A}_m = \frac{[\mathbf{I} - f_i \mathbf{A}_i]}{f_m} \quad (5)$$

138 By introducing the linear elastic constitutive relation for different phases contained in V_p , the linear
139 homogenization formula for the macroscopic elasticity tensor can be determined as follows:

140
$$\mathbf{C}_h = \langle \mathbf{C} : \mathbf{A} \rangle = \sum_r f_r \mathbf{C}_r : \mathbf{A}_r = f_m \mathbf{C}_m : \mathbf{A}_m + f_i \mathbf{C}_i : \mathbf{A}_i \quad (6)$$

141 According to Mori-Tanaka theory²¹ the localization tensor of the GO phase can be determined as
142 follows:

143
$$\mathbf{A}_i = [\mathbf{I} + f_m \mathbf{S} : \mathbf{C}_m^{-1} : (\mathbf{C}_i - \mathbf{C}_m)]^{-1} \quad (7)$$

144 For isotropic elastic spheres, the Hooke's law can be expressed in terms of stiffness tensor $\mathbf{C}_{r=i,m}$
145 and $\mathbf{C}_h$ as follows:

$$\mathbf{C}_r = 3K_r \mathbf{R} + 2\mu_r \mathbf{T} \quad (8a)$$

$$\mathbf{C}_h = 3K_h \mathbf{R} + 2\mu_h \mathbf{T} \quad (8b)$$

where $K_{r=i,m}$ and $\mu_{r=i,m}$ are the bulk moduli and shear moduli of phase inclusion and matrix respectively; K_p and μ_p are the homogenized bulk and shear moduli.

$\mathbf{R}$ and $\mathbf{T}$ are the volumetric part and the deviator part of the fourth-order unit tensor $\mathbf{I}$ respectively and $\mathbf{I} = \mathbf{R} + \mathbf{T}$ where,

$$\mathbf{R} = R_{ijkl} = 1/3 \delta_{ij} \delta_{kl} \quad (9)$$

For isotropic elastic spheres, the Eshelby tensor for the inclusion phase can be expressed in the form as follow,

$$\mathbf{S}_i = \alpha \mathbf{R} + \beta \mathbf{T} \quad (10)$$

where

$$\alpha = \frac{1+\nu}{3(1-\nu)} = \frac{3k_i}{3K_i+4\mu_i} \quad (11a)$$

$$\beta = \frac{8-10\nu}{15(1-\nu)} = \frac{6(k_i+2\mu_i)}{5(3K_i+4\mu_i)} \quad (11b)$$

Substituting Equations 8 and 9 and into Equation 7,

$$\mathbf{A}_i = \frac{1}{f_m(\alpha \frac{K_i}{K_m} - \alpha) + 1} \mathbf{R} + \frac{1}{f_m(\beta \frac{\mu_i}{\mu_m} - \beta) + 1} \mathbf{T} \quad (12)$$

Combining Equation 9, 10 and 11 leads to the relationship as follows,

$$\mathbf{C}_h = \mathbf{C}_m + f_i[\mathbf{C}_i - \mathbf{C}_m] : \mathbf{A}_i$$

$$= (3K_m \mathbf{R} + 2\mu_m \mathbf{T}) + f_i[(3K_i \mathbf{R} + 2\mu_m \mathbf{T}) - (3K_m \mathbf{R} + 2\mu_m \mathbf{T})] : \mathbf{A}_i$$

$$= 3K_m \mathbf{R} + \frac{f_i \cdot 3(K_i - K_m)}{\alpha \frac{K_i}{K_m} - \alpha + 1} \mathbf{R} + 2\mu_m \mathbf{T} + \frac{f_i \cdot 2(\mu_i - 2\mu_m)}{\beta \frac{\mu_i}{\mu_m} - \beta + 1} \mathbf{T}$$

$$165 \quad \text{And } C_h = 3K_h R + 2\mu_h T$$

$$166 \quad \text{Hence } 3K_h R + 2\mu_h T = 3K_m R + \frac{f_i \cdot 3(K_i - K_m)}{\alpha \frac{K_i}{K_m} - \alpha + 1} R + 2\mu_a T + \frac{f_i \cdot 2(\mu_i - 2\mu_m)}{\beta \frac{\mu_i}{\mu_m} - \beta + 1} T \quad (13)$$

167 Therefore, the homogenized bulk elastic modulus k_h and shear moduli μ_h can be determined as
168 follow,

$$169 \quad k_h = k_{CSH} + \frac{f_{GO}(k_{GO} - k_{CSH})}{1 + f_{CSH} \alpha \left(\frac{k_{GO}}{k_{CSH}} - 1 \right)} \quad (14)$$

$$170 \quad \mu_h = \mu_{CSH} + \frac{f_{GO}(\mu_{GO} - \mu_{CSH})}{1 + f_{CSH} \beta \left(\frac{\mu_{GO}}{\mu_{CSH}} - 1 \right)} \quad (15)$$

171 Finally, the effective Young's modulus after homogenization E_h can be derived as follows,

$$172 \quad E_h = \frac{9k_h\mu_h}{3k_h + \mu_h} = \frac{9 \left[k_{CSH} + \frac{f_{GO}(k_{GO} - k_{CSH})}{1 + f_{CSH} \alpha \left(\frac{k_{GO}}{k_{CSH}} - 1 \right)} \right] \left[\mu_{CSH} + \frac{f_{GO}(\mu_{GO} - \mu_{CSH})}{1 + f_{CSH} \beta \left(\frac{\mu_{GO}}{\mu_{CSH}} - 1 \right)} \right]}{3 \left[k_{CSH} + \frac{f_{GO}(k_{GO} - k_{CSH})}{1 + f_{CSH} \alpha \left(\frac{k_{GO}}{k_{CSH}} - 1 \right)} \right] + \left[\mu_{CSH} + \frac{f_{GO}(\mu_{GO} - \mu_{CSH})}{1 + f_{CSH} \beta \left(\frac{\mu_{GO}}{\mu_{CSH}} - 1 \right)} \right]} \quad (16)$$

173 The elastic modulus of C-S-H (i.e., k_h and μ_h) can be obtained from nano-indentation test or
174 molecular dynamics simulation ²². The modulus of GO (i.e., k_{GO} and μ_{GO}) are usually available
175 from commercial producers; it can also be computed or experimentally tested.

176

177 The same method can be applied to the next level homogenization for GO-cement paste. As shown
178 in Figure 1b, the cement paste can be considered as a three-phase composite. GO-CSH is treated as
179 the matrix containing calcium hydroxide (CH) and voids (V). Un-hydrated cement is not present in
180 the homogenization process as complete hydration is assumed for water-to-cement (w/c) ratio above
181 0.4. The homogenized strain can be linked to the individual strain at different phases in terms of the
182 linear strain localization tensors which are shown as follows,

$$183 \quad \varepsilon_r = \mathbf{A}_r : \bar{\varepsilon} \quad (17)$$

$$\varepsilon_h = \mathbf{A}_h : \bar{\varepsilon} \quad (18)$$

$$\varepsilon_{CH} = \mathbf{A}_{CH} : \bar{\varepsilon} \quad (19)$$

$$\varepsilon_V = \mathbf{A}_V : \bar{\varepsilon} \quad (20)$$

The concentration tensor $\mathbf{A}_r$ can also be expressed as follows,

$$\langle \mathbf{A}_r \rangle_{V_p} = \sum_r f_r \langle \mathbf{A}_r \rangle = \mathbf{I} \quad (21)$$

Therefore,

$$\mathbf{A}_h = 1/f_h [\mathbf{I} - (f_{CH} \mathbf{A}_{CH} + f_V \mathbf{A}_V)] \quad (22)$$

By introducing the linear elastic constitutive relation for different phases contained in V_p , the linear homogenization formula for the macroscopic elasticity tensor can be determined as follows,

$$\begin{aligned} \mathbf{C}_u &= \langle \mathbf{C} : \mathbf{A} \rangle = \sum_r f_r \mathbf{C}_r : \mathbf{A}_r \\ &= f_h \mathbf{C}_h : \mathbf{A}_h + f_{CH} \mathbf{C}_{CH} : \mathbf{A}_{CH} + f_V \mathbf{C}_V : \mathbf{A}_V \end{aligned} \quad (23)$$

The Young's modulus of voids is taken as 0. For a high w/c ratio of higher than 0.38, the clinker phase of the unhydrated cement can be ignored. Therefore the above equation can be simplified as follows,

$$\begin{aligned} \mathbf{C}_h + f_{CH} \left[\frac{3K_{CH} - 3K_h}{f_m (\alpha \frac{K_{CH}}{K_h} - \alpha) + 1} \mathbf{R} + \frac{(2\mu_{CH} - 2\mu_h)}{f_m (\beta \frac{\mu_{CH}}{\mu_h} - \beta) + 1} \mathbf{T} \right] \\ = (3K_h \mathbf{R} + 2\mu_h \mathbf{T}) + f_{CH} \left[\frac{3K_{CH} - 3K_h}{f_m (\alpha \frac{K_{CH}}{K_h} - \alpha) + 1} \mathbf{R} + \frac{(2\mu_{CH} - 2\mu_h)}{f_m (\beta \frac{\mu_{CH}}{\mu_h} - \beta) + 1} \mathbf{T} \right] \end{aligned}$$

Therefore

$$3K_u \mathbf{R} + 2\mu_u \mathbf{T} = (3K_h \mathbf{R} + 2\mu_h \mathbf{T}) + f_{CH} \left[\frac{3K_{CH} - 3K_h}{f_m (\alpha \frac{K_{CH}}{K_h} - \alpha) + 1} \mathbf{R} + \frac{(2\mu_{CH} - 2\mu_h)}{f_m (\beta \frac{\mu_{CH}}{\mu_h} - \beta) + 1} \mathbf{T} \right] \quad (24)$$

The homogenized bulk modulus and shear modulus for the second step can therefore be derived as

203 follows:

$$204 \quad k_u = k_h + \frac{f_{CH}(k_{CH}-k_h)}{1+f_h\alpha(\frac{k_{CH}}{k_h}-1)} \quad (25)$$

$$205 \quad \mu_u = \mu_h + \frac{f_{CH}(\mu_{CH}-\mu_h)}{1+f_h\beta(\frac{\mu_{CH}}{\mu_h}-1)} \quad (26)$$

206 The homogenized Young's modulus at the macroscale E_u can be obtained as follows,

$$207 \quad E_u = \frac{9k_u\mu_u}{3k_u + \mu_u} = \frac{9(k_h + \frac{f_{CH}(k_{CH}-k_h)}{1+f_h\alpha(\frac{k_{CH}}{k_h}-1)})(\mu_h + \frac{f_{CH}(\mu_{CH}-\mu_h)}{1+f_h\beta(\frac{\mu_{CH}}{\mu_h}-1)})}{3(k_h + \frac{f_{CH}(k_{CH}-k_h)}{1+f_h\alpha(\frac{k_{CH}}{k_h}-1)}) + (\mu_h + \frac{f_{CH}(\mu_{CH}-\mu_h)}{1+f_h\beta(\frac{\mu_{CH}}{\mu_h}-1)})} \quad (27)$$

208 Equation (27) shows the Young's modulus of GO-cement at macroscale as a function of a number
209 of parameters at different length scales. All the key material and geometric factors have been
210 considered in this formulation. The elastic modulus of CH can be obtained from experimental test
211 or molecular dynamics simulation. The volume fraction of voids can be estimated from porosity
212 usually obtained from MIP test.

213

214 3. EXPERIMENTAL PROGRAM

215 As shown in Figure 4(a), in-situ SEM three-point bending tests were performed on beams of 6mm
216 $\times$ 10mm $\times$ 40mm using Tungsten Filament Scanning Electron Microscope (SEM) incorporated with
217 a three-point bending testing mechanism to determine their Young's modulus and fracture
218 mechanisms. A notch of 2 mm was placed in the middle of each beam. A commercially available
219 GO solution with a GO concentration 4 mg/ml was used in this investigation. The chemical
220 composition of GO provided by the manufacturer is Carbon 49-56%, Hydrogen 0-1%, Nitrogen
221 0-1%, Sulfur 0-2% and Oxygen 41-50%. GO-cement composites with w/c = 0.4 were prepared by
222 mixing cement, water and GO. The dosages of GO were 0.00%, 0.02%, and 0.035% by weight.

223 These dosages were obtained by adjusting the concentration of the as received GO solution. For
224 each GO dosage, the required amount of water was added to the GO solution and the resulting
225 solution was sonicated for 30 minutes using a bath sonicator. The GO-cement composites were
226 prepared by simply mixing the GO solution and the cement powder in a mixer for 3 minutes. The
227 fresh GO-cement composite was then poured into a 6mm × 10mm × 40mm moulds and kept for 24
228 hours at room temperature. The samples were then de-moulded and cured under water for 28 days
229 at temperature of 20°C. 3 specimens were produced for each batch. The samples were subjected to
230 load in a displacement-control mode with a speed of 0.05mm/min. The load-deflection curves were
231 recorded and used to determine the Young's modulus and morphology of the GO-cement
232 composites at different scales. The testing arrangement and the geometric parameters are illustrated
233 in Figure 4. The morphology of the GO-cement composites was examined with the SEM. In
234 addition, porosity tests (MIP) were conducted on broken samples obtained from the micro
235 three-point bending test to determine the effect of GO on the porosity of the GO-cement
236 composites.

237

238 **4. EXPERIMENTAL RESULTS AND DISCUSSION**

239 Figure 5 shows the load-deflection curves obtained from the micro three-point bending tests. As in
240 this figure, the flexural response of the composites can be divided into three parts: elastic
241 deformation, plastic deformation and fracture stage. Figure 5 indicates that the failure load of the
242 composites increases with increasing GO dosage. This is due to the microscale enhancement of
243 cement by the GO through crack bridging mechanism, cement porosity reduction, chemical reaction
244 between the functional groups of GO and cement to form stronger interfaces, etc.

245

246 The microstructures of the GO-cement with different GO dosages are presented in Figure 6. All
247 samples have shown considerable amount of needle-like Ettringite minerals. The GO wrapped with

248 cement has been identified on the surface of the sample with 0.035% and 0.06% GO inclusions by
 249 the SEM test. It has been found that the fracture surface for pure cement is relatively smoother,
 250 whilst the 0.035% GO-cement sample shows rougher surface, especially around the GO, whose
 251 length ranges from 3 μm to 30 μm in its presence of GO-cement. It is believed that the existence of
 252 GO in cement can change the hydration process or packing of cement particles. Due to the
 253 functional groups attached, GO tends to react with the C-S-H, the main binding phase of the cement,
 254 forming chemically-bound interface between oxygen in GO and calcium in cement ²³. Such a
 255 chemically-bound cementitious nanocomposite can provide higher stress transfer through the
 256 interfaces and hence stronger strength of the material. Moreover, Figure 7 illustrates the fracture
 257 process obtained for the 0.035% GO-cement sample from the micro three-point bending test. The
 258 crack is developed as the loading increases. The fracture process shows some kind of shielding
 259 effect, since the fracture path is tortuous. The loads are in Figure 7 for each stage of the crack and
 260 all these loads are in the softening curve of the load-deflection relationship in Figure 5. The results
 261 obtained from the porosity tests indicate that GO decreases the porosity of the cementitious
 262 composites. For example, the percentage of porosity decreased from 15.57% at a GO dosage of
 263 0-wt% to 14.56% at a GO dosage of 0.035-wt%. This is due the fact that GO tends to amplify the
 264 hydration products, and fill and cover the pores in the matrix, thus densifying the cement pastes
 265 with less porosity. This is consistent with results reported in ^{10, 11}.

266

267 5. Model Verification

268 To verify the developed analytical model, the results are compared with those from the experiments.
 269 The measured Young's modulus of the GO-cement composite was determined using the elastic
 270 deformation phase, can be calculated as follows ²⁴:

$$271 \quad E = \frac{P_a D^3}{4t(b-a_0)^3 d} \quad (28)$$

272 where P_a is the load within the elastic stage, D is the distance between the two supports, t is the
273 width of the specimen, b is the depth of specimen, a_0 is the notch and d is the deflection of
274 specimen.

275

276 The Young's modulus of the GO-cement composites was predicted using the materials properties
277 given in Table 1. The predicted and measured Young's modulus of the GO-cement composites are
278 given in Table 2. Table 2 shows that the predicted results are in a good agreement with the
279 experimental results. For 0.02-wt% of GO inclusion by weight, the Young's modulus of cement
280 determined from the test increases from 11.63 GPa to 12.63 GPa and from the model increases to
281 12.99GPa. The enhancement in Young' modulus is 8.6% and 11.7% respectively. The difference
282 could be partially due to the assumption that the interfaces between GO and cement are perfected
283 bonded. This means there is no slip at the interfaces and thus loss in stress transfer between these
284 two materials is minimal. This leads to slightly higher Young's modulus in numerical results.
285 However, for 0.035-wt% of GO inclusion, the Young's modulus from both the experiment and the
286 model agree very well. Moreover, it is very interesting to see that the relationship between the
287 increase of GO dosage and the enhancement of Young's modulus is not proportional; the increase of
288 Young's modulus of GO-cement is much faster than that of GO dosage.

289

290 **6. Parametric Study**

291 One of the advantages of the analytical model is that the effects of a number of factors can be
292 investigated. In this paper a few key parameters were chosen from the derived analytical model to
293 examine the sensitivity of those parameters to the elasticity of GO-cement. From the model, the
294 volume fractions and Young's modulus for GO, C-S-H and CH were selected, as well as the volume
295 fraction of void, in order to study their effects on the homogenized Young's modulus of GO-cement.
296 Figure 8 presents the macro scale Young's modulus of GO-cement as a function of Young's

297 modulus of GO. It can be seen that the Young's modulus of GO-cement increases as the Young's
298 modulus of GO increases. Three different percentages of GO addition are also plotted in the figure.
299 As expected, the increase in volume fraction of GO can also increase the homogenized Young's
300 modulus of the GO-cement. The increase is roughly in linear relationship. It is interesting to see that
301 the Young's modulus of GO does not change the macroscopic Young's modulus too much for the
302 same volume fraction of the GO inclusion investigated; but higher volume fraction of GO can
303 increase the elastic modulus of the GO-cement a lot more. This demonstrates that for a very small
304 amount of GO inclusion in cement, the mechanical property of the inclusion is less important.
305 Nevertheless, compared with the normal cement, the Young's modulus of GO-cement can still be
306 enhanced significantly for a small GO inclusion.

307

308 Figure 9 illustrates the effects of the volume fraction as well as the elastic modulus of C-S-H on the
309 global elastic modulus of the GO-cement. It can be seen that the Young's modulus of GO-cement
310 decreases with the increase of the volume fraction of C-S-H. The reason is because the matrix phase
311 of C-S-H has lower Young's modulus than its inclusion phase GO; the increase in the volume of
312 C-S-H would decrease the volume of the GO and hence the decrease in global elastic modulus.
313 Meanwhile, the increase in the Young's modulus of the C-S-H can significantly increase of the
314 Young's modulus of the GO-cement, as shown in Figure 9. The Young's modulus of C-S-H is
315 investigated between 15 and 45 GPa since it is the range that the literature suggests. It can be seen
316 that the overall Young's modulus is very sensitive to that of C-S-H. This can be easily understood
317 since C-S-H is the dominate phase material in the composite. Figure 10 shows the relationship
318 between the homogenized elastic modulus of the GO-cement and that of the CH phase, as well as its
319 volume. The homogenized Young's modulus of GO-cement can increase as either the Young's
320 modulus of CH rises or the volume fraction of CH does.

321

322 As discussed, GO in the cement composites can be in the form of either folding or stacking. These
323 two mechanisms are not separately considered in the analytical model for the homogenized elastic
324 property of GO-cement. This is because the homogenization scheme employed in this study only
325 allows one inclusion phase. As such, a single phase of GO is assumed in the modeling. However,
326 the mechanical properties of the folding GO and the stacking GO are not identical and to roughly
327 estimate the effects of different volumes of these two types of GO, Figure 11 is plotted. The simple
328 weighted average method was employed for the estimation. The assumption is based on that the
329 Young's modulus of the folding and stacking GO are 350GPa and 300GPa, respectively. These
330 values are estimated since there are no experimental results yet. It can be seen that with the increase
331 of the volume fraction of the relevant GO, the elastic modulus for both scenarios increase and the
332 increase for the folding GO is higher than that of stacking GO, as expected. The difference between
333 the two scenarios is significant for larger fraction of GO inclusion while relatively small for low GO
334 fraction.

335

336 **5. CONCLUSIONS**

337 In this paper a multiscale analytical model has been derived for the elastic modulus of the
338 GO-cement. Young's modulus and volume fractions for different composition at different scales, i.e.,
339 micro, meso and macro scales, are formulated in the developed model. In-situ three-point bending
340 SEM test was also undertaken to determine the Young's modulus of GO-cement experimentally and
341 the results have been compared with the analytical model. It has been found that the results from the
342 derived model and the experimental tests are in good agreement. Moreover, the in-situ SEM tests
343 have shown the crack propagation process and the cracking bridging mechanism was observed and
344 discussed. MIP test has also been conducted to determine the porosity of the GO-cement with
345 different concentrations. It can be concluded that the model developed is perhaps the only analytical
346 model that can predict the elastic mechanical performance of GO-cement by considering all

347 possible scales. The addition of GO can significantly change the morphology and substantially
348 enhance the mechanical properties of the cement with respect to the amount of GO added. The
349 developed model can be used as a useful tool to evaluate the global elastic mechanism of
350 GO-cement based on the microscale mechanical behavior of the materials.

351

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406 2. Comparison of the results from the experiments and the model

407 Table 1: Material properties for GO and C-S-H as input for the model

Properties	GO	C-S-H	CH
Young’s modulus E	350 GPa	24 GPa	38 GPa
Poisson’s ratio ν	0.197	0.24	0.31

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409

410 Table 2: Comparison of the results from the experiments and the model

Weight fraction of GO		0%	0.02%	0.035%
Experiment	Young's Modulus	11.63 GPa	12.63 GPa	14.64 GPa
	Improvement	n.a.	8.6%	25.9%
Model	Young's Modulus	11.63 GPa (assuming)	12.99 GPa	14.89 GPa
	Improvement	n.a.	11.7%	28.0%

411

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- 424 modulus of GO-cement
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Figure 1 The scale range of GO-cement (a) microscale (b) mesoscale (c) macroscale

429

Folding GO

Stacking GO

Figure 2 The schematic of folding GO and stacking GO in C-S-H

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Figure 3 The proposed RVE and the upscaling process

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Figure 4 The schematic of three-point bending test

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442

Figure 5 Load-deflection curves obtained from the three-point bending tests

(a)

(b)

(c)

(d)

443 Figure 6 SEM pictures of SEM pictures of (a) 0% GO-cement (b) 0.02% GO-cement, (c) 0.035%
 444 GO-cement and (d) 0.06% GO-cement

445

446

(a) 5.95N

(b) 5.51N

(c) 5.05N

(d) 4.44N

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448 Figure 7 Fracture process of the sample of 0.035% GO-cement

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454 Figure 8 Relationship between Young's modulus of GO and Young's modulus of GO-cement

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457 Figure 9 Relationship between Young's modulus of C-S-H and Young's modulus of GO-cement

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461 Figure 10 Relationship between Young's modulus of CH and Young's modulus of GO-cement

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464 Figure 11 Relationship between the volume fraction of two different existences of GO and Young's
465 modulus of GO-cement

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