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Multiscale characterization of effective thermal properties of graphene/polymer composite aerogels

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Abstract

1 This work involves the characterization of effective thermal conductivity of polymer aerogel rein-
2 forced by graphene and graphene oxide elaborated by replacing the liquid phase with a gas phase
3 through an environmentally friendly freeze-drying process. For characterizing the developed aerogel,
4 multiscale geometrical configurations were constructed based on the experimental characterizations
5 of the prepared aerogels. Following that, a homogenization procedure was applied, moving from
6 smaller to larger scales. At the nanoscale, the Milton method was used, while at the micro- and
7 macroscales, the asymptotic method was employed in combination with the finite element method.
8 Problems posed on a domain called the representative unit cell were formulated at both micro-
9 and macroscales, and their resolution using the finite element method allows the calculation of
10 characteristic functions of the problems, thereby obtaining effective thermal conductivity of the
11 material. To the best of our knowledge, no studies have been reported in the literature on the
12 multiscale characterization of the effective properties of polymer aerogels, hence the motivation
13 for this work. To address this gap, a novel numerical approach has been developed to investigate
14 aerogel properties across multiple scales. The multiscale approaches have revealed the influence
15 of various microstructural characteristics on the effective thermal conductivity properties of the
16 hybrid aerogel. The results show that graphene and graphene oxide nanoinclusions do not signifi-
17 cantly affect the thermal conductivity, but they do significantly improve the mechanical properties
18 of the polymer-based aerogel. Furthermore, this study has also demonstrated that aerogels with
19 superinsulating properties can be obtained by reducing the pore size to the nanometer scale and
20 lowering the gas pressure to below 0.01 atm.

Keywords: Asymptotic homogenization, effective thermal properties, finite element method,
composite aerogel, graphene, biopolymer

1. Introduction

2 The continuous increase in global energy consumption has always been a major concern for
3 decades. Buildings were the most consuming sector, accounting for approximately a third of global
4 energy consumption [1] and even as much as 41% of the total energy consumption in Europe [2].

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5 Hence, reducing energy consumption in buildings through the use of insulation materials is consid-
6 ered as one of the solutions to this issue, simultaneously contributing to maintaining human comfort
7 in daily lives. It should be noted that materials without high thermal insulation performance will
8 require substantial thickness, which can lead to a reduction in living space. Therefore, increas-
9 ing thermal insulation performance by reducing thermal conductivity will be a crucial objective
10 in the development of insulation materials. Several commonly used insulation materials include
11 polyurethane foam, mineral wool, and vacuum insulation panels (VIP) providing a range of insu-
12 lation solutions that can be tailored to specific needs. Closed-cell structure of polyurethane foams
13 reduces significantly heat transfer, resulting in excellent thermal resistance required for residential
14 applications. Mineral wool combines thermal insulating properties with fire resistance and sound-
15 proofing qualities. VIP offer the highest thermal resistance through vacuum-driven minimization
16 of conductive and convective heat transfer. Additionally, their thin profile allows for exception-
17 ally effective insulation in tight spaces based on factors such as thermal performance, fire safety,
18 moisture resistance, and space limitations. However, these materials still have limitations, such as
19 problems related to aging for VIPs [3]. Therefore, aerogels, known for their extremely low internal
20 thermal conductivity ranging from 0.0034 to 0.022 W/(m·K), have attracted increasingly more at-
21 tention in the building sector [4]. In recent years, it has been demonstrated that graphene-reinforced
22 polymer composite aerogels are a promising alternative to silica aerogels due to their low cost and
23 improved mechanical properties [5, 6, 7]. Caring for environmental sustainability, abundant natural
24 biopolymers, notably chitosan, was used as a polymer matrix in combination with an environmen-
25 tally friendly freeze-drying method for the development of aerogels [5, 6]. Indeed, the freeze-drying
26 method offers various advantages, especially cost-effectiveness, due to the direct use of water as a
27 solvent and, the simple drying process through sublimation [8]. We firmly believe that freeze-drying
28 can be regarded as an environmentally friendly process as it operates at low temperatures avoiding
29 the need for high-energy inputs required for supercritical conditions which involves temperatures
30 above 30°C and pressures of 70 bar or more. Additionally, freeze-drying primarily uses water as
31 a solvent, which is abundant, non-toxic, non-flammable, and environmentally benign, producing
32 no hazardous waste as compared to some organic solvents. These factors significantly reduce the
33 environmental impact associated with solvent production, handling, and disposal, unlike the solvent
34 exchanges often used in supercritical drying, such as replacing ethanol or acetone with CO₂.

35 There are various experimental methods that can be employed to characterize the thermal con-
36 ductivity of aerogels, such as the transient plane source (TPS) [9], the hot-wire method [10] and
37 the heat flow method [11, 12, 13], etc. However, experimental works are either unfeasible or may
38 require significant efforts when conducting parametric studies related to changes of parameters at
39 the nano- and microscales. Hence, numerical simulations become essential for predicting the effec-
40 tive thermal conductivity of aerogels and simultaneously for optimizing the material manufacturing
41 processes.

42 In the literature, several analytical methods are often used to predict the thermal conductivity
43 of aerogels, such as the models by Zeng *et al.* [14], Dan *et al.* [15] and Xie *et al.* [16]. The
44 limitations of these models include their inability to flexibly describe the microstructure of aere-
45 gels, particularly the complex multiscale structure of nanoinclusion-reinforced polymer composite
46 aerogels. Furthermore, the asymptotic homogenization method allows for predicting the effective
47 thermal conductivity of heterogenous materials based on representative unit cells [17]. This implies
48 that this method allows for the calculation of the effective thermal conductivity of the solid phase,
49 including nanoinclusions (namely fillers), and the polymer matrix at the microscale, as well as the

50 effective thermal conductivity of the aerogels created by the pores and the solid network at the
51 macroscale. Therefore, the homogenization theory is highly useful for establishing the relation-
52 ship between parameters at low scales, such as nano- and microscales, and the effective thermal
53 conductivity of aerogels.

54 Regarding the effects of graphene and its derivatives, namely graphene oxide (GO) and reduced
55 graphene oxide (rGO), it has been reported that these bidimensional materials can significantly
56 enhance the thermal conductivity of polymer-based composite materials [12, 18, 19, 20, 21, 22].
57 Furthermore, it is known that graphene and graphene oxide sheets dispersed within a polymer ma-
58 trix form different structures, such as aggregates, intercalated and exfoliated structures, influencing
59 the effective properties of the materials [23, 24, 25]. As far as we know, no studies have hitherto in-
60 vestigate the effect of microstructure on the thermal conductivity of polymer-based aerogels. In the
61 context of graphene and graphene oxide commonly being used to enhance the mechanical properties
62 of polymer-based insulation materials, experimental studies have primarily provided information
63 about the impact of the filler content on the thermal conductivity of the material [26, 27, 5]. How-
64 ever, other parameters such as porosity and microstructure may also change with filler content
65 [27, 25], which can lead to misconceptions regarding the effects of graphene and graphene oxide.
66 Considering the pore size, it is evident that nanometric pores significantly reduce the thermal
67 conductivity of aerogels due to the Knudsen effect. Although aerogels typically consist of both
68 nanometric and micrometric pores with varying volume fractions, previous researches have mainly
69 focused on materials with nanometric pores [28] or with a fixed volume fraction of these pores
70 [29], thus lacking in-depth understanding of the influence of nanometric pores in aerogels. Closely
71 related to the effect of pore size, reducing gas pressure will increase the mean free path of gas
72 molecules, resulting in a decrease in the gas thermal conductivity as this mean free path reaches
73 values in the same order of the pore size. Therefore, the influence of gas pressure on effective
74 thermal conductivity of aerogels needs to be considered in conjunction with the effect of pore size.

75 The main objective of this study is to perform numerical characterization of the effective thermal
76 conductivity of chitosan aerogels reinforced by graphene or graphene oxide, which were synthesized
77 through the freeze-drying method. The numerical studies will focus on the effect of the microstruc-
78 tural morphology, such as aggregates, intercalated and exfoliated structures, on the effective thermal
79 conductivity of this aerogel, which has not been investigated so far in the literature to date. We
80 are also interested in investigating the influence of pore size and gas pressure on the thermal con-
81 ductivity of aerogels, taking into account the simultaneous presence of nanometric and micrometric
82 pores with varying volume fractions, which has not been addressed in previous works.

83 Due to the lack of studies in the literature on the multiscale characterization of the effective
84 properties of polymer aerogels, this work aims to fill this gap. A novel numerical approach has been
85 developed to examine the properties of aerogels at multiple scales, and the key contributions of the
86 paper are as follows:

- 87 1. chitosan aerogels incorporating variously structured graphene inclusions, ranging from mono-
88 layer to aggregates were elaborated and thoroughly characterized.
- 89 2. experimental characterization parameters enabled construction of geometrical configurations
90 at various scales and model validation further supported by literature.
- 91 3. it is the first attempt that a multiscale characterization of the effective thermal properties of
92 graphene/polymer-based hybrid aerogels is carried out.

93 4. we conduct extensive studies on the effect of the microstructural morphology, such as ag-
94 gregate, intercalated and exfoliated structures, on the effective thermal conductivity of these
95 aerogels.

96 In order to estimate the effective thermal conductivity of the developed aerogels, multiscale
97 geometrical configurations will be constructed based on the experimental characterization, followed
98 by a homogenization process carried out at each scale, progressively from smaller to larger scales.
99 In this contribution, nanopores refer to pores with size below 100 nm, while micrometric pores are
100 defined as larger pores, above 100 nm, and with typical size from a few micrometers to several
101 hundreds of micrometers in size. The aggregate structure of graphene and the exfoliated and
102 intercalated structures of graphene oxide have been examined. Additionally, the variation in aerogel
103 porosity and the presence of nano-sized pores within the polymer matrix with different volume
104 fractions are also considered in this study. In parallel, the numerical results are also compared to
105 experimental data in the literature to check the validity of the proposed model.

106 The paper is organized as follows. Section 2 introduces the elaboration method and experimental
107 characterization of the aerogels under investigation. Sections 3 and 4 present the construction
108 of geometrical configuration and homogenization methods at different scales, respectively. The
109 numerical results and a discussion about the thermal conductivity are reported in section 5. In this
110 section, the obtained numerical results are also compared with previous experimental work in the
111 literature. Finally, section 6 summarizes the main conclusion of this work.

112 2. Material elaboration and characterization

113 2.1. Materials

114 Graphene nanoplatelets (G, quality level 100: grade C-750, thickness a few nm, particle size
115 $< 2\mu\text{m}$, bulk density $0.2-0.4\text{ g/cm}^3$ and surface area $750\text{ m}^2/\text{g}$), chitosan with low molar mass and a
116 deacetylation degree of $75-85\%$ (CS), graphite flakes (particle size $< 150\mu\text{m}$), glacial acetic acid,
117 sulphuric acid (H_2SO_4 , $\geq 97.0\%$), sodium nitrate (NaNO_3 , $\geq 99.0\%$), potassium permanganate
118 (KMnO_4 , $\geq 99.0\%$) and hydrogen peroxide 30% (H_2O_2) were purchased from Sigma-Aldrich and
119 used without further purification. Graphene oxide (GO) was prepared starting from natural graphite
120 using Hummers' method [30].

121 2.2. Instruments used in the tests

122 The aerogels were characterized using X-ray Diffraction (XRD), Scanning and Transmission
123 Electron Microscopy (SEM, TEM). XRD measurements were performed on a Bruker D8 Advance
124 diffractometer equipped with a Cu $K\alpha$ source ($\lambda = 1.5418\text{ \AA}$), operating at 45 kV and 44 mA.
125 Diffractograms were recorded from thin aerogel disks, scanned at a rate of 0.2° per minute across a
126 2θ range of 5° to 60° . The interlayer distance (d-spacing) of graphene was calculated using Bragg's
127 equation:

$$n\lambda = 2d\sin\theta,$$

128 where $n = 1$ and θ is the diffraction angle.

129 TEM analysis was carried out on a FEI Tecnai F20 electron microscope at an accelerating
130 voltage of 200 kV. The samples were prepared by dispersing the aerogels in absolute ethanol through
131 ultrasonication, followed by drop-casting the suspension onto copper grids coated with a Formvar-
132 carbon film. SEM analysis was carried out using a Zeiss Merlin microscope (Carl Zeiss, Germany)

133 equipped with an SE2 detector and operated at 10 kV. Prior to SEM analysis, the aerogels were
 134 sectioned with a razor, thoroughly dried, and coated with a 5 nm thin layer of Pd to enhance
 135 conductivity. Pore sizes were measured using ImageJ software and addressed in two perpendicular
 136 directions for each pore. A total of 30 pores were analyzed per SEM image, with a minimum of
 137 10 SEM images evaluated.

138 To assess the mechanical properties, uniaxial compression tests were performed using a universal
 139 testing machine (Instron model 5567, Boston, Massachusetts, USA) equipped with a 2 kN load cell.
 140 Cylindrical aerogel samples (diameter ~ 30 mm, height ~ 20 mm) were compressed to 70% of their
 141 original height and then unloaded at 0.5 mm/min.

142 2.3. Elaboration method

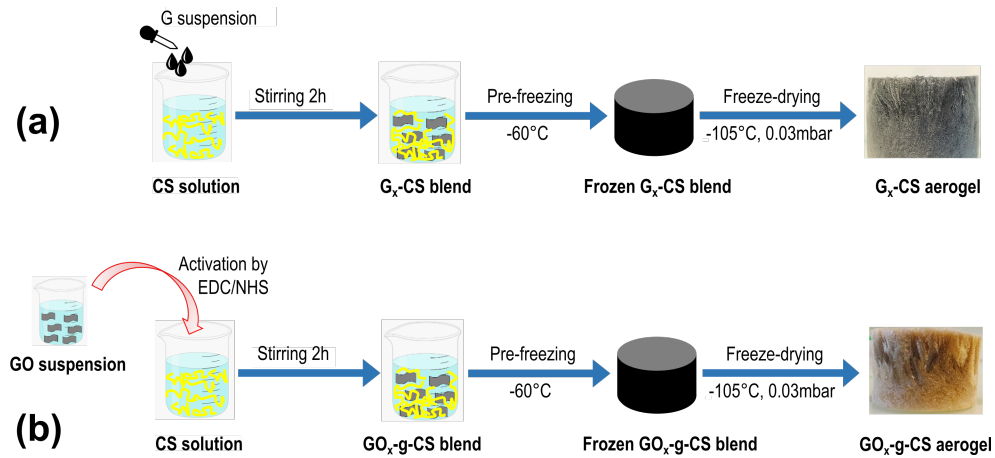


Figure 1: Schematic fabrication diagram of (a) G_x -CS and (b) CS_g - GO_x aerogels using the freeze-drying method.

143 The studied hybrid aerogels based on biopolymer (chitosan) and nanoinclusions (graphene or
 144 graphene oxide) were prepared through an environmentally friendly freeze-drying process. The
 145 aerogels' preparation process involved three main steps, including dispersing the nanoinclusions in
 146 the polymer matrix to form a homogeneous solution, freezing the sample and finally drying the
 147 sample by replacing the liquid phase with a gas phase. In order to prevent the skeleton from
 148 collapsing during the drying process, freeze-drying allows us to convert water from the solid phase
 149 to a gas phase (sublimation) in a low-temperature and low-pressure environment while keeping
 150 the shape of the skeleton intact [31]. The graphene-chitosan composite aerogels, denoted by G_x -
 151 CS aerogels with $x\%$ representing the percentage by weight of graphene relative to chitosan, were
 152 prepared based on previously reported methods [22], as shown in Fig. 1a. Typically, the chitosan
 153 solution was prepared by dissolving 2.4 g of chitosan powder in 100 mL of acetic acid aqueous
 154 solution (1% v/v). Then, the homogeneous graphene suspension with a desired amount of graphene
 155 nanoinclusions ($x\%$ weight ratio with respect to the amount of chitosan), as prepared through
 156 ultrasonic treatment was added to the chitosan solution.

157 The mixture was then vigorously stirred for 2 h. The homogeneous mixture obtained was then
 158 poured into molds and pre-frozen at -60 °C for 24 h in a temperature-controlled freezer. Finally,
 159 the sample was completely dried by freeze-drying after 48 h.

160 For chitosan grafted graphene oxide aerogel, denoted by GO_x -g-CS with $x\%$ representing the
 161 percentage by weight of graphene oxide relative to chitosan, the synthesis process is similar to

162 that of graphene-chitosan aerogel. However, the graphene oxide suspension was activated using the
163 1-(3-Dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide
164 (NHS) coupling agents before being added to the chitosan solution (see Fig. 1b).

165 The grafted aerogels were soaked in a mixture of ethanol/water with a ratio of 9/1 under
166 ultrasonic treatment to remove excess of EDC/NHS, then freeze-dried for 48 hours to complete the
167 process. Moreover, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDC, purity >
168 98%), N-Hydroxysuccinimide (NHS, purity > 98%) were obtained from TCI. Ethanol was purchased
169 from Alfa-Aesar.

170 2.4. Experimental characterization

171 To predict the arrangement of graphene and graphene oxide sheets in the chitosan matrix, X-
172 ray diffraction (XRD) analysis was used. According to the XRD results (see Fig. 2a), the original
173 graphene and graphene oxide powder exhibited a typical diffraction peaks at 26.6° and 11.3° that
174 corresponded to interlayer spacing of 0.335 nm and 0.780 nm, respectively. In the G₁₀-CS aerogel,
175 a weak peak at 26.3° demonstrates the presence of graphene with an interlayer spacing of 0.338 nm.
176 The graphene interlayer distance was almost constant indicating that graphene sheets existed as
177 aggregates in polymer matrix. In contrast, the XRD pattern of GO₁₀-g-CS aerogel did not show
178 any peak of GO indicating that the graphene oxide sheets were highly exfoliated. To determine the
179 number of layers in the aggregates, transmission electron microscopy (TEM) technique was carried
180 out on the G₁₀-CS aerogel sample. The TEM images (see Fig. 2b-c) showed that graphene sheets
181 form aggregates in which the graphene sheets were arranged parallel to each other. There were
182 4 – 12 layers in each assembly with interlayer spacing ranging between 0.33 and 0.35 nm, which
183 coincided with the results obtained from the XRD analysis above. In addition, these aggregates
184 were randomly distributed in the chitosan matrix with a length varying from 30 to 90 nm.

185 In fact, although graphene oxide was easily dispersed into single sheets (exfoliated structure)
186 in the polymer matrix due to its surface functionality [23], the intercalated structure of graphene
187 oxide had been obtained in some cases. In the work of Blanton *et al.* [24], the distance between two
188 graphene oxide sheets in composites with various polymers and different polymer content were valid
189 in the range of 1.5 – 5.3 nm. Therefore, to expand the scope of our research, two types (intercalated
190 and exfoliated) of graphene oxide structures were also considered.

191 The pore features were preliminarily characterized through scanning electron microscopy (SEM)
192 analysis. SEM images were processed using ImageJ software to determine the pore size. An
193 average of 10 SEM images was considered for each analyzed sample resulting in a total number
194 of pores for determining the pore size of the materials of 300. The pore size was measured twice
195 in two perpendicular directions for each pore. According to the SEM micrographs (see Fig. 3), a
196 three-dimensional structure composed of a network of thin alveolus can be found in both types of
197 aerogels. The alveolus form interconnected pores with average diameters ranging from several tens
198 of micrometers to several hundreds of micrometers. The average diameter of the pores in G₁₀-CS
199 aerogel was approximately equal to 76 μm . Besides, the interconnection of pores was characterized
200 by a void with an average diameter of 12 μm in both aerogels. The obtained structures of our
201 aerogels closely resemble those of aerogels synthesized using freeze-drying methods in previous
202 works [5, 6].

203 Mechanical tests of graphene-chitosan and graphene oxide-grafted chitosan aerogels were con-
204 ducted using a universal testing machine at room temperature (Instron 5567, Boston, Massachusetts,
205 America). The samples were cylinder-shaped with a diameter of 30 mm and a height of 20 mm.

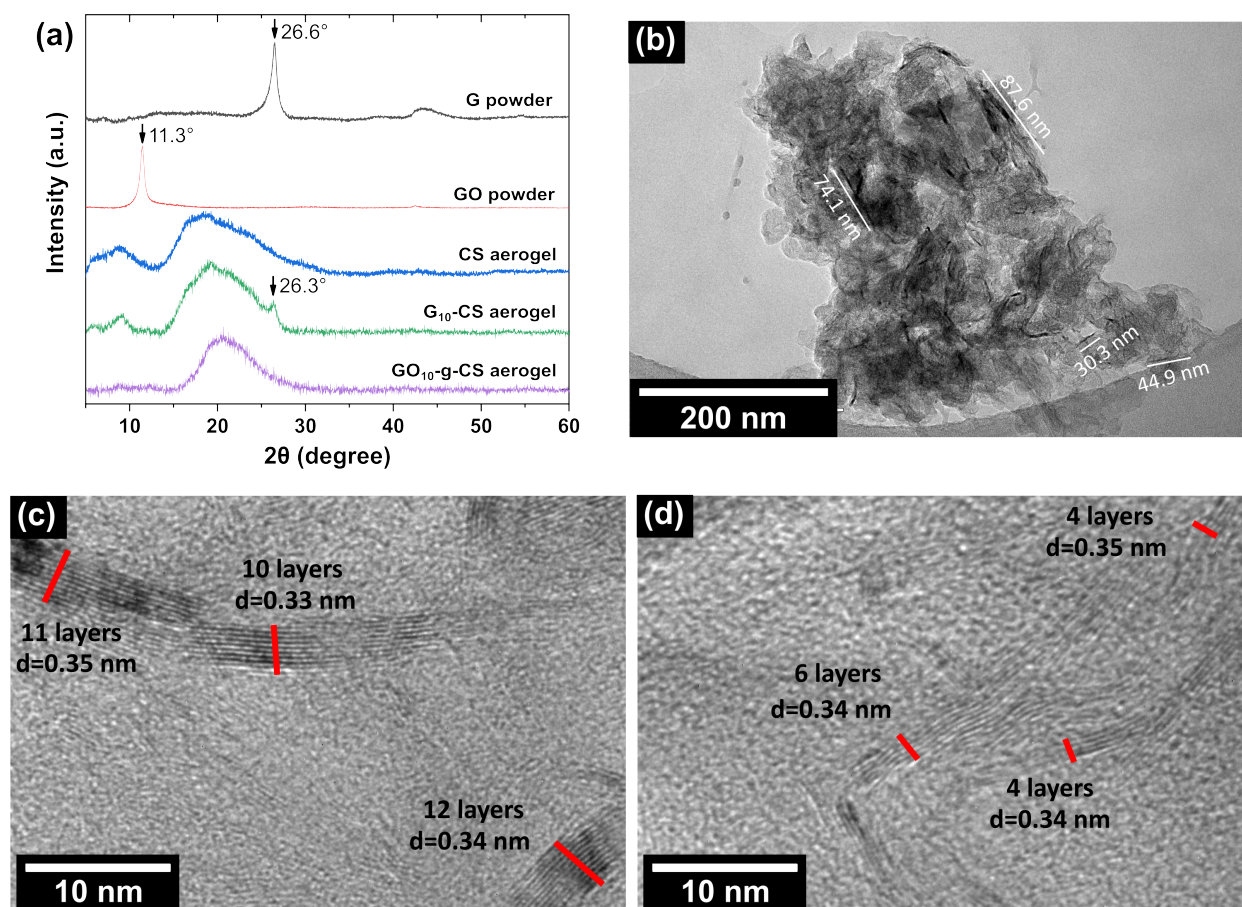


Figure 2: (a) XRD patterns of graphene powder, graphene oxide powder, pure chitosan aerogel, G₁₀-CS aerogel and GO₁₀-g-CS aerogel, (b) low-resolution TEM image, (c) first example of a high-resolution TEM image of G₁₀-CS aerogel, (d) second example of a high-resolution TEM image of G₁₀-CS aerogel.

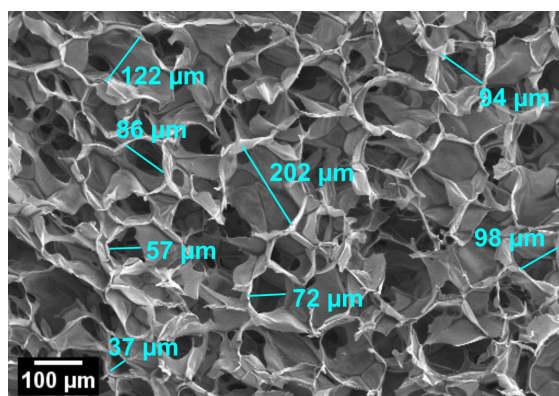


Figure 3: SEM micrograph of G₁₀-CS aerogel.

206 Cylindrical samples were subjected to a vertical compression test as shown in Fig. 4a. The compressive modulus was calculated as the ratio between stress and strain in the elastic domain, and the
 207 resulting value was then averaged from the compression tests conducted on 3 samples. Figure 4b
 208

209 presents the compressive modulus of graphene-chitosan and chitosan grafted graphene oxide aero-
 210 gels with varying filler contents, *i.e.* graphene and graphene oxide contents. It is easily seen that the
 211 compressive modulus increases as the filler content rises. Specifically, the compressive modulus of
 212 the graphene-chitosan aerogel is 0.38 MPa at 10% by weight of graphene, which is approximately 2.8
 213 times higher than the compressive modulus of 0.14 MPa of the pure chitosan aerogel. Meanwhile,
 214 a compressive modulus of 0.61 MPa is recorded for the graphene oxide-grafted chitosan aerogel at
 215 10% by weight of graphene oxide, indicating it is around 4.5 times higher than the pure chitosan
 216 aerogel. This enhancement can be attributed to the excellent intrinsic stiffness of both graphene
 217 and graphene oxide [32, 33], which increases the stiffness of the framework, resulting in improved
 218 overall mechanical properties of the aerogel. Furthermore, it can be observed that chitosan grafted
 219 graphene oxide aerogels consistently exhibit higher compressive modulus than graphene-chitosan
 220 aerogels with the same filler content. This result can be explained by the fact that graphene oxide,
 221 due to its abundant functional groups on the surface, can easily be dispersed in the chitosan matrix,
 222 forming an exfoliated structure. Simultaneously, graphene oxide also forms covalent bonds through
 223 EDC/NHS-mediated reactions with the amino groups in chitosan chains, significantly enhancing
 the mechanical properties of the aerogels.

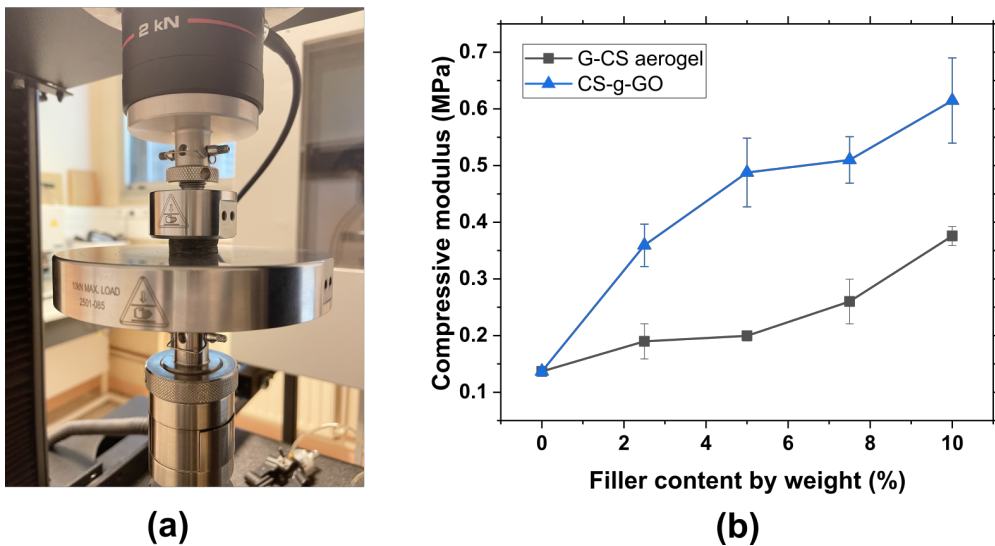


Figure 4: (a) Photographs of the compression test on cylindrical aerogels and (b) compressive modulus as function of filler contents.

224

225 3. Multiscale geometrical configuration and materials properties

226 Based on the experimental results presented in the previous section, the multiscale structure of
 227 aerogels was divided into three separate scales. The first scale (scale qualified of nanoscale) was
 228 related to the aggregation of graphene sheets (named graphene blocks) or the intercalated structure
 229 of graphene oxide (named graphene oxide blocks), the second one corresponded to the microscale
 230 where the graphene blocks or graphene oxide blocks dispersed in the chitosan matrix form the solid
 231 phase of the aerogel and finally the macroscale was made of gas phase and solid phase as shown in
 232 Fig. 5. In this section, the geometrical configurations at different scales are presented and discussed
 233 as well as the material properties of the constituents.

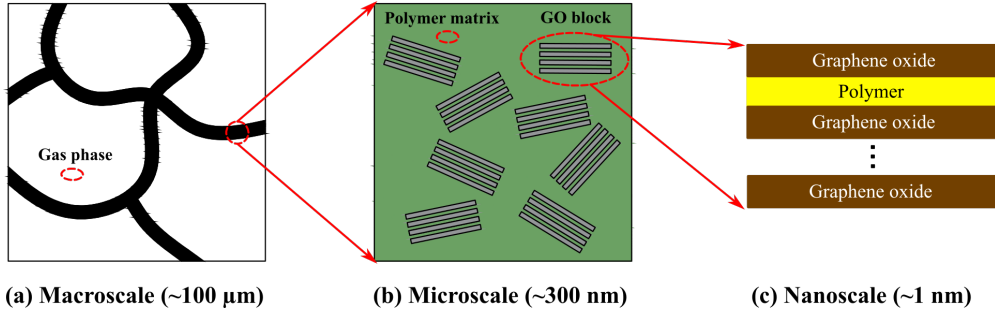


Figure 5: Schematic illustration of the multiscale structure of graphene-chitosan composite aerogels including (a) macroscale depicting solid and gas phases, (b) microscale depicting the distribution of graphene blocks in chitosan matrix and (c) nanoscale describing the graphene sheets in graphene block.

234 3.1. Construction of multiscale geometrical configuration

235 3.1.1. Geometrical configuration at the nanoscale

236 As demonstrated by XRD results and TEM images, the graphene block consists of graphene
 237 sheets arranged parallel to each other with a distance of 0.335 nm caused by van der Waals in-
 238 teractions. The number of graphene layers in the blocks was found to vary from 4 to 12 layers.
 239 The structure of the graphene block resembles that of crystalline graphite, with different thermal
 240 conductivity between the parallel and perpendicular directions to the graphene sheets. Therefore,
 241 the geometrical configuration of the graphene block is a homogeneous multilayered assembly with
 equivalent anisotropic thermal conductivity (see Fig. 6a).

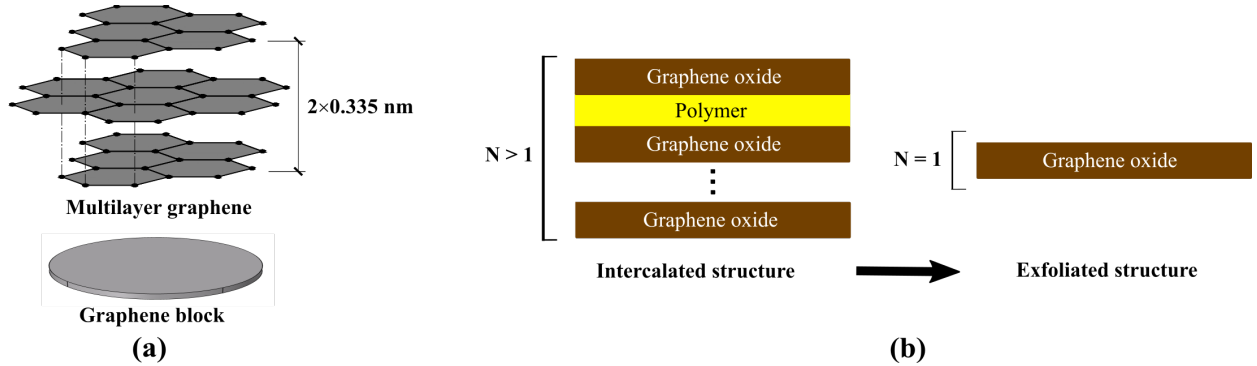


Figure 6: Description of three geometrical configurations at the nanoscale including (a) the aggregate structure of graphene corresponding to graphene block and (b) the intercalated and exfoliated structure of graphene oxide corresponding to graphene oxide block and monolayer graphene oxide, respectively.

242 For graphene oxide, the intercalated and exfoliated structures are considered as discussed in
 243 section 2. The XRD results of graphene oxide powder show that the distance between the sheets is
 244 equal to 0.78 nm, which is approximately the thickness of graphene oxide monolayer experimentally
 245 measured in previous works [34, 35]. Therefore, the thickness of the graphene oxide sheet is taken
 246 as 1 nm. The number of graphene oxide layers per block, denoted by N is greater than 1 for
 247 intercalated structure and equal to 1 for exfoliated structure (see Fig. 6b). In the intercalated
 248 structure, since the distance between the two graphene oxide layers is in the range of 1.5 – 5.3 nm
 249 [24], the thickness of the polymer (chitosan) interlayer between the graphene oxide layers is taken
 250 to be 2 nm.
 251

3.1.2. Geometrical configuration at the microscale

The shape of graphene and graphene oxide is considered to be that of a disc as in previous works [36, 37]. Therefore, each graphene block, graphene oxide monolayer and graphene oxide blocks are also included in the geometrical configuration as disc-shaped inclusions.

With this shape, the diameter and thickness of these inclusions need to be determined. The results from the TEM image in subsection 2.4 show that the graphene blocks have a length of 30.3 – 87.6 nm and a thickness of 1.36 – 4.04 nm. Therefore, the aspect ratio of the graphene blocks, defined by the ratio between diameter and thickness, can be estimated in the range of 8 – 65, which is consistent with the results in previous works [38, 39]. It can be noted that graphene sheets can be disrupted by ultrasonic treatment during graphene dispersion [39], and that the aggregation of graphene layers results in a rather low aspect ratio.

In this work, the typical value of the number of graphene layers and the aspect ratio of the block are taken as 5 and 40, respectively. In addition, it can be seen that the graphene blocks are randomly arranged in the chitosan matrix, they are therefore modeled as discs with arbitrary orientation and position in the polymer matrix.

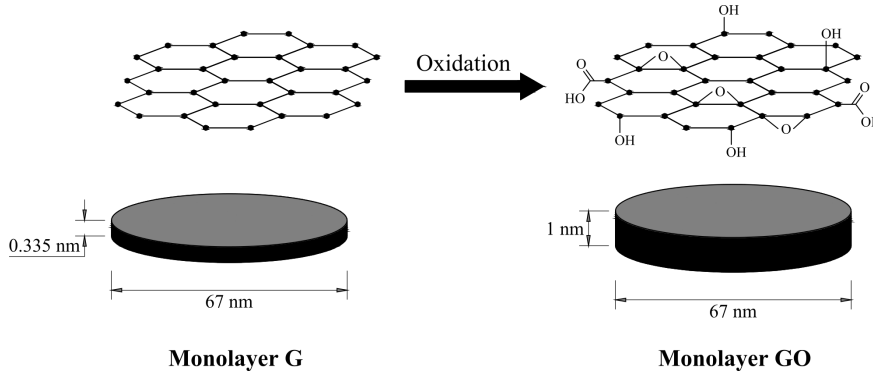


Figure 7: Illustration of the oxidation of graphene to graphene oxide with the lateral dimension unchanged at the nanoscale.

For graphene oxide, the monolayer has an aspect ratio that varies from 10 [40] to more than 1000 [35], depending on the graphene oxide preparation method or the graphene oxide dispersion method in the polymer matrix.

In order to compare the influence of graphene oxide *versus* graphene on the thermal conductivity of aerogels, we assume that the graphene blocks after oxidation form graphene oxide monolayer with constant lateral dimensions. For example, within a typical graphene block having an aspect ratio of 40 and five graphene layers, the monolayered graphene sheets are evaluated to be of equal size with thicknesses and diameters of 0.335 nm and 67 nm, respectively. Therefore, the diameter of the monolayer graphene oxide sheet is also taken to be equal to 67 nm. With a thickness of 1 nm, the aspect ratio of monolayer graphene oxide is equal to 67 (see Fig. 7). For the intercalated structure of graphene oxide, the number of graphene oxide layers per block is investigated at 3 and 5. Additionally, similarly to graphene, the monolayer graphene oxides or graphene oxide blocks are arranged with an arbitrary orientation in the polymer matrix.

Collectively, the representative volume element (RVE) at the microscale consists of disc-shaped inclusions randomly distributed in the polymer matrix with three types of inclusions: graphene block, graphene oxide monolayer and graphene oxide blocks with 3 or 5 layers per block (see

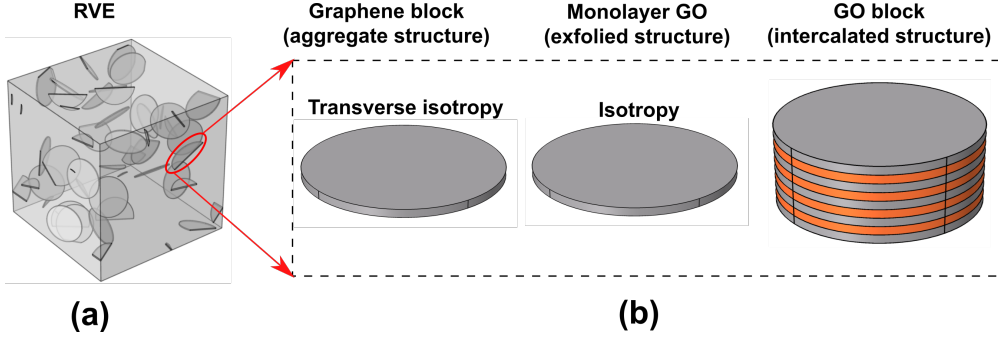


Figure 8: Description of (a) representative volume element at the microscale for 1% concentration by volume of randomly oriented inclusions and (b) three types of inclusions: graphene block, monolayer graphene oxide and graphene oxide block.

283 Fig. 8).

284 3.1.3. Geometrical configuration at the macroscale

285 The geometrical configuration at the macroscale is a periodic structure formed by a single type of
 286 repetitive unit cells. The characteristics that must be considered when building this unit cell include
 287 pore shape, pore size, and porosity in such a way that the unit cell must represent the material
 288 properties of the entire material. According to the application of aerogels, two main morphologies
 289 of aerogels are taken into consideration in the literature, leading to an anisotropic or isotropic
 290 behavior of the structure that is obtained by using different freezing techniques. Two controlled
 291 freezing techniques are utilized to create the anisotropic structure: unidirectional freezing produces
 292 a structure with tubular pores parallel to the freezing direction [5], while bidirectional freezing
 293 affords a structure with parallel layered lamellars [41]. For the isotropic structure, the aerogels
 294 were frozen by ensuring freezing in all directions at the same freezing rate. By using this freezing
 295 method, the aerogels obtained in our research featured a cellular structure with an interconnected
 296 pore network whose average pore diameter was equal to $76 \mu\text{m}$. This conclusion agreed with other
 297 studies [6, 5] that used the same freezing procedure and observed a pore size ranging from a few
 298 tens to several hundreds of micrometers.

299 Next, the Cartesian reference system is used in which the orthonormal basis is denoted by
 300 $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ and the position vector at macroscopic scale by $\mathbf{x} = (x_1, x_2, x_3)$.

301 In this study, the unit cell representing the macrostructure of the material is a hollow sphere
 302 with a diameter of $76 \mu\text{m}$ as shown in Fig. 9c. Six holes with a diameter of $12 \mu\text{m}$ were made on
 303 the wall of the hollow sphere to create the interconnected pore network among the unit cells.

304 In addition to the aforementioned factors, the wall thickness of the hollow sphere must be
 305 determined to fully describe the unit cell. This thickness is determined by introducing the porosity
 306 of the unit cell which is the volume fraction of gas phase in the unit cell. Due to the periodicity, the
 307 relationship between aerogel porosity and aerogel density has been used to calculate the porosity
 308 of aerogel. This relationship is expressed by the following expression:

$$\phi_a = 1 - \frac{\rho_a}{\rho_s}, \quad (1)$$

309 where ϕ_a and ρ_a are the porosity and the apparent mass density of aerogel, respectively. The
 310 quantity ρ_s is the mass density of the solid phase related to the mass density of the graphene ρ_G

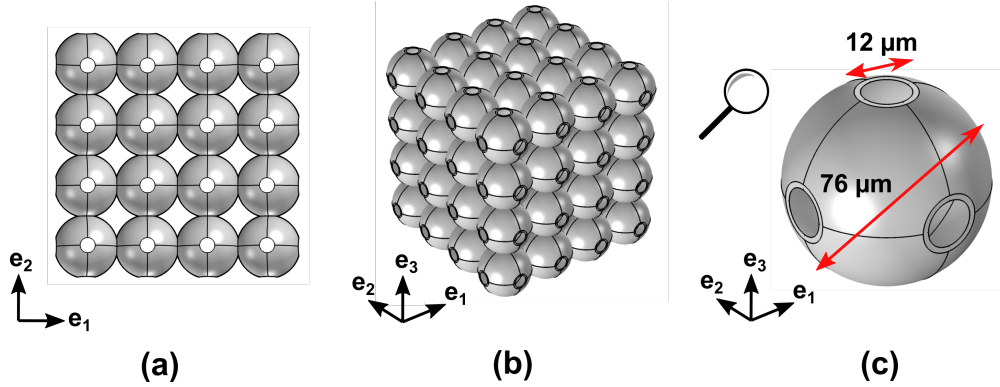


Figure 9: (a) The three-dimensional view of the overall geometrical configuration as an array consisting of periodic unit cells along the e_1 , e_2 and e_3 directions; (b) the representative unit cell and (c) the vertical view of the geometrical configuration at the macroscale.

311 and chitosan ρ_{CS} components by the following expression:

$$\rho_s = f_v \rho_G + (1 - f_v) \rho_{CS}, \quad (2)$$

312 where f_v is the graphene volume fraction, defined as the ratio of the volume of graphene to the
 313 volume of the RVE. In the experiment, graphene was added to the polymer as a percentage by mass
 314 of polymer f_w . Therefore, for instance, the relation between f_v and f_w in aerogel is given by the
 315 relation:

$$f_v = \frac{\rho_{CS} f_w}{\rho_{CS} f_w + \rho_G}. \quad (3)$$

Table 1: Apparent mass density and calculated porosity of aerogels.

Graphene weight fraction f_w (%)	Graphene volume fraction f_v (%)	Apparent mass density ρ_a (g.cm^{-3})	Porosity ϕ_a (%)
0	0	0.0256 ± 0.0012	98.25 ± 0.08
2.5	1.59	0.0261 ± 0.0010	98.23 ± 0.06
5	3.13	0.0262 ± 0.0002	98.24 ± 0.01
7.5	4.62	0.0277 ± 0.0006	98.15 ± 0.04
10	6.06	0.0290 ± 0.0014	98.08 ± 0.09

316 For pure chitosan aerogel, the value of ρ_{CS} is taken to be equal to 1.463 g.cm^{-3} [42]. The
 317 mass density of graphene is taken to be equal to the mass density of crystalline graphite which is
 318 equal to $\rho_G = 2.267 \text{ g.cm}^{-3}$ [43]. Given the measured apparent mass densities of the aerogels, their
 319 overall porosity is shown in Tab. 1. It can be seen that the porosity of the aerogel does not change
 320 significantly as the graphene weight fraction f_w varies; especially when the graphene weight ratio is
 321 below 5% (corresponding to the graphene volume fraction below 3%), the porosity barely varies by
 322 98.231 to 98.250%. This results is consistent with previous works [5, 44]. For the graphene oxide-
 323 grafted aerogel, its porosity was calculated in a similar way, where the mass density of graphene
 324 oxide is taken to be 2 g.cm^{-3} (see [45]). Similar results have also been obtained for this type of
 325 aerogel.

326 Therefore, in the parametric study, the value of aerogel porosity is taken with an average value
 327 of 98.24% and the values of graphene and graphene oxide volume fraction f_v are taken in the range
 328 of 0 – 3%.

329 3.2. Material properties of the constituents

330 Graphene is known for its high in-plane thermal conductivity. At room temperature, the in-
 331 plane thermal conductivity of graphene is in the range of 2000 – 4000 W/(m·K) [46]. However,
 332 when graphene sheets are closely packed due to weak van der Waals interactions forming blocks,
 333 the thermal conductivity of these multilayer blocks in the out-of-plane direction (the direction
 334 perpendicular to the sheets) is much weaker than in the in-plane direction. Indeed, the out-of-plane
 335 thermal conductivity of pyrolytic graphite at room temperature is only about 6 W/(m·K) [46]. In
 336 this work, graphene blocks are introduced into the model with in-plane and out-of-plane thermal
 337 conductivity values of 2500 W/(m·K) and 6 W/(m·K), respectively.

338 It has been indicated that graphene oxide has significantly lower thermal conductivity compared
 339 to graphene due to the phonon-defect scattering at the surface oxidized groups, which reduces the
 340 overall phonon mean free path of graphene oxide [47, 48]. The thermal conductivity of graphene
 341 oxide is taken as 18 W/(m·K), as measured experimentally in the work of Mahanta and Abramson
 342 [48]. Therefore, the graphene oxide monolayer is considered as an isotropic material with thermal
 343 conductivity of 18 W/(m·K) [48]. For graphene oxide blocks, the effective thermal conductivity is
 344 calculated using Milton’s method, which will be detailed in the following section.

345 Most of polymers are thermally insulating exhibiting thermal conductivity ranging from 0.1 to
 346 0.5 W/(m·K) [49]. In this study, the polymer matrix is considered as isotropic and homogeneous
 347 with a thermal conductivity of 0.2 W/(m·K).

348 4. Homogenization method

349 4.1. Determination of material properties of graphene oxide block at the nanoscale

350 In this section, we calculate the effective thermal conductivity of the graphene oxide blocks for
 351 the intercalated structure which will be used at the microscale to describe homogeneous inclusions
 352 embedded in the polymer matrix. With a laminate structure of graphene oxide blocks consisting of
 353 alternating graphene oxide and polymer layers, the Milton’s method [50] is relevant to determine
 354 the effective thermal conductivity of a graphene oxide block. By using the Milton’s method, the
 355 effective thermal conductivity tensor of laminate materials with arbitrary layer orientations can
 356 be obtained. This is in perfect agreement with our model where stratified inclusions are oriented
 357 randomly in a matrix.

358 The following paragraph introduces the method principle for calculating the effective thermal
 359 conductivity tensor of a two-phase laminate material. We consider a laminate domain Ω consisting
 360 of two phases, assuming that there is no volumetric heat source, the steady state heat conduction
 361 equations of each phase are given as follows:

$$\mathbf{q}(\mathbf{x}) = \mathbf{K}(\mathbf{x}) \mathbf{G}(\mathbf{x}), \quad (4)$$

$$\mathbf{G} = -\text{grad } T, \quad (5)$$

$$\text{div } \mathbf{q} = 0, \quad (6)$$

362 where the thermal heat flux is denoted by \mathbf{q} , \mathbf{G} denotes the temperature gradient, T is the temper-
 363 ature, \mathbf{K} is the second-order thermal conductivity tensor, div is the divergence operator and grad

364 is the gradient operator. These equations are derived from the physical laws of conduction of heat
 365 by using Fourier's law and conservation of energy.

366 The main idea of this method involves seeking solutions to the partial differential equations by
 367 assuming that specific components of the fields are constant or, equivalently, that specific projections
 368 of the fields are uniform. It is assumed that \mathbf{q} , \mathbf{G} and \mathbf{K} vary only in the direction of the layers,
 369 characterized by the unit vector \mathbf{n} :

$$\mathbf{q} = \mathbf{q}(y), \quad \mathbf{K} = \mathbf{K}(y), \quad \mathbf{G} = \mathbf{G}(y) \quad \text{where } y = \mathbf{x} \cdot \mathbf{n}. \quad (7)$$

370 It is easily obtained that there are no variations in the component of \mathbf{q} and \mathbf{G} that are parallel
 371 and perpendicular to \mathbf{n} , respectively, that is:

$$\mathbf{n} \cdot \mathbf{q} = \mathbf{n} \cdot \langle \mathbf{q} \rangle_{\Omega}, \quad \mathbf{G} = \langle \mathbf{G} \rangle_{\Omega} + \frac{d\tilde{T}(y)}{dy} \mathbf{n}, \quad (8)$$

372 where $d\tilde{T}(y)/dy$ is the fluctuating part of the temperature gradient in the direction parallel to \mathbf{n}
 373 ensuring the condition $\tilde{T}(y)$ is periodic over Ω and the symbol $\langle \star \rangle_{\Omega}$ denotes the volume average of
 374 \star over domain Ω .

375 Introducing the two matrices $\mathbf{\Gamma}_1(\mathbf{n})$ and $\mathbf{\Gamma}_2(\mathbf{n})$ which are the projections on the out of plane
 376 and the plane of normal \mathbf{n} , Eq. (8) implies that:

$$\mathbf{\Gamma}_1(\mathbf{n})\mathbf{q} = \mathbf{\Gamma}_1(\mathbf{n})\langle \mathbf{q} \rangle_{\Omega}, \quad \mathbf{\Gamma}_2(\mathbf{n})\mathbf{G} = \mathbf{\Gamma}_2(\mathbf{n})\langle \mathbf{G} \rangle_{\Omega}, \quad (9)$$

377 where $\mathbf{\Gamma}_1(\mathbf{n})$ and $\mathbf{\Gamma}_2(\mathbf{n})$ are represented as functions of the vector \mathbf{n} as follows:

$$\mathbf{\Gamma}_1(\mathbf{n}) = \mathbf{n} \otimes \mathbf{n}, \quad \mathbf{\Gamma}_2(\mathbf{n}) = \mathbf{I} - \mathbf{n} \otimes \mathbf{n}, \quad (10)$$

378 with \mathbf{I} is the second-order identity tensor and the symbol \otimes denotes the tensor product (also called
 379 dyadic product of two vectors).

380 It is noteworthy that $\mathbf{\Gamma}_1(\mathbf{n})$ and $\mathbf{\Gamma}_2(\mathbf{n})$ are projections onto mutually orthogonal subspaces
 381 satisfying the expected properties:

$$\mathbf{\Gamma}_i(\mathbf{n})\mathbf{\Gamma}_j(\mathbf{n}) = \delta_{ij}\mathbf{\Gamma}_i(\mathbf{n}), \text{ for } i, j = 1, 2 \quad \text{and} \quad \mathbf{\Gamma}_1(\mathbf{n}) + \mathbf{\Gamma}_2(\mathbf{n}) = \mathbf{I}, \quad (11)$$

382 where δ_{ij} is Kronecker's symbol.

383 To determine the effective conductivity tensor, the polarization field \mathbf{p} is introduced:

$$\mathbf{p}(\mathbf{x}) = (\mathbf{K}(\mathbf{x}) - c_0 \mathbf{I})\mathbf{G}(\mathbf{x}) = \mathbf{q}(\mathbf{x}) - c_0 \mathbf{G}(\mathbf{x}), \quad (12)$$

384 where c_0 is an arbitrary constant that can be freely chosen. From Eq. (12), the temperature gradient
 385 $\mathbf{G}(\mathbf{x})$ and its average $\langle \mathbf{G}(\mathbf{x}) \rangle_{\Omega}$ can be expressed in terms of the polarization field \mathbf{p} and its average
 386 $\langle \mathbf{p}(\mathbf{x}) \rangle_{\Omega}$:

$$c_0 \mathbf{G}(\mathbf{x}) = -\mathbf{M}(\mathbf{x}) \mathbf{p}(\mathbf{x}), \quad c_0 \langle \mathbf{G}(\mathbf{x}) \rangle_{\Omega} = \mathbf{M}^e \langle \mathbf{p}(\mathbf{x}) \rangle_{\Omega}, \quad (13)$$

387 where the following two second-order tensors have been introduced:

$$\mathbf{M}(\mathbf{x}) = c_0 (c_0 \mathbf{I} - \mathbf{K}(\mathbf{x}))^{-1}, \quad \mathbf{M}^e = c_0 (c_0 \mathbf{I} - \mathbf{K}^e)^{-1}, \quad (14)$$

388 where the superscript e designates the average of the field.

389 By using Eq. (12), one shows that the polarization field average can be formulated as follows:

$$\langle \mathbf{p}(\mathbf{x}) \rangle_{\Omega} = [\mathbf{M}^e - \mathbf{\Gamma}_1(\mathbf{n})]^{-1} \mathbf{v} = \langle [\mathbf{M}(\mathbf{x}) - \mathbf{\Gamma}_1(\mathbf{n})]^{-1} \rangle_{\Omega} \mathbf{v}, \quad (15)$$

390 for all uniform fields \mathbf{v} .

391 Since Eq. (15) holds for all fields \mathbf{v} , this relation implies the general formula given by:

$$[\mathbf{M}^e - \mathbf{\Gamma}_1(\mathbf{n})]^{-1} = \langle [\mathbf{M}(\mathbf{x}) - \mathbf{\Gamma}_1(\mathbf{n})]^{-1} \rangle_{\Omega}. \quad (16)$$

392 With these relations, the calculus of the effective thermal conductivity tensor \mathbf{K}^e is carried out
393 as follows:

- 394 1. evaluation of: $\mathbf{L} = \langle [\mathbf{M}(\mathbf{x}) - \mathbf{\Gamma}_1(\mathbf{n})]^{-1} \rangle_{\Omega}$,
- 395 2. from Eq. (16), evaluation of: $\mathbf{M}^e = \mathbf{L}^{-1} + \mathbf{\Gamma}_1(\mathbf{n})$,
- 396 3. from Eq. (14), evaluation of: $\mathbf{K}^e = c_0 (\mathbf{I} - (\mathbf{M}^e)^{-1})$.

397 4.2. Asymptotic homogenization procedure for micro- and macroscales homogenization

398 The asymptotic method is a powerful tool for solving periodic domain problems. The details
399 of the homogenization method can be easily found in the literature, for example in the books of
400 Auriault *et al.* [17] and Mei *et al.* [51]. In this subsection, the principle and the main results of
401 this method are presented.

402 We consider a two-phase composite material with a periodic domain. The microscopic domain
403 of a unit cell is denoted by Y (include in the three-dimensional space), corresponding to the period
404 l_c which is the microscopic characteristic length. In contrast, the characteristic length at the
405 macroscale, as denoted by L_c , is noticeably separated from the microscopic length, that is, $l_c/L_c =$
406 $\epsilon \ll 1$. Domain Y is composed of phase a and phase b , occupying the domains Y^a and Y^b ,
407 respectively, and their interface Γ .

$$Y = Y^a \cup Y^b, \quad Y^a \cap Y^b = \emptyset, \quad \partial Y^a \cup \partial Y^b = \Gamma. \quad (17)$$

408 4.2.1. Microscopic scale governing equations

409 In this subsection, in each phase $\alpha = a, b$, the temperature is denoted by T^α and the second-order
410 thermal conductivity tensor is denoted by \mathbf{K}^α .

411 Assuming that there is no volumetric heat source, the steady-state heat conduction problem is
412 described by the following equations:

$$\operatorname{div}(\mathbf{K}^\alpha \operatorname{grad} T^\alpha) = 0 \quad \text{in } Y^\alpha, \text{ for } \alpha = a, b. \quad (18)$$

413 Assuming perfect thermal contact between phase a and phase b , the continuity conditions in
414 the heat transfer problem are as follows:

$$T^a = T^b, \quad \text{on } \Gamma, \quad (19)$$

$$(\mathbf{K}^a \operatorname{grad} T^a - \mathbf{K}^b \operatorname{grad} T^b) \cdot \mathbf{n} = 0, \quad \text{on } \Gamma, \quad (20)$$

415 where \mathbf{n} is the outward-pointing unit vector locally normal to the boundary Γ .

416 *4.2.2. Asymptotic expansions*

417 As we defined above, l_c represents the unit length of the periodicity and L_c represents the length
 418 at the macroscale so that the condition $l_c/L_c = \epsilon \ll 1$ is satisfied. We introduce now the fast and
 419 slow coordinates $\mathbf{x} = (x_1, x_2, x_3)$ and $\mathbf{y} = (y_1, y_2, y_3)$ for coordinates at macro- and microscales,
 420 respectively, with the relationship $y_i = x_i/\epsilon$.

421 The asymptotic expansion of temperature is expanded as a power series of ϵ as follows:

$$T^\alpha = T^{\alpha(0)}(\mathbf{x}, \mathbf{y}) + \epsilon T^{\alpha(1)}(\mathbf{x}, \mathbf{y}) + \epsilon^2 T^{\alpha(2)}(\mathbf{x}, \mathbf{y}) + \dots \quad (21)$$

422 where $T^{\alpha(0)}, T^{\alpha(1)}, T^{\alpha(2)}, \dots$ are Y -periodic in the variable \mathbf{y} . Terms of the order of ϵ^n are represented
 423 by the upper index (n), where macroscale variables are expressed in the order of ϵ^0 .

424 *4.2.3. Cell problem and effective properties*

425 By substituting Eq. (21) into Eqs. (18) at order ϵ^{-2} , Eq. (19) at order ϵ^0 and Eq. (20) at order
 426 ϵ^{-1} , we get $T^{\alpha(0)}$ is a constant with respect to \mathbf{y} , that is, $T^{\alpha(0)}(\mathbf{x}, \mathbf{y}) = T^{b(0)}(\mathbf{x}, \mathbf{y}) = T^{(0)}(\mathbf{x})$.

427 Grouping ϵ^{-1} terms of Eq. (18), ϵ terms of (19) and ϵ^0 terms of (20), in virtue of the linearity
 428 of the problem, the Y -periodic characteristic vector-valued function $\mathbf{w}^\alpha(\mathbf{y})$ (whose the components
 429 are given by $w_l^\alpha(\mathbf{y})$) is introduced so that:

$$T^{\alpha(1)}(\mathbf{x}, \mathbf{y}) = w_l^\alpha(\mathbf{y}) \frac{\partial T^{(0)}(\mathbf{x})}{\partial x_l} + \bar{T}^{\alpha(1)}(\mathbf{x}), \quad (22)$$

430 where $\bar{T}^{\alpha(1)}(\mathbf{x})$ is a constant field with respect to \mathbf{y} . This relation leads to the cell problem defined
 431 by:

$$\frac{\partial}{\partial y_i} \left[K_{ij}^\alpha \left(\frac{\partial w_l^\alpha}{\partial y_j} + \delta_{jl} \right) \right] = 0, \quad \text{in } Y^\alpha, \quad \alpha = a, b \quad (23)$$

$$w_i^a = w_i^b, \quad \text{on } \Gamma \quad (24)$$

$$K_{ij}^a \left(\frac{\partial w_l^a}{\partial y_j} + \delta_{jl} \right) n_i = K_{ij}^b \left(\frac{\partial w_l^b}{\partial y_j} + \delta_{jl} \right) n_i, \quad \text{on } \Gamma \quad (25)$$

$$\langle \mathbf{w} \rangle_Y = 0, \quad (26)$$

432 where δ_{ij} is Kronecker symbol and $\langle \star \rangle_Y$ denotes the volume average of \star over domain Y :

$$\langle \star \rangle_Y = \frac{1}{Y} \left\{ \int_{Y^a} (\star) dV + \int_{Y^b} (\star) dV \right\}. \quad (27)$$

433 The condition given in Eq. (26) is a normalization condition to render the solution for \mathbf{w}^α
 434 unique.

435 At order ϵ^0 of Eq. (18), order ϵ^2 of Eq. (19) and order ϵ of Eq. (20), the macroscopic equation
 436 can be written as:

$$\text{div}(\mathbf{K}^e \text{grad } T^{(0)}(\mathbf{x})) = 0 \quad \text{in } Y, \quad (28)$$

437 where the components of the effective thermal conductivity tensor are given by

$$K_{ij}^e = \left\langle K_{il}^\alpha \left(\frac{\partial w_j^\alpha}{\partial y_l} + \delta_{jl} \right) \right\rangle_Y. \quad (29)$$

438 The effective thermal conductivity tensor can be determined from Eq. (29) from the solution of
 439 the cell problem defined by Eqs. (23)-(26).

440 5. Results and discussion

441 5.1. Numerical implementation

442 To perform numerical studies on the effective thermal conductivity of materials using a multi-
443 scale approach, problems were solved successively from the small to the larger scale by introducing
444 the result of the smaller scale into the subsequent larger scale. In addition, the interface between
445 the inclusions and the polymer matrix was considered perfectly bonded in this modelling.

446 At the nanoscale, the thermal conductivity of the graphene blocks was assumed to be the same
447 as that of graphite with experimentally measured values [46], implying that the graphene block
448 exhibited transverse isotropic characteristics. Besides, the effective thermal conductivity tensor of
449 graphene oxide block was easily obtained by the semi-explicit formulas. Specifically, the effective
450 thermal conductivity of the graphene oxide blocks exhibited transverse isotropy, similarly to the
451 graphene blocks. The thermal conductivity of the graphene oxide blocks with 3 layers in the
452 parallel and perpendicular directions to the sheets were equal to 7.8 W/(m·K) and 0.3 W/(m·K),
453 respectively. Meanwhile, these values were equal to 7.0 W/(m·K) and 0.3 W/(m·K) for the graphene
454 oxide block with 5 layers, respectively.

455 For the calculation of the effective thermal conductivity tensor at the micro- and macroscales
456 through Eq. (29) in the asymptotic approach, the function \mathbf{w}^α must first be determined in the cell
457 problem given by Eqs. (23)-(26). To do so, the finite element method was used and simulations
458 were carried out using the Comsol Multiphysics software [52]. The following paragraphs summarize
459 the problem solving process at the micro- and macroscales by using the finite element (FE) method.

460 At the microscale, the algorithm used to implement the 3D FE model results from the com-
461 bination of seamless integration of Comsol Multiphysics with Matlab. The algorithm written in
462 Matlab allows for the generation of the representative volume element (RVE) with randomly dis-
463 tributed inclusions as well as the introduction of effective thermal conductivity values of inclusions
464 and polymer matrix into the model. These two processes are described in detail below.

465 **Generation of random disc-shaped inclusions**

466 The geometrical construction of disc-shaped inclusions randomly placed in a given volume do-
467 main is carried out by using a method proposed elsewhere [53]. This method, which has previously
468 been introduced [54] for discs-shaped in 2D and spheres-shaped in 3D, uses an algorithm based
469 on molecular dynamics. In this algorithm, all particle (inclusions) are randomly created with a
470 null volume within a cube of specified dimensions. A random velocity vector is prescribed at each
471 particle. The particles are then set in motion and each volume gradually increases from zero. Two
472 types of incidents are checked at each iteration: binary collisions and collisions between particles
473 and the cell faces. When a binary collision occurs, with respect to the kinetic energy conserva-
474 tion principle, the velocities of the two concerned particles are updated. Nevertheless, if a particle
475 leaves the volume domain through a face, it must appear from the opposite side to carry out the
476 periodicity conditions. The simulation stops when the imposed volume fraction is reached. This
477 algorithm is more efficient than the random sequential adsorption algorithm [55, 56], in particular,
478 it can generate very dense packings in a low computation time.

479 The principal steps of the algorithm are summarized hereafter.

- 480 (i) N ellipsoids are randomly created within a cube domain of side L . The volume of each
481 ellipsoid is initially null. At each ellipsoid is attributed a random velocity, an angular velocity
482 and a random orientation.

- 483 (ii) The growth rates of the semi-principal axes a_0, b_0, c_0 of ellipsoid are chosen in such a way that
484 $b_0 = a_0/r_1$ and $c_0 = a_0/r_2$, where r_1 and r_2 denote respectively the two aspect ratios that
485 serve as inputs in the algorithm.
- 486 (iii) The elliptical particles are then put in translational and rotational motion and their volumes
487 gradually increase. At each step, two types of collisions are checked and computed: binary
488 collision between two ellipsoids and collision between a particle and a cube domain face. If
489 the first type of collision occurs, the velocity and angular velocity of the involved particles are
490 updated. However, if an ellipsoid intersects a cube domain face, its periodic image is created
491 on the opposite side.
- 492 (iv) The algorithm stops when the volume fraction ϕ is reached.
- 493 (v) The ellipsoid is then completely replaced by discs by keeping their position, orientation, aspect
494 ratio and volume. The model is then returned to the actual size with the reference of the
495 thickness of the graphene sheet.
- 496 (vi) Finally, a visual check is performed to check the presence of overlaps among the particles or
497 between the particles and the RVE surface.

498 **Input properties of the inclusions**

- 499 (i) It should be noted that this process is only necessary when the inclusions are not isotropic,
500 that is, for graphene block and graphene oxide blocks.
- 501 (ii) A loop is created, where the effective thermal conductivity tensor of each graphene oxide block
502 is calculated using Milton's equation directly (as described in section 4.1). For the graphene
503 block, its effective thermal conductivity tensor is applied to the model using the rotation of
504 its unit vector towards the corresponding direction in the matrix polymer.

505 For the finite element method, the domain and the equations were discretized on an unstructured
506 mesh of tetrahedral finite elements with quadratic Lagrange interpolating polynomials. The meshing
507 process was conducted in 2 steps starting by the inclusions then the polymer matrix with the
508 maximum element size of the inclusion of 5 nm, and the maximum element size of the matrix of 1/5
509 of the RVE size. The MUltifrontal Massively Parallel sparse direct Solver (MUMPS) method with
510 the relative tolerance of 0.001 was used for the final linear system. In addition, periodic boundary
511 conditions were imposed due to the periodicity of the model. An example of a meshed specimen of
512 a RVE at the microscale with inclusions being graphene oxide monolayers is shown in Fig. 10a.

513 At the macroscale, the surface thickness of the hollow sphere was controlled to construct the
514 unit cell with the desired porosity. Here, the effective thermal conductivity tensor obtained from the
515 results of microscale is introduced into the solid phase. Then, the cell problem solving procedure
516 for calculating the function \mathbf{w}^α for the unit cell and followed by the effective thermal conductivity
517 tensor is carried out with the same finite element method as that in the microscale. For meshing,
518 the maximum element size of the solid and gas phases is equal to twice the surface thickness of
519 the hollow sphere and 1/5 of the representative unit cell size, respectively. Figure 10b presents
520 an example of a meshed specimen of representative unit cell at the macroscale with a porosity of
521 98.24% corresponding to a surface thickness of 1.24 μm .

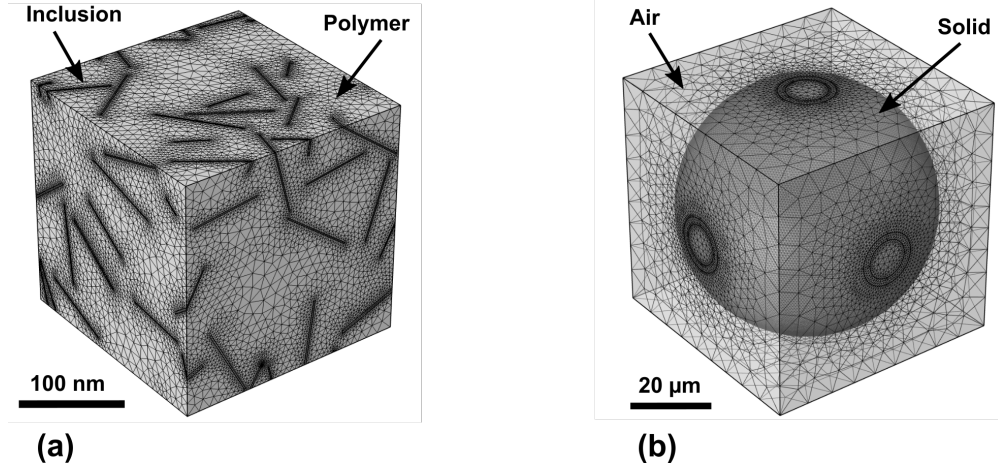


Figure 10: Example of a meshed specimen of (a) a RVE at the microscale with 2% inclusion volume fraction and 40 inclusions and (b) a representative unit cell at the macroscale consisting of solid and gas phases with porosity of 98.24%.

522 In the following section, for the sake of brevity, the exponent e referring to the effective properties
 523 is dropped. Instead, the exponents (2) and (3) characterize computational quantities at the micro-,
 524 and macroscales, respectively.

525 5.2. Effective thermal conductivity of composite aerogels at the microscale

526 5.2.1. RVE size sensitivity

527 At the microscale, we start by testing the influence of RVE size on the estimated effective
 528 thermal conductivity. Given the determined shape and volume fraction of inclusions, the size of
 529 the RVE is directly related to the number of inclusion considered. Therefore, in small RVEs, the
 530 random inclusion distribution can be distorted due to the low number of inclusions, resulting in a
 531 variation in the results obtained. Nevertheless, too large RVE size also requires high computational
 532 cost. Finding a reasonable size of the RVE to exhibit convergence of the outcome was therefore the
 533 target of this subsection. To do that, we consider the case of graphene oxide monolayer with volume
 534 fraction $f_v = 1\%$, the RVE size was thus determined by varying the number of inclusions from 10 to
 535 60, with increments of 10. At each defined number of inclusions, we calculate all the components K_{ij}
 536 of the effective thermal conductivity tensor $\mathbf{K}^{(2)}$ of 5 RVEs where the microstructural morphology
 537 was independently generated. Here, the thermal conductivity of graphene oxide and polymer are
 538 spherical tensors characterized by scalar values of 18 W/(m·K) and 0.2 W/(m·K), respectively.

539 Figure 11a presents the components K_{ij} of the effective thermal conductivity tensor $\mathbf{K}^{(2)}$ in
 540 all 5 cases in which 30 inclusions were generated. It is easy to see that the composite at the
 541 microscale is almost isotropic, that is $\mathbf{K}^{(2)} = K^{(2)} \mathbf{I}$. This complies with the principle of random
 542 inclusion distribution in the polymer matrix, partly demonstrating the validity of the proposed
 543 model. Moreover, the variations of K_{11} , K_{22} and K_{33} are also observed. By introducing this
 544 variation as a function of the number of inclusions, the effect of RVE size on the convergence of the
 545 results can be observed.

546 Figure 11b shows the variation of the effective thermal conductivity normalized by the thermal
 547 conductivity of the polymer matrix $\mathbf{K}_m = K_m \mathbf{I}$ as a function of the number of inclusions from 10
 548 to 60. The results indicate that the effective thermal conductivity is insensitive to the RVE size

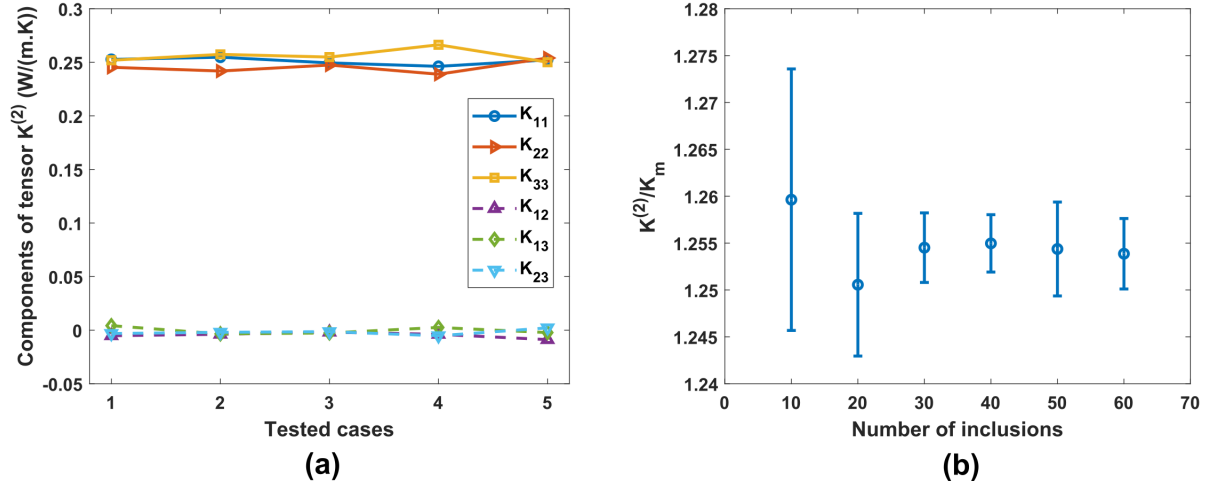


Figure 11: (a) Variation of the components of the effective thermal conductivity tensor for different configurations of graphene oxide monolayer with $f_v = 1\%$ (RVE sizes were built with 30 inclusions) and (b) effect of number of inclusion (RVE size) on the effective thermal conductivity at the microscale.

549 when more than 30 inclusions were present in the domain. This number of inclusions is consistent
 550 with previous reports in the literature [57, 58]. In the subsequent study, the number of inclusions
 551 in the RVE will be used from 30 to 50 corresponding to the inclusion volume fraction from 1 to 3%.

552 5.2.2. Effect of graphene oxide on the thermal conductivity of composite

553 Although graphene oxide has a low thermal conductivity (18 W/(m·K)) [48], it is still used
 554 to enhance the heat transfer capacity of polymer matrix due to its low production cost and good
 555 dispersion ability as well as its stability in the polymer matrix [59, 60]. This subsection draws on
 556 experimental works on the thermal conductivity of composite materials based on graphene oxide
 557 and polymer (epoxy resin) [59, 60] in order to comprehend the effect of structural factors, *i.e.*
 558 exfoliated or intercalated structures, on the effective thermal conductivity of composite materials
 559 at the microscale and to validate the robustness of the proposed model at this scale. For this
 560 purpose, the effective thermal conductivity of composites with exfoliated structure (1 single layer)
 561 or intercalated structure (3 or 5 layers per block) at the microscale is depicted as a function of the
 562 volume fraction of graphene oxide (as shown in Fig. 12a). It is clearly observed that in all cases the
 563 thermal conductivity increases as the volume fraction of graphene oxide increases with a (nearly)
 564 linear relationship. Additionally, the exfoliated structure can improve the thermal conductivity
 565 of the composite substantially more than the intercalated structure. In particular, the composite
 566 with onelayer, 3 layers, and 5 layers of graphene oxide per block at 3% graphene oxide volume
 567 fraction improved in the thermal conductivity by 82%, 45%, and 35%, respectively, compared to
 568 the pure polymer. This may be explained by the fact that when the number of graphene oxide
 569 layers per block increases, the aspect ratio of the block (inclusion) decreases, thus lowering the heat
 570 conductivity of the composite [61]. The mechanical properties of graphene-reinforced polymer have
 571 also been shown to follow a similar trend [62]. These results demonstrate the effectiveness of using
 572 graphene oxide to simultaneously improve the heat transfer capacity and mechanical properties
 573 of the polymer matrix. With the aim of producing a material with improved thermal insulation
 574 and high mechanical strength, the latter statement raises the question of whether, the addition of

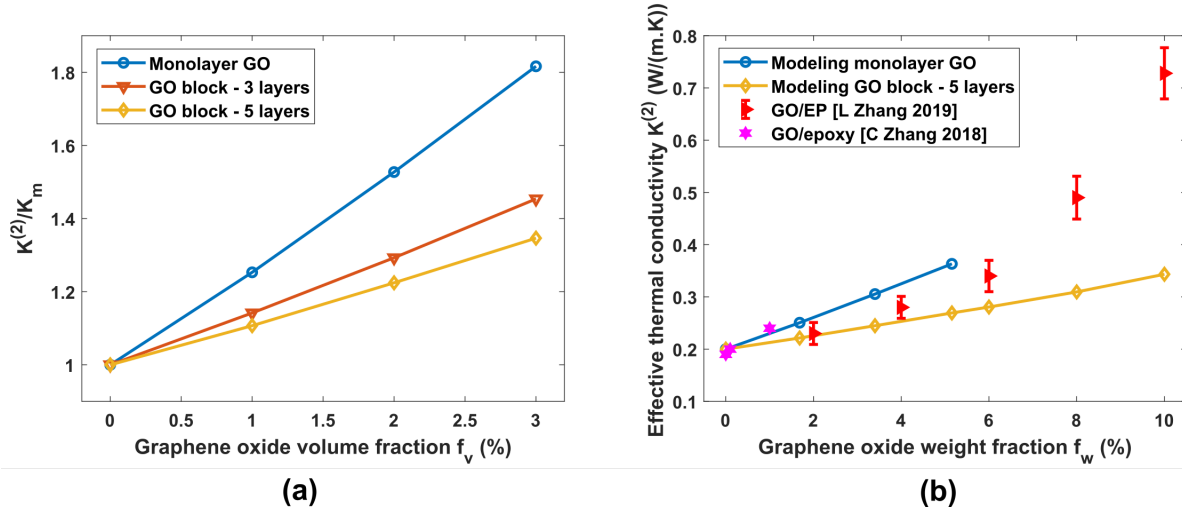


Figure 12: (a) Effect of the inclusion type-related structural parameter on the thermal conductivity of aerogel and (b) numerical predictions of the effective thermal conductivity at the microscale compared to the experimental data of graphene oxide/epoxy composites from [59, 60].

575 graphene or graphene oxide to enhance the mechanical properties of polymer-based aerogels leads
 576 to an increase of its thermal conductivity as well. In other words, how will the amount of graphene
 577 or graphene oxide affect the thermal conductivity of this aerogel at the macroscale, where the gas
 578 phase occupies most of the material's volume? In the following section, the estimated thermal
 579 conductivity at the macroscale will be presented, which will answer this question.

580 Before proceeding to the next larger scale, we also compared the thermal conductivity of the
 581 material at the microscale predicted by our model with that extracted from experimental measure-
 582 ments in literature. To do that, the graphene oxide volume fraction was converted to graphene
 583 oxide weight fraction using relation (3), where the mass density of chitosan and graphene were re-
 584 placed by epoxy resin $\rho_{EP} = 1.2 \text{ g.cm}^{-3}$ [63] and graphene oxide $\rho_{GO} = 2 \text{ g.cm}^{-3}$ [64], respectively.
 585 Figure 12b presents the experimentally measured thermal conductivity of the graphene oxide-epoxy
 586 composite from the works of Zhang *et al.* [59] and Zhang *et al.* [60], alongside the predicted val-
 587 ues by our model at the microscale in two cases as the exfoliated structure and the intercalated
 588 structure (5 layers per block).

589 One may state that the results of the two experimental works are different, where Zhang *et al.*
 590 [60] obtained composites with higher thermal conductivity per graphene oxide content than
 591 those elaborated by Zhang *et al.* [59]. This may be due to the different dispersion of graphene
 592 oxide sheets in these two composites, which has not been described in detail in the two cited
 593 works. Indeed, in order to get comprehensive information on the microstructural morphology of
 594 the composite or the distribution of graphene oxide sheets, observations must be made at the
 595 nanoscale and in many different regions. Consequently, this information is usually not reported
 596 in detail in experimental works that do not focus on it. However, one can confirm that the three
 597 morphologies can be obtained for the composites upon dispersion of graphene oxide in the polymer
 598 matrix, namely the exfoliated structure, the intercalated structure and the partially exfoliated
 599 structure (which is the co-existence of the two previous structures) [23]. For $f_w < 5\%$, the models
 600 of exfoliated structure and intercalated structure, corresponding to the upper and lower bounds,
 601 may envelop the experimental results, implying the validity of the proposed model. On the other

602 hand, there were difficulties to generate RVEs containing more than 3% graphene oxide volume
603 fraction (corresponding to $f_w > 5\%$) for the exfoliated structure. This issue arose due to the
604 random orientation of the inclusions, leading to the lack of intersections between them; as a result,
605 the monolayered graphene oxide sheets characterized with high aspect ratio became entangled
606 preventing the creation of RVEs with a large graphene oxide volume fraction. Hbaieb *et al.* [58]
607 encounters the same difficulty in creating clay inclusions with an aspect ratio of 50 for a clay volume
608 fraction greater than 5%. In this study, the volume fraction of monolayer graphene oxide sheets
609 that can be generated is limited to about 3% due to its larger aspect ratio of 67. In summary, our
610 numerical model at the microscale is suitable for estimating the thermal conductivity of graphene
611 oxide-polymer composites at the filler volume fraction from 0 to 3%.

612 5.3. Effective thermal conductivity of composite aerogels at the macroscale

613 After validating the model and performing simulations at the microscale, we transitioned to the
614 macro scale by introducing these results into the model. At this scale, we investigated studies on
615 the influence of structural parameters, including porosity, morphology, and presence of nanopores
616 on the thermal conductivity of the aerogel. Additionally, a comparison with experimental data
617 from the literature was also performed to validate the model.

618 5.3.1. Effect of porosity

619 Here, we investigated the effect of porosity on the thermal conductivity of aerogels while concur-
620 rently establishing a comparison between these numerical results and experimental measurements
621 extracted from the literature. To mitigate the influences arising from the fillers (such as their dis-
622 tribution and intrinsic thermal conductivity, etc.), which are difficult to precisely control through
623 experimental techniques, the thermal conductivity measurements obtained from pure polymer aero-
624 gels [65, 10, 11, 12, 13] were selected as the reference systems. Hence, the model employed here
625 features a filler volume fraction of $f_v = 0\%$, meaning that the solid phase only consists of the poly-
626 mer matrix with a thermal conductivity of $k_m = 0.2 \text{ W}/(\text{m}\cdot\text{K})$. The porosity of aerogel is considered
627 in the range of 90-99.6%. With the purpose of verifying the model's robustness, we present here
628 the predicted effective thermal conductivity by our model for two cases: one without nanopores
629 and the other considering their presence.

630 In the first case, the aerogel is considered to have only micrometric pores. In the second case,
631 there are 12% nanometric pores and 88% micrometric pores combined in the total pore volume
632 of the aerogel. It is noteworthy that the terms "nanopores" and "macropores" used in this work,
633 respectively to refer to the nanometric and micrometric pores. The thermal conductivity of the air
634 confined in nanopores, which is significantly smaller than that of the free air, may be calculated
635 using relation (30). Detailed procedures for calculating the effective thermal conductivity of aerogel
636 while taking into account effect of nanopores will be provided in subsection 5.3.3.

637 Figure 13 shows the thermal conductivity estimated by our numerical model and the experimen-
638 tally measured thermal conductivity of polyimide (PI) aerogel [10], chitosan (CS) aerogel [66], and
639 cellulose nanofibril (CNF)-emulsion aerogel [9]. It should be noted that the nonzero components
640 (i.e. diagonal components) of the effective thermal conductivity tensor at the macroscale $\mathbf{K}^{(3)}$ are
641 the same due to the isotropic properties of solid phase and the symmetry of the hollow spherical
642 unit cell.

643 From the numerical results, it can be observed that the effective thermal conductivity decreases
644 as the porosity increases. At the same porosity, aerogels with 12% nanopore always have a lower
645 thermal conductivity than aerogels composed only of macropores (0% nanopore). Furthermore,

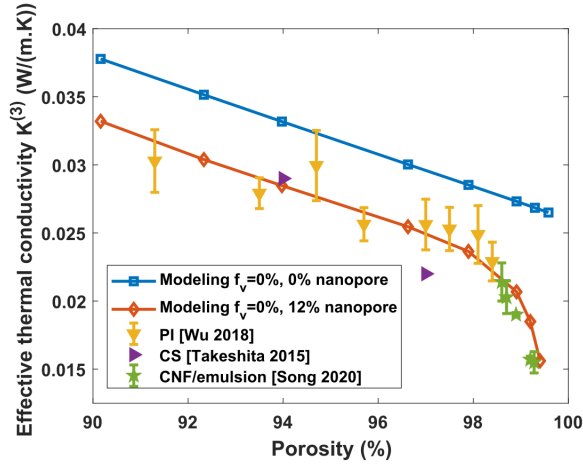


Figure 13: Numerical predictions of the effective thermal conductivity at the macroscale compared to the experimental data of polymer-based aerogel from literature [10, 66, 9].

646 a linear relationship between the effective thermal conductivity and porosity for the case of 0%
 647 nanopore can also be seen in the figure. On the contrary, this relationship becomes strongly non-
 648 linear in the case of 12% nanopore when the porosity is higher than 96%. This phenomenon
 649 is correlated with the Knudsen effect within nanopores [67], causing a reduction in the effective
 650 thermal conductivity of the aerogel below the free air thermal conductivity of 0.026 W/(m·K) when
 651 the porosity exceeds 96%. This effect will be discussed in more detail in subsection 5.3.3.

652 In relation to porosity, various methods can be employed to control the porosity of aerogels.
 653 Specifically, the referenced experimental works have reported that porosity can be influenced by
 654 factors such as crosslinking [10, 66], polymer concentration [10, 66] and emulsion templating [9],
 655 where the effect of polymer concentration is found to be the most significant. Accordingly, the
 656 porosity of aerogels can rise from 91.3 to 98.1% with a decrease in polyimide concentration from 10
 657 to 1.1% (by weight), as previously reported [10], and from 86 to 97% with a corresponding decrease
 658 in chitosan concentration from 1.6 to 0.4% (by weight), as described elsewhere [66]. Therefore, the
 659 simulation results suggest that in order to reduce the effective thermal conductivity and enhance
 660 the insulation performance of the aerogel, it is advisable to decrease the polymer concentration.

661 The comparison between simulation results and experimental data indicates that the model of
 662 0% nanopore overestimate the experimental data in most cases. This phenomenon can be explained
 663 by the fact that this case does not account for the impact of nanopores on the thermal conductivity
 664 of aerogels. Indeed, all three referenced experimental works report the existence of nanopores with
 665 diameters ranging from 3 to 50 nm. Besides, the results of the model with 12% nanopores match
 666 well with the experimental ones. This result suggests the significant influence of nanopores on the
 667 effective thermal conductivity of aerogels, which will be further investigated in detail in the following
 668 section. It is noted that the volume fraction of nanopores relative to the total pore volume has not
 669 been reported in these experimental works, thus only qualitative comparisons could be conducted
 670 and further investigations are needed. However, these results have also, to some extent, showcased
 671 the reliability of the proposed model for predicting the effective thermal conductivity of aerogels.

672 5.3.2. Effect of microstructural morphology

673 To investigate the effect of the structural parameters on the effective thermal conductivity
674 of aerogels, the porosity was fixed at 98.24%, corresponding to the computed average value in
675 subsection 3.1.3. As presented in subsection 3.1.1, 3 structures were considered, including graphene
676 block with 5 layers per block (aggregate structure), monolayer graphene oxide (exfoliated structure)
677 and graphene oxide block with 3 or 5 layers per block (intercalated structure). The volume fraction
678 of the fillers (graphene and graphene oxide) was examined in the range of 0% – 3%. Here, the
679 estimated effective thermal conductivity at the macroscale has been normalized by the effective
680 thermal conductivity of the pure polymer aerogel (*i.e.* $f_v = 0$) for ease of observation. The effective
681 thermal conductivity tensor of this pure polymer aerogel is denoted by $\mathbf{K}_0^{(3)}$.

682 Figure 14a illustrates the normalized effective thermal conductivity at the macroscale as a
683 function of the filler volume fraction for different structure types. It is evident that the effective
684 thermal conductivity of aerogels increases as the volume fraction of the fillers rises. However, the
685 extent of this increase varies among the different structural types. Specifically, graphene block
686 contributes to the highest increase in thermal conductivity, followed by graphene oxide monolayer,
687 and finally, graphene oxide blocks. It's interesting to consider that, at the macroscale, graphene
688 oxide monolayer, graphene oxide blocks with 3 layers and graphene oxide block with 5 layers, only
689 increases the effective thermal conductivity of aerogel by 6.4%, 3.6% and 2.8%, respectively, when
690 the graphene oxide volume fraction is 3%. Meanwhile, these increments are recorded as 82%,
691 45%, and 35% at the microscale, as elucidated in subsection 5.2.2. It is noteworthy that in this
692 study, the effective thermal conductivity at the micro- and macroscales respectively characterize
693 the effective thermal conductivity of the composite (with extremely little to no pores) and the
694 aerogel (ultraporous). These results provide a response to the question posed in subsection 5.2.2,
695 indicating that graphene oxide can significantly enhance the thermal conductivity of polymer-based
696 composites, while it does not substantially alter the thermal conductivity of polymer-based aerogels.
697 This implies that graphene oxide can be employed flexibly for various applications.

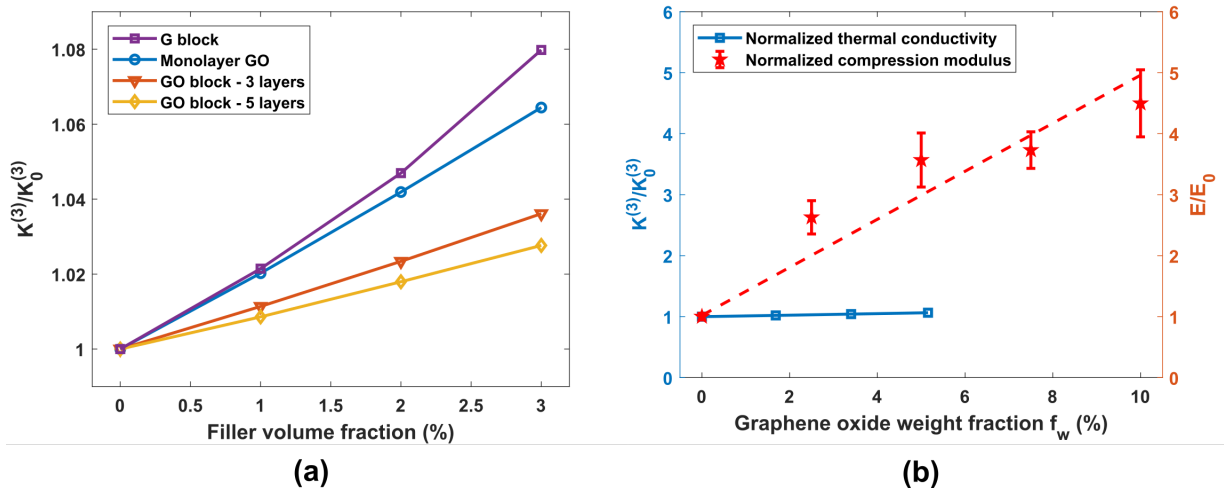


Figure 14: (a) Effect of the inclusion type-related structural parameter on the effective thermal conductivity of aerogel at the macroscale with a porosity of 98.24% and (b) estimated effective thermal conductivity by simulation and compressive modulus by experimentally measured as a function of graphene oxide weight fraction. The red dashed line represents to the line fitted by linear regression of the compressive modulus.

698 Regarding the comparison between graphene and graphene oxide, as observed in Fig. 14a, the
699 polymer aerogel reinforced with graphene (aggregate structure) exhibits slightly higher thermal
700 conductivity than that reinforced with graphene oxide (exfoliated structure). However, the results
701 of the compression test demonstrate that graphene oxide exhibits a better capability for reinforcing
702 mechanical properties compared to graphene (see Fig. 4). This result can be explained by the fact
703 that, at high degree of oxidation, graphene oxide has a significantly lower thermal conductivity
704 of about 1% compared to graphene [47], while its Young's modulus is only about 50% lower than
705 that of graphene [68]. Furthermore, thanks to its functional groups on the surface, graphene oxide
706 exhibits a strong dispersibility and may form covalent bonds with polymers, contributing to the
707 enhancement of the mechanical properties of the aerogels.

708 In order to understand the impact of graphene oxide on the thermal conductivity and mechani-
709 cal properties of the aerogels, we simultaneously represented both the effective thermal conductivity
710 estimated by simulations and the compressive modulus that is experimentally measured as a func-
711 tion of graphene oxide weight fraction f_w (see Fig. 14b). It is noteworthy that both quantities were
712 normalized by the effective thermal conductivity and compressive modulus of pure polymer aerogel
713 ($f_w = 0$), respectively. The graphene oxide volume fraction f_v can be transformed into graphene
714 oxide weight fraction f_w using Eq. (3). Figure 14b clearly illustrates that the compressive modulus
715 increases with the weight fraction of graphene oxide, while the thermal conductivity remains nearly
716 unchanged. Specifically, by employing linear regression on experimental results, the linear rela-
717 tionship obtained between compressive modulus and graphene oxide weight fraction indicates that
718 the compressive modulus increases by 39% for each 1% weight fraction of graphene oxide added.
719 Meanwhile, the rate of increase in effective thermal conductivity is only 1% for every 1% weight
720 fraction of graphene oxide added. Furthermore, aerogels with an exfoliated structure of graphene
721 oxide also exhibit more favorable characteristics compared to aerogels with an aggregate structure
722 of graphene, such as improved thermal insulation and enhanced mechanical strength.

723 Based on the results of this section, it can be highlighted that the addition of graphene oxide
724 significantly enhances the mechanical properties and reasonably increases the thermal conductiv-
725 ity of polymer-based aerogels. In the context where monolayer graphene sheets are prohibitively
726 expensive and challenging to manufacture [69], monolayer graphene oxide, which can be readily
727 produced on a massive scale at a reasonable cost, emerges as a promising candidate for reinforcing
728 polymer-based aerogels.

729 5.3.3. Effect of nanopores occurrence

730 As discussed in subsection 5.3.1, porosity and presence of nanopores to various degrees are two
731 critical factors that significantly affect the thermal conductivity of aerogels. Nevertheless, it should
732 be noted that increasing the porosity to enhance thermal insulation performance also reduces the
733 mechanical properties of the material, which should be taken into account in construction appli-
734 cations. Therefore, nanopore occurrence has, to be considered when developing porous materials
735 with excellent thermal insulation while maintaining high rigidity. Indeed, with the same porosity,
736 nanoporous materials possess lower thermal conductivity than common porous materials thanks to
737 the extremely low gas thermal conductivity in the nanopores through the Knudsen effect [70]. This
738 effect occurs when the mean free path (MFP) of the gas molecules is larger than the pore diameter,
739 meaning that the gas molecules collide with the pore wall more frequently than with other gas
740 molecules. As a result, the thermal conductivity of the gas becomes lower than the value for free
741 gas. The gas thermal conductivity, denoted by k_g , taking into account the Knudsen effect, can be

742 written as follows [71]:

$$k_g = \frac{k_g^0}{1 + 2\beta \ell_m/D}, \quad (30)$$

743 where k_g^0 is the thermal conductivity of the free gas, $K_n = \ell_m/D$ is the Knudsen number in which
 744 ℓ_m is the MFP of gas molecules and D is the characteristic size of pores, β is a coefficient varying
 745 between 1.5 and 2.0 characterizing the molecule-wall collision energy transfer efficiency (~ 2 for
 746 air). The quantity ℓ_m has been simply expressed by Stewart and Leiser as a function of temperature
 747 and pressure [72] as follows:

$$\ell_m = 2.303 \times 10^{-8} \times \frac{T}{P_g}, \quad (\text{cm}) \quad (31)$$

748 where T is the temperature and P_g is the gas pressure. From Eq. (31), it can be calculated that
 749 the MFP of gas molecules at room conditions ($T = 293$ K, $P_g = 1$ atm) is 67 nm. Therefore, an
 750 important impact of the Knudsen effect can be predicted for pores smaller than 67 nm in diameter.

751 In fact, nanopores and macropores coexist in the majority of aerogels, with sizes ranging from 1
 752 to 50 nm and from a few micrometers to several hundreds of micrometers, respectively [73, 74, 75].
 753 Additionally, the contribution of nanopores to the total pore volume is much lower than that of
 754 macropores, specifically ranging from 4 to 22%, as reported in previous studies [73, 74]. Hence, this
 755 study investigates the influence of nanopores on the overall thermal conductivity of aerogels from
 756 two aspects: (i) nanopore size and (ii) nanopore volume fraction. Here, due to the negligible impact
 757 of the Knudsen effect on the macropores, their diameter will be fixed at 76 μm . To accomplish
 758 this, the multiscale homogenization procedure introduced in section 4 requires an additional step.
 759 This step is employed at the nanoscale to calculate the effective thermal conductivity of the equiv-
 760 alent polymer matrix, where the spherical nanopores are regularly arranged within the polymer
 761 matrix. At this scale, the thermal conductivity of the gas phase within the nanopores, calculated
 762 by Eq. (30) and the thermal conductivity of the polymer matrix $k_p = 0.2$ W/(m·K) will be used
 763 for the homogenization issue. It should be noted that graphene oxide monolayer with a thermal
 764 conductivity $k_{GO} = 18$ W/(m·K) has been taken as a reference case; therefore, it is unnecessary
 765 to compute the effective thermal conductivity of the inclusion at the nanoscale. Next, the thermal
 766 conductivity of the equivalent homogenized matrix is used as input properties of the matrix at the
 767 microscale, and the homogenization process at both the micro- and macroscales is conducted as
 768 described in subsection 4.2. Furthermore, aerogels maintaining a total porosity of 98.24% and 2%
 769 volume fraction of graphene oxide monolayer are used throughout the studies in this section.

770 Figure 15 shows the pore size versus air thermal conductivity relationship at room conditions
 771 where 1 – 50 nm is the range of the pore size investigation. It is clear that the thermal conductivity
 772 of the confined air decreases from 0.0042 W/(m·K) to 0.0001 W/(m·K) as the pore size decreases
 773 from 50 nm to 1 nm, and it is much smaller than that of free air (0.026 W/(m·K)). Next, the
 774 influence of pore size on the effective thermal conductivity of aerogel with 2% and 12% nanopore
 775 volume fractions is illustrated in Fig. 16a. It can be observed that a reduction in pore size leads
 776 to a decrease in the effective thermal conductivity of the aerogel, and this effect becomes more
 777 significant at higher nanopore volume fractions. The effective thermal conductivity in the case
 778 of 2% nanopore volume fraction appears to remain nearly constant, decreasing by 0.4% when the
 779 nanopore size decreases from 50 to 1 nm, whereas the case of 12% nanopore volume fraction records
 780 a reduction of 5.4%. This implies that enhancing the thermal insulation of the aerogel by reducing

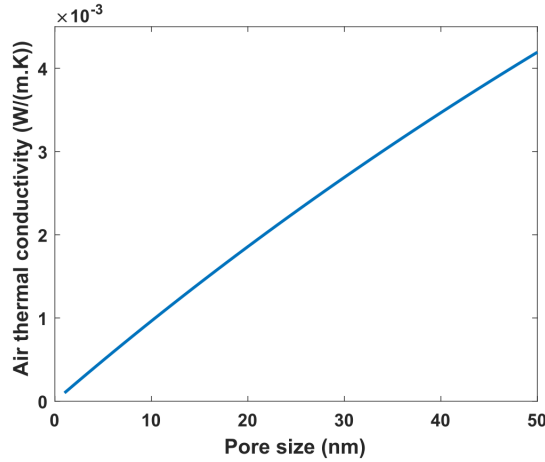


Figure 15: Air thermal conductivity as a function of the pore size at room condition.

781 the nanopore size is only significant when a substantial nanopore volume fraction is present within
 782 the aerogel. Furthermore, it is noteworthy that the volume fraction of nanopores has a significantly
 783 more pronounced impact on the effective thermal conductivity of the aerogel than the nanopore
 784 size. Indeed, at nanopore size of 1 nm, the thermal conductivity of the aerogels in the case of 12%
 785 nanopore volume fraction is 0.023 W/(m·K), decreasing by 20% compared to 0.027 W/(m·K) of
 786 the case of 2% nanopore volume fraction. To investigate the effect of nanopore volume fraction on
 787 the effective thermal conductivity of aerogel, we fixed the nanopore size at 4 nm and varied the
 788 nanopore volume fraction from 0 to 22% (see Fig. 16b).

789 One can observe that as the nanopore volume fraction increases from 0 to 22%, the effective
 790 thermal conductivity of aerogel decreases from 0.030 W/(m·K) to 0.017 W/(m·K), indicating a 43%
 791 of reduction. Moreover, a weak nonlinear relationship between the effective thermal conductivity
 792 and nanopore volume fraction can also be found. The influence of nanopore volume fraction dimin-
 793 ishes slightly as the effective thermal conductivity approaches the value of 0.026 W/(m·K), which
 794 is free air thermal conductivity. Beyond this threshold, the effective thermal conductivity continues
 795 to decrease significantly as the nanopore volume fraction increases.

796 In fact, the nanopore volume within aerogels can be increased through various techniques. For
 797 instance, aerogels prepared by pyrolysis of resorcinol–furfural (RF) gel containing salt (ZnCl_2) will
 798 contain numerous nanopores as ZnCl_2 is removed [76]. Furthermore, cross-linkers can be employed
 799 to enhance the stability of the three-dimensional network structure, limiting the continuous growth
 800 of ice crystals during the freezing process, which results in the reduction in pore size of the aerogel
 801 [77]. It has also been demonstrated that the incorporation of graphene oxide into the polymer matrix
 802 creates favorable conditions for the formation of nanopores within the aerogel [7]. The numerical
 803 results in this section provide motivation for enhancing the thermal insulation performance of
 804 aerogels by increasing the volume of nanopores. Furthermore, in conjunction with the findings in
 805 subsection 5.3.2, it can be inferred that incorporating graphene oxide into polymer-based aerogels
 806 not only enhances their stiffness but also reduces their thermal conductivity, as the number of
 807 nanopores in the aerogel increases.

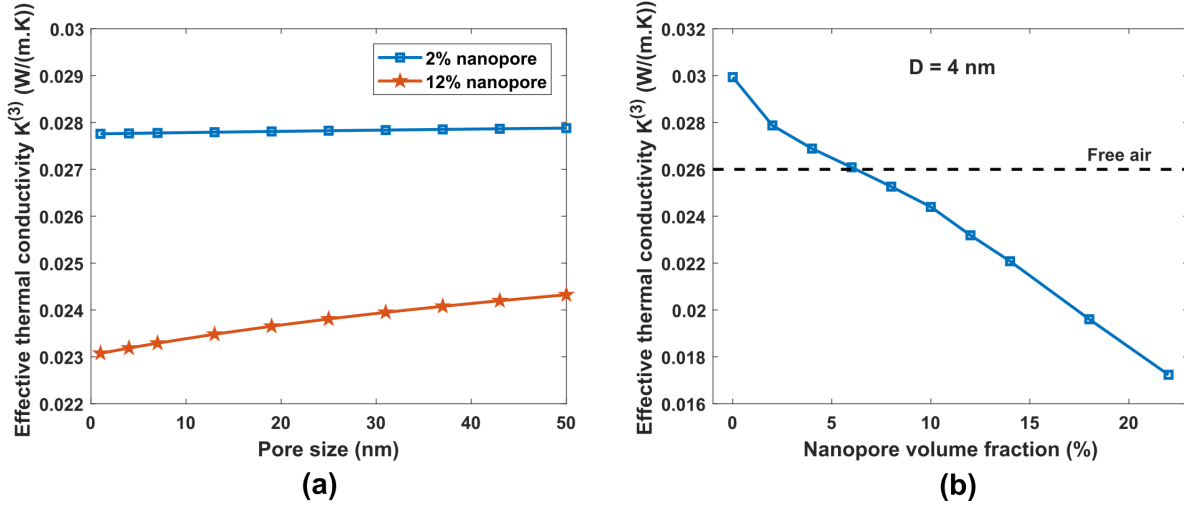


Figure 16: Effect of two parameters on effective thermal conductivity of aerogels at porosity of 98.24% and 2% graphene oxide volume fraction: (a) pore size with different volume fractions of nanopores, (b) nanopore volume fraction with pore size of 4 nm.

5.3.4. Effect of gas pressure

Gas pressure P_g has an important influence on the thermal conductivity of air. As the pressure decreases, the mean free path of the gas molecules l_m increases, leading to an increase in the impact of the Knudsen effect and thus a decrease in the gas thermal conductivity. The relationship between P_g and l_m has been shown in Eq. (31). It can be deduced that during a decrease in gas pressure, the gas thermal conductivity is virtually unaffected until the MFP of gas molecules reaches values in the same order of size as the pore size. Therefore, the effect of gas pressure on the thermal conductivity of gas within smaller pores occurs earlier than in the case of gas within larger pores. Figure 17a illustrates the thermal conductivity of air contained within two types of pores of different sizes, including macropore ($D = 76 \mu\text{m}$) and nanopores ($D = 4 \text{ nm}$), as a function of gas pressure in the range of $10^{-5} - 10$ atm. It is easy to see that the thermal conductivity of the air in the macropores is equal to that of the free air ($\sim 0.026 \text{ W}/(\text{m}\cdot\text{K})$), in other words there is no Knudsen effect. Its value decreases sharply when the gas pressure begins to decrease below 0.01 atm and approaches zero at vacuum pressure. Meanwhile, the thermal conductivity of the air in the nanopores was almost zero at room conditions ($P_g = 1 \text{ atm}$), indicating that the effect of gas pressure has already occurred due to the small diameter of the nanopores.

In order to investigate the effect of gas pressure on the effective thermal conductivity of aerogel, we varied the gas pressure within the pores of aerogel from 10^{-5} to 10 atm. Here, aerogels have a constant porosity 98.24% and 2% graphene oxide volume fraction, with various cases of nanopore volume fractions considered. Figure 17b shows the variation of the effective thermal conductivity with respect to gas pressure for 3 cases of nanopore volume fractions, *i.e.* 0%, 6% and 12%. It is easy to see that the effective thermal conductivity decreases as the gas pressure decreases, following the same trend in all 3 cases. This effect becomes noticeable only when the pressure drops below 10^{-2} atm. Specifically, the thermal conductivity of aerogel can reach the values of 0.0025 W/(m·K), 0.0012 W/(m·K) and 0.0009 W/(m·K) at a pressure of 10^{-5} atm, respectively, for the cases of 0%, 2% and 3% nanopore volume fraction. Moreover, one can also observe that aerogels with large nanopore volume always have lower thermal conductivity at the same pressure. In other words,

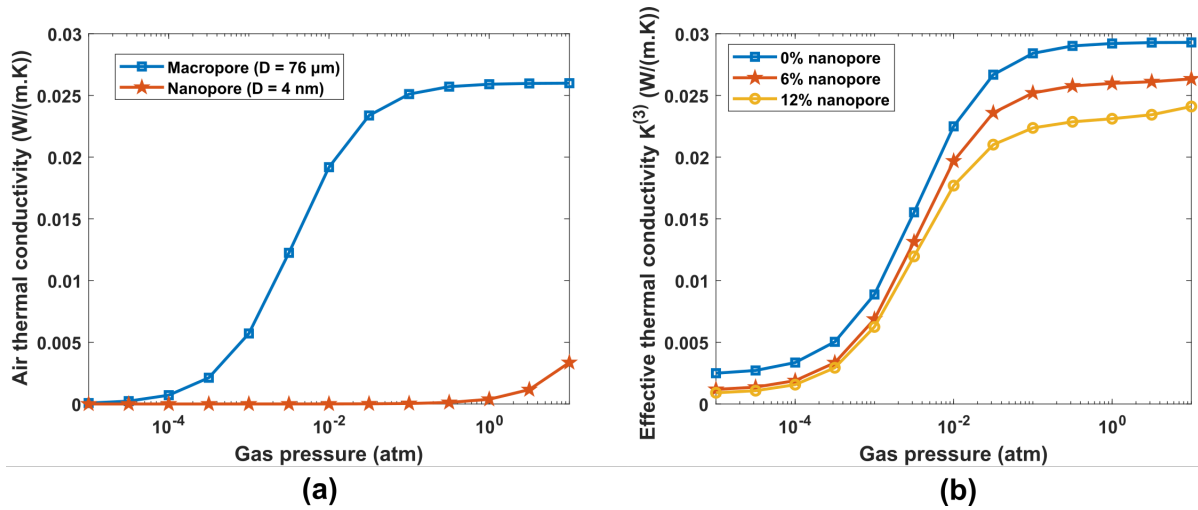


Figure 17: Effect of air pressure on (a) air thermal conductivity in nanopore with a diameter of 4 nm and in macropore with a diameter of 76 μm , and on (b) the thermal conductivity of aerogels at porosity of 98.24% and 2% graphene oxide volume fraction with different volume fractions of nanopores.

835 to achieve the same insulation performance, aerogels with a large nanopore volume need lower gas
 836 pressure than vacuum pressure. In essence, this is a compromise between the vacuum requirement
 837 and the nanopore volume to achieve optimal thermal insulation performances of porous materials.
 838 Indeed, it has been reported that VIPs cannot maintain a low inner pressure for a long period [3].
 839 This suggests that the incorporation of aerogel as the core material for VIPs to achieve optimal
 840 insulation performance could be a promising solution to this problem. It should also be noted
 841 that the core material in VIPs needs to possess sufficient mechanical properties to withstand the
 842 pressure of the envelope without collapsing. One can increase the mass density of aerogel, meaning
 843 reduce porosity, to ensure a certain mechanical strength, although solid phase conduction increases.
 844 However, with the Knudsen effect in nanopores and the low gas pressure, the effective thermal
 845 conductivity of the porous material can be decreased. This is a multifaced issue involving a delicate
 846 compromise between three factors, namely: mechanical strength, nanopore volume fraction, and
 847 gas pressure, all of which requires further research.

848 6. Conclusion

849 This work employed a multiscale approach for the numerical characterizations of the effective
 850 thermal conductivity of polymer aerogels reinforced by graphene and graphene oxide. This compos-
 851 ite aerogel type has gained tremendous attention due to its environmentally friendly manufacturing
 852 process, which combines the use of biopolymers and freeze-drying techniques. In the proposed mul-
 853 tiscale approach to characterize the effective thermal properties of the studied aerogels, geometrical
 854 configurations were constructed at three scales, referred to as nano-, micro-, and macroscales, based
 855 on experimental characterization. Subsequently, the homogenization process was conducted from
 856 smaller to larger scales, wherein Milton's method was employed at the nanoscale, and the asympt-
 857 otic homogenization method combined with the finite element method was utilized at the micro-
 858 and macroscales. Three types of inclusions forms related to the aggregate structure of graphene,
 859 exfoliated and intercalated structures of graphene oxide were investigated. By randomly generating

860 these inclusions in the polymer matrix at the microscale and employing a hollow spherical repre-
861 sentative unit cell at the macroscale, the relationship was established between the effective thermal
862 conductivity of the aerogel and microstructure characteristics, namely microstructural morphology,
863 porosity, pore size, as well as gas pressure.

864 Comparisons between simulation results and experimental data validated the accuracy of the
865 proposed model. It was shown that the addition of graphene and graphene oxide did not signifi-
866 cantly alter the effective thermal conductivity of the aerogel while notably enhancing its mechanical
867 properties. The numerical results demonstrated that the exfoliated structure of graphene oxide of-
868 fered the most beneficial application for enhancing the stiffness of the polymer aerogel and ensuring
869 a reasonable increase in thermal conductivity compared to other structures. The numerical results
870 also suggested that reducing the polymer concentration in the precursor solution increased the
871 porosity of the aerogel, leading to a decrease in its effective thermal conductivity. Furthermore, the
872 thermal insulation performance of the materials could be significantly enhanced by reducing the
873 pore size to below 50 nm, or in other words, increasing the number of these nanopores through the
874 introduction of cross-linkers or the increase in the graphene oxide content. In relation to the effect
875 of gas pressure, it was demonstrated that reducing the gas pressure below 10^{-2} atm significantly
876 decreased the effective thermal conductivity of the aerogels, and concurrently, aerogels with numer-
877 ous nanopores required less vacuum demand for the same thermal insulation performance. Based
878 on these numerical results, it is suggested to integrate aerogels as the core material of vacuum in-
879 sulation panels to achieve optimal thermal insulation performance while ensuring that the aerogels
880 are sufficiently rigid to withstand the pressure of the envelope without collapsing.

881 To obtain initial estimates of the effective thermal properties of the studied aerogels, the multi-
882 scale approach herein focusing on the ideal disc-shaped of graphene and graphene oxide has proven
883 to be useful in the material development phase. Nonetheless, graphene and graphene oxide pre-
884 dominantly exhibit defects in their two-dimensional structures, such as the out-of-plane wrinkles
885 and hole defects [78]. These factors may provide deeper insights into the effects of graphene and
886 graphene oxide on the effective thermal properties of polymer-based materials, which will be the
887 topic of a further investigation. Additionally, the proposed integration of aerogels with nanopores
888 as cores for VIPs demands more in-depth research on both experimental and simulation aspects.
889 This constitutes a complex challenge in finding a compromise between three key factors, *i.e.* ther-
890 mal conductivity, gas pressure, and mechanical properties. Specifically, experimental work must
891 provide sufficient data on the stiffness, porosity, and corresponding volume fraction of nanopores,
892 while simulation work will estimate the effective thermal conductivity of these materials under
893 varying gas pressure conditions. With the target insulation performance corresponding to a specific
894 gas pressure, the optimal material will be suitable for application as a core material provided its
895 stiffness is adequate to withstand the pressure exerted by the envelope at this pressure level.

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