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Sustainable assembling of graphite flakes into graphite/carbon composite foams with thermal percolative interfaces for active heat dissipation

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ABSTRACT

Current methods for producing open-pore graphite foams with heat dissipation potential involve costly graphitization processes, limiting their widespread use. This study presents a sustainable approach to fabricate high-performance graphite/carbon composite foams with porosities in the range of 49 - 82%. The method involves the densification and carbonization of solid mixtures comprising natural graphite flakes, sucrose, and NaCl particles. The dissolution of NaCl creates coarse pores, while carbonized sucrose contributes fine porosity and serves as a binder to impart mechanical stability, ensuring the maintenance of thermally conductive percolative contacts between flakes. The composite foams exhibit thermal conductivities of up to 91 Wm⁻¹K⁻¹, permeability values in the range of 10⁻¹¹ - 10⁻¹⁰ m², and excellent mechanical properties. Experimental and computational findings demonstrate that the developed materials surpass the heat dissipation capabilities of conventional heat sinks based on graphite and aluminum foams by about 3 and 1.5 times, respectively, making them excellent candidates for thermal management applications.

KEYWORDS: composite foam, graphite flake, percolative interface, thermal management.

1. Introduction

The rapid technological advancements in the electrical and electronics industries have led to the development of devices capable of handling increasing electrical power. However, these devices generate significant heat, which needs efficient dissipation to prevent premature deterioration [1]. Consequently, the scientific community seeks materials with high heat dissipation capabilities [2,3]. The latest generation of heat sink materials comprises composite materials with extremely high thermal conductivities (up to 1000 Wm⁻¹K⁻¹) [4,5]. These materials effectively transfer heat from hot zones to active heat sinks, where it is convectively transferred to a fluid (usually air or water) for dissipation in a suitable environment. One promising approach involves using high thermal conductivity particulate materials, like synthetic diamond,
combined with pure metal matrices through nanotechnology-engineered interfaces [4,6,7]. However, the potential for further property improvement in future materials is limited to about 20 percent [5].

The coming generation of heat dissipation materials will mainly consist of open-pore foam materials with high convective potential used as active heat sinks. These materials should have a target thermal conductivity greater than 50 Wm\(^{-1}\)K\(^{-1}\), be environmentally sustainable, and adhere to green processing standards. Open-pore graphite foams are particularly suitable for heat dissipation due to their high thermal conductivity, low density, high specific surface area, and acceptable mechanical properties [8,9]. Three main categories of methods are used to produce these foams: (i) blowing methods of graphitizable precursors, (ii) methods employing templating agents, and (iii) assembly/compression of graphitic units [8,9]. Template-based methods offer certain advantages over blowing-based methods as they enable precise control over the shape and distribution of pores, facilitating the adjustment of permeability to specific requirements and achieving thermal conductivity values of up to 60 Wm\(^{-1}\)K\(^{-1}\). Nevertheless, these two methods have disadvantages, including high costs and unsustainability due to energy consumption and graphitization processes [10–13]. The assembly/compression method, which avoids graphitization treatments, has shown promise, but materials with sufficiently high permeability and thermal conductivity are still required for effective thermal management [14–16]. Recent research suggests combining natural graphite flakes with an aqueous solution of blowing/binder agent (sucrose) and NaCl (template) to produce graphite composite foams [17]. However, these foams have low thermal conductivities (< 4 Wm\(^{-1}\)K\(^{-1}\) for pore volume fractions of 0.4-0.8) and do not meet the requirements for demanding thermal management applications. Therefore, there is a need to develop new, cost-effective, sustainable methods to produce highly permeable open-pore graphite composite foams with improved thermal conductivity and mechanical behavior.

In this paper, the authors propose a novel class of graphite/carbon composite foams with exceptional thermal performance. These materials are fabricated in three steps: (i) preparation of self-standing preforms by pressure densification of a solid mixture of natural graphite flakes, sodium chloride (NaCl) as a template, and sucrose particles as a blowing/binder agent; (ii) caramelization and carbonization of sucrose; and (iii) dissolution of NaCl template. Different combinations of graphite flakes, NaCl, and sucrose were investigated to produce composite foams with pore volume fractions similar to those developed for thermal management (ranging from 0.49 to 0.81). The carbonized sucrose contributes to dimensional stability, while the contacts between flakes facilitate efficient heat transport, resulting in a high thermal conductivity of up to 91 Wm\(^{-1}\)K\(^{-1}\), which is over 20 times higher than previous graphite foams [17].

2. Experimental procedures

2.1. Materials

Natural graphite flakes (Gf, average diameter: 420 μm, average thickness: 50 μm) were purchased from Graphitwerk Kropfmühl AG (Hauzenberg, Germany). Specific details regarding the characterization of the graphite flakes can be found in the Supplementary Material section. Analytical-grade sodium chloride particles (NaCl, 99.5 wt%) were provided by Panreac Química S.L.U. (Barcelona, Spain) with a fraction size of 355-500 μm after sieving. The selection of NaCl particles as a templating agent stems from both their proficiency in facilitating material processing at elevated temperatures, while still remaining below their melting point of 801 °C, and their facile removal via dissolution in water. Ordinary sucrose (culinary quality) was also sieved, resulting in two fractions of 150-200 μm and 38-45 μm, herein referred to as large and small sucrose particles, respectively. The sucrose particles serve the purpose of acting as binders for graphite flakes once they undergo carbonization. Although the thermal conductivity of the resulting carbon is low, its application is noteworthy due to the superior wetting capability of sucrose on graphite in its caramelized state, which is achieved at relatively low temperatures (below 200 °C). Figure 1 showcases micrographs displaying the dimensions and morphology of these raw materials.
2.2. Fabrication of Gf/C composite foams

The Gf/C composite foam fabrication process is illustrated in Figure 1. The first step consists of the preparation of self-standing preforms. To achieve this, precise amounts of Gf, NaCl, and sucrose particles were first hand-mixed in a vessel and then transferred to an assisted powder mixer operating at 60 rpm (Stuart STR4, Staffordshire, UK). After 15 minutes of physical mixing, the mixtures were placed in a 10 × 50 mm mold and gently vibrated for 1 minute to ensure optimal Gf orientation. It was noted that longer vibration times caused particle segregation. Self-standing preforms were then created by applying a pressure of 20 MPa perpendicular to the Gf orientation plane for 2 minutes using a manual hydraulic workshop press. The volume percentages of each phase used for the specimens in this study can be found in Table 1. At temperatures above 160 ºC, sucrose particles undergo a complex process known as caramelization, breaking down into smaller volatile aromatic molecules or combining to form larger molecules. Sucrose, a renewable resource that melts at low temperatures, serves as an excellent non-graphitizable carbon precursor. To achieve this, self-standing preforms were pyrolytically treated, heating them at a rate of 6.67 ºCmin⁻¹ to 600 ºC under vacuum (0.1 bar) for 15 minutes, followed by cooling at a rate of 2.15 ºCmin⁻¹ to room temperature. This sucrose carbonization process contributes to the creation of part of the final porosity, hereafter referred to as carbonization-generated porosity. In the final step of composite foam fabrication, NaCl particles were dissolved to achieve a structured material with interconnected porosity, known as template-generated porosity. To facilitate access to the NaCl particles, the outer surfaces of the resulting materials are roughened. The samples are then immersed in magnetically stirred distilled water at room temperature (400 rpm), and their mass loss is monitored. Once the mass stabilizes, the samples are dried and stored for further characterization.

2.3. Characterization of microstructure and chemical composition

Microstructure and chemical composition characterization utilized an optical microscope (Olympus PME3-ADL) and a Scanning Electron Microscope (SEM-Hitachi S3000N) operating at 20 keV for examining self-standing preforms and Gf/C composite foams, respectively. To avoid deformation of the porous structures caused by standard cutting methods, composite foams were fractured via hammer impact. Fragments resulting from the impact, with approximate dimensions of 5 × 5 × 5 mm and devoid of direct hammer contact, were collected and their fractured surfaces within the inner zone were examined. Three complementary techniques were employed to determine composite foam porosities at different scales: (i) image analysis using the software Buehler-Omnimet Enterprise to examine the largest pores, (ii) mercury porosimetry (Poremaster-60 GT Quantachrome Instruments) for measuring intermediate porosity, and (iii) gas adsorption (Quantachrome Instruments equipment) to determine the fine porous structure. The carbon precursor and selected Gf/C composite foams were subjected to thermogravimetric measurements using a simultaneous thermogravimetry-differential scanning calorimetry instrument (TG-DSC Mettler Toledo) operating in a nitrogen atmosphere between 100 ºC and 600 ºC, providing differential TG values (DTG) automatically.

2.4. Determination of composite foam density and pore volume fraction

The determination of open and closed porosity volume fractions in the developed materials involved the calculation of three densities. Initially, material densities ($\delta_{m}$) were established by computing the mass-to-volume ratio, geometrically determined based on the dimensions of the foam pieces. Furthermore, skeletal densities ($\delta_{sk}$) were obtained using an automated He ultra-pycnometer provided by Quantachrome Instruments. The solid body densities ($\delta_{b}$) were subsequently determined by subjecting the samples to uniaxial pressing using a manual hydraulic workshop press at a pressure of 50 MPa, enough to ensure a consistent density value. The following equations were used to relate $\delta_{m}$, $\delta_{b}$ and $\delta_{sk}$:

$$\delta_{sk} = \delta_{b}(1 - V_{cp})$$

(1)
\[ \delta_m = \delta_b (1 - V_{cp} - V_{op}) \] (2)

where \( V_{cp} \) and \( V_{op} \) represent the closed porosity and open porosity, respectively, within the composite foams. Five individual density measurements were performed for each material, and the resultant average values were reported.

### 2.5. Pressure drop and permeability characterization

The pressure drop of the composite foam specimens was measured using a homemade setup introduced in [18]. This setup includes two ±0.001 bar precision pressure gauges connected to both ends of the sample with 1 m of polymer tubing to ensure fully developed fluid flow. An air flow meter recorded the flow rate through the foams within a range of 0-8 lmin\(^{-1}\). The pressure drop across the material is determined by the Darcy-Forchheimer equation, accounting for permeability and the inertial coefficient [19,20]:

\[ \frac{\Delta P}{\Delta L} = \frac{\mu}{K} v + \rho C_F v^2 \] (3)

where \( \Delta P(\Delta L)^{-1} \) represents the relative pressure drop across the porous material, \( \mu \) is the dynamic viscosity of the fluid, \( K \) is the permeability of the foam, \( C_F \) is the inertial coefficient, and \( v \) and \( \rho \) are the superficial velocity and density of the fluid, respectively. Permeability was calculated using second-degree fittings of the relative pressure drop versus superficial air velocity plots. The overall uncertainty of the permeabilities was estimated to be less than 15%.

### 2.6. Thermal, mechanical, and thermo-mechanical characterization

To measure the thermal conductivity, an experimental setup was assembled at the University of Alicante, following the relative steady-state (equal-flow) technique and complying with ASTM E-1225-0. The heat transfer coefficient was determined using an established experimental setup inspired by [19]. The sample was heated at a constant temperature through one of its bases, and air was passed through it while measuring the temperature before and after passing through the sample. The temperature was monitored using K-type thermocouples (with an associated error of ±0.1 °C). The heating control of the sample base was achieved using four copper blocks arranged in series, each containing a thermocouple and connected to a direct current (DC) power supply to maintain a temperature of 50 °C in each block. The tests were conducted with a constant pumping power and specimens of size 10 × 10 × 10 mm. After 20 minutes of stabilization, measurements were taken with an initial air temperature of 25 °C. The heat transfer coefficient \( h \) was calculated using Newton's cooling law and the following equations [19,21]:

\[ h = \frac{\dot{q}}{(T_{base} - T_{in})} \] (4)

\[ \dot{q} = \frac{q}{S_{base}} = \dot{m} C_p (T_{out} - T_{in}) \] (5)

where \( q \) is the heat flow rate, \( T_{base} \) is the temperature of the heated base, \( T_{in} \) and \( T_{out} \) are the temperatures of the incoming and outgoing air, respectively, \( S_{base} \) is the area of the heated base, \( \dot{m} \) is the mass flow rate of the fluid, and \( C_p \) is the specific heat of the air at constant pressure.

The compressive strength was determined using an Instron-4411 universal testing machine, conducting
compressive tests on specimens of size 10 × 20 × 5 mm at a constant crosshead speed of 2 mm·min\(^{-1}\). The compressive strength of each sample was derived from the stress-strain curves obtained, specifically identifying it as the stress at the peak subsequent to the initial nearly linear regime. The reported compressive strength for each material is presented as the mean of three independent tests, with an associated estimated error of 15%. The thermal expansion of preforms was measured using thermomechanical analyses (TA Instruments Q400) under a nitrogen atmosphere up to 600 °C with a heating rate of 3 °Cmin\(^{-1}\) and 0.03 N.

2.7. Computational Fluid Dynamics (CFD) simulations

3D computational simulations were performed using the ANSYS Fluent software, with the following assumptions: (i) the fluid flow (air) is incompressible, laminar, and steady, (ii) the solid and fluid phases in the porous domain are in local thermal equilibrium, (iii) heat losses due to convection and radiation are negligible, and (iv) the material properties remain constant within the temperature range under study. The governing equations for the porous media are as follows [22]:

**Continuity equation**

\[ \nabla \cdot (\varepsilon \rho_f \nu) = 0 \]  \hspace{1cm} (6)

**Momentum equation**

\[ \frac{\rho_f}{\varepsilon^2} (\nu \nabla) \nu = -\nabla P + \frac{\mu_f}{\varepsilon} \nabla^2 \nu + \frac{\mu_f}{K} \nu - \frac{\rho_f C_F}{\sqrt{K}} |\nu| \nu \]  \hspace{1cm} (7)

**Energy equation**

\[ (\rho C_p)_f (\nu \cdot \nabla T) = k_{pm} \nabla^2 T \]  \hspace{1cm} (8)

Here, \( \varepsilon \) represents porosity, \( k \) is thermal conductivity, and \( T \) denotes temperature. The subscripts \( f \) and \( pm \) refer to the fluid and porous media, respectively. Additionally, the governing equation for the solid domains is given as (\( s \) is the subscript for the solid phase):

\[ 0 = k_s \nabla^2 T^s \]  \hspace{1cm} (9)

The aim of these simulations was to understand the thermal behavior of the materials under realistic operating conditions. To achieve this, we focused on a simplified version of a power electronic module, comprising layers of a heat source (electronic chip with four hot spots), a passive heat sink (heat spreader domain), and an active heat sink (porous domain). **Figure 2** illustrates the power module domains, their dimensions, and the packaging configuration. **Table 2** summarizes the solid and fluid properties of the 3D power module considered for simulation. The boundary conditions used were as follows: (i) constant velocity at the inlet (25 °C), (ii) pressure-outlet with a zero-pressure gauge, and (iii) adiabatic walls on all surrounding surfaces. Each hot spot was assigned to emit 200 kWcm\(^{-3}\).
3. Results and discussion

3.1. Preparing Gf:NaCl:sucrose self-standing preforms

Table 3 presents volume fractions of the constituent phases, along with their density, thermal conductivity, and absolute volume before and after heat treatment of the prepared preforms. The composition significantly influences preform compaction, as indicated by their density values.

Microstructures of the preforms exhibit distinct characteristics (Figure 3). Preforms with large sucrose particles hinder proper Gf alignment, causing the flakes to encircle both sucrose and NaCl particles (Figure 3A). In contrast, preforms containing small sucrose particles display improved Gf alignment, as these particles do not obstruct the flakes, leading to better thermal conductivity potential [20,23]. However, some small sucrose particles get trapped between the Gf (Figure 3B), resulting in fewer flake-flake contacts and decreased thermal conductivity for PC-i preforms compared to PA-i or PB-i (Table 3). The thermal conductivity increases with Gf content, reaching a maximum of 96 Wm⁻¹K⁻¹ for PB-1 preform.

3.2. Conversion of preforms into composite foam materials

To transform the preforms into composite foam materials, a heat treatment at 600 ºC was performed, causing sucrose to melt and undergo complex decomposition processes, leading to carbon formation. During this treatment, a significant volume increase occurred, primarily in the pressing direction (Table 3). The volume increase was influenced by sucrose content and particle size (Figure 3C). The heat treatment resulted in a series of expansion and contraction processes, as observed in thermomechanical analysis (TMA) curves (Figure 3D-F). Differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses were conducted to understand the behavior of sucrose powder during heat treatment (Figure 3G-H). The DSC results showed an endothermic peak at 183 ºC, corresponding to sucrose melting [24]. An endothermic process with a peak at 198 ºC was attributed to sucrose dehydration [25]. In the temperature range of 200-450 ºC, mass loss occurred due to caramelization, producing gaseous volatile species [17,26]. The study conducted by [26] revealed that caramel plays a significant cohesive role in materials processed with clay-sucrose mixtures, leading to a reduction in active surface area. This cohesive impact is evident in the considerable volume decrease observed in the Thermomechanical Analysis (TMA) curves. The pyrolysis of sucrose involves a complex reaction scheme due to the generation of numerous products [25]. The results presented in [26], demonstrated through TMA curves, indicate that the conversion of caramel to carbon at temperatures above 450 ºC causes a substantial expansion of the material. Moreover, the preforms retain their structural integrity even after subjecting them to thermal cycling following treatment at the maximum temperature of 600 ºC (as depicted by the TMA curves showing temperature drop to 50 ºC and subsequent rise to 600 ºC).

Figure 3I illustrates the DTG curves of sucrose and selected preforms (PA-1, PB-1, and PC-1) within the temperature range of 100-350 ºC. The preforms show an earlier onset of mass loss compared to sucrose, likely due to the presence of adsorbed water from the manufacturing process in addition to compositional water in sucrose. Furthermore, the second DTG peak progressively shifts from sucrose (271 ºC) to PA-1 (264 ºC), PB-1 (260 ºC), and PC-1 (252 ºC) due to the catalytic effect of NaCl on sucrose degradation [24]. In contrast to the findings of [24], which reported peak shifts across the entire temperature range when incorporating salts (LiCl, KCl, Na₂B₄O₇, and NaI) into sucrose samples, our observations reveal significant peak shifts only at the second DTG peak. This shift is proportional to the extent of sucrose and NaCl interaction. Notably, the PA-1 preform, with the same sucrose particle size as PB-1, exhibits the second peak at a higher temperature due to its lower NaCl content. Similarly, the PC-1 preform displays a lower second DTG peak temperature than PB-1, attributed to its smaller sucrose particle size, which enables greater interaction with NaCl particles due to its higher specific surface area per unit volume. Moreover, the catalytic effect of certain salts at the onset of sucrose degradation, as found in [24], diminishes the significance of subsequent pyrolytic reactions. This suggests that the expansion occurring during caramel carbonization (temperatures above 450 ºC) decreases as the second peak of the DTG curve shifts to lower temperatures. These experimental observations align with the heat treatment results, where the preforms exhibit the expansion order: PC-1 < PB-1 < PA-1.

To further investigate the impact of NaCl particles on sucrose degradation, two additional series of experiments were conducted. In the first experiment, preforms with the same composition as PB-1 were
produced at two different compaction pressures (2 and 4 MPa). Increasing the compaction pressure by a factor of two resulted in a slight shift of the second peak in the DTG curve to lower temperatures, indicating enhanced sucrose degradation due to increased contact between sucrose particles and NaCl (Figure 3J).

In the second experiment, 67:33 vol.% NaCl:sucrose mixtures were subjected to heat treatment in quartz tubes with varying particle characteristics and mean sucrose diameters. The samples included: NaCl and sucrose of 150-200 μm (sample S-1), NaCl and sucrose of 63-80 μm (sample S-2), NaCl and sucrose of 38-45 μm (sample S-3); graphite-coated NaCl and sucrose of 150-200 μm (sample T-1), graphite-coated NaCl and sucrose of 63-80 μm (sample T-2), and graphite-coated NaCl and sucrose of 38-45 μm (sample T-3). The results after heat treatment revealed a clear correlation between increased NaCl-sucrose interaction and lower total volume increase, as the graphite coating prevented interaction between NaCl and sucrose particles (Figure 7K-L).

3.3. Obtaining Gf/C composite foams - dissolution kinetics of NaCl template

Figure 4 displays the mass loss of carbonized preforms as the NaCl template dissolves over time. The curves reveal that preforms with higher NaCl and sucrose contents (preforms PA-3, PB-3, and PC-3) experience more rapid NaCl template dissolution. Comparing PA-i and PB-i preforms, both with 150-200 μm sucrose, highlights the impact of sucrose and NaCl contents on dissolution time. PA-i preforms exhibit longer dissolution times than PB-i preforms, suggesting that NaCl content primarily controls the dissolution process. Higher NaCl content leads to better interconnection between NaCl particles, facilitating dissolution. Additionally, comparing PB-i and PC-i preforms, prepared with the same NaCl and sucrose contents, indicates that PC-i preforms require longer dissolution times, possibly due to a finer size distribution in the carbonization-generated porosity (see results in the following section).

3.4. Microstructural characterization of Gf/C composite foams

Figure 5 displays photographs of the nine Gf/C composite foams produced in this study, illustrating the total volume increase due to heat treatment (Table 3 and Section 3.2). Table 4 summarizes the volume fractions and properties (material density, skeletal density, solid body density and thermal conductivity) of the Gf/C composite foams. Material density decreases significantly as template-generated and carbonization-generated porosities increase in each group of foams. Skeletal densities decrease for the same group with the decrease in Gf content, rendering the carbon volume fraction negligible. Further phase identification and crystallinity information can be found in the Supplementary Material section. Microstructures of composite foams A-1, B-1, and C-1 fracture surfaces are shown in Figure 5, confirming the complete dissolution of the NaCl template. Two types of pores are evident: coarse pores originating from NaCl particles with quasi-spherical geometry and homogeneous distribution, and smaller pores from sucrose carbonization. These are illustrated and labelled for selected characteristic instances in the micrographs. The template-originated pores closely resemble the geometry of the NaCl particles, akin to cellular materials processed by liquid infiltration in the replication method [12,13].

A comprehensive investigation of porosity at different scales was conducted. Image analysis and optical microscopy examined the coarsest pores (200 to 700 μm), demonstrating agreement with the particle size distribution of an epoxy resin-embedded sample, confirming NaCl as the origin of these pores (Figure 6A). Mercury porosimetry measured intermediate porosity (0.05 to 200 μm). Figure 6B displays the mercury intrusion curves, which represent the relationship between mercury saturation and applied pressure, for foams B-1, B-3, and C-1. The presence of S-shaped curves indicates porous samples with a varied pore size distribution. While the curves for B-1 and B-3 foams exhibit remarkable similarity, they differ from the curve for C-1 foam. Moving on to Figure 6C, the Brooks-Corey plots (log (1-S) versus log P) for the three foams are depicted. These materials exhibit both shared and distinctive characteristics. Notably, the C-1 foam curve is shifted to higher pressures compared to the B-1 and B-3 foam curves, suggesting greater infiltration difficulty. However, all three curves show two distinct slope sections, with the slope being identified as the negative of the pore size distribution index, conventionally denoted as λ. Around 300 kPa (log P=2.48), λ in each curve changes from approximately 0.7-0.8 to 0.2-0.4. These λ values, lower than the literature-reported values for commercial graphite foams (typically around 2-3 [27]), indicate that these preforms possess a more intricate pore structure and present greater infiltration challenges. The variations
in $\lambda$ for each preform indicate changes in the pore size distribution. By the time this transition occurs, mercury saturation reaches approximately 90%, indicating infiltration of pores larger than 4.5 $\mu$m. The pore size distributions derived from the mercury intrusion curves are shown in Figure 6D. These curves illustrate that the pore size distribution of C-1 foam is narrower and skewed towards smaller values compared to B-1 and B-3 foams. Consequently, the size and content of sucrose used are critical factors influencing the formation of a specific intermediate porous microstructure. Fine porosity analysis using nitrogen adsorption curves and the BET theory yielded specific surface areas for B-1, B-3, and C-1 foams. The microporosity of B-3 was greater due to higher sucrose content, while C-1 exhibited higher microporosity despite containing the same sucrose content as B-1 foam but with smaller particle size. The microstructural characterization of Gf/C composite foams provided valuable insights into their porosity, pore size distribution, and surface area, which are crucial factors influencing their thermal performance. The observed variations in material and skeletal density among the different foams underscore the significance of the starting preform composition and processing parameters in tailoring their microstructures. The presence of coarse pores resulting from the dissolution of NaCl templates and smaller pores from sucrose carbonization highlights the effectiveness of the fabrication process in creating interconnected porosity in the composite foams. The analysis of fine porosity was conducted by studying nitrogen adsorption curves at 77 K, employing the BET (Brunauer-Emmet-Teller) theory (Figure 6E). The results obtained from the BET analysis indicate surface areas of 21.7 m$^2$g$^{-1}$ for sample B-1, 47.5 m$^2$g$^{-1}$ for sample B-3, and 30.1 m$^2$g$^{-1}$ for sample C-1 (with an estimated error of <0.5%). Furthermore, the desorption curves were utilized to calculate size distributions using the NLDFT model (Figure 6F). The micropore size for all three foams falls within the range of 0.3-2 nm. Notably, the higher sucrose content in the initial preform resulted in greater microporosity for foam B-3 compared to foams B-1 and C-1. Additionally, a comparison between foams B-1 and C-1 highlights the impact of sucrose particle size on microporosity, as foam C-1 exhibits greater microporosity despite having the same sucrose content as foam B-1 but with smaller particles.

3.5. Pressure drop and permeability

Figures 7A show how the relative pressure drop of the composite foam materials varies with the superficial air velocity. As expected, materials with higher porosity exert lower pressure drop on fluid flow, making them more permeable. The permeability ($K$) values were derived from the fitting parameters of the pressure drop versus velocity curves (Table 5), representing the viscous and inertial losses (first and second terms in Equation (3)). In Figure 7B, the composite foams from series 3 demonstrate the highest permeability. Permeability results from the intricate interplay between the larger, interconnected template-generated porosity and the carbonization-generated porosity, which may contain some closed, fluid-impermeable pores. Remarkably, the obtained permeabilities are several orders of magnitude higher than those reported in other studies on densified graphitic materials [14–16]. The thermal conductivity of these materials remains below 2 Wm$^{-1}$K$^{-1}$ when their permeabilities are similar to those observed in the composite foams investigated in our study.

3.6. Thermal conductivity of Gf/C composite foams - measurements and modeling

The thermal conductivity of the developed Gf/C composite foams achieves remarkable values of up to 91 Wm$^{-1}$K$^{-1}$ (Table 4), representing a significant advancement in high conductivity materials without the need for expensive graphitization. This magnitude of thermal conductivity has not been reported in the literature for foam materials prepared through assembly/compression of graphitic units. Analytical expressions, inspired by those originally developed by Deng et al. [28,29] for carbon nanotube inclusions, were derived by Mahanta et al. [30] for materials consisting of an epoxy matrix and n-type graphite-based inclusions arranged parallel to one of the three coordinate planes (x-y, y-z, or x-z):

$$k_c = k_m V_m + k_m \sum_{i=1}^{n} V_i \frac{2/3}{\left( (k_i/k_m) - 1 \right)^{2/3}}$$

(10)
where $k$ is the thermal conductivity, $V$ is the volume fraction, $R_k$ is the interfacial resistivity (due to the absence of a matrix-inclusion interface, it refers to the resistivity between two consecutive inclusions in contact), and $L$ is the length of the inclusion in a particular direction. Among the subscripts, $i$ represents a specific inclusion, $eff$ refers to effective, while $c$ and $m$ denote the composite and matrix, respectively. In the case of the materials developed here, Equation (10) can be greatly simplified by assuming the following: (i) there is only one type of inclusion (n=1) and, (ii) the matrix is air, which has a much lower thermal conductivity than graphite inclusions ($k_m << k_i$). Under these conditions, Equation (10) simplifies to:

$$k_c = \frac{2}{3} V_r k_{r_{eff}}$$

(12)

where $r$ denotes the only inclusion considered (Gf). This expression can be applied to both the preforms and the developed composite foam materials, with the difference being that the graphite flakes, the only thermally conductive phase (the other phases can be considered thermally non-functional), are present at a lower volume fraction in the composite foam specimens due to the sucrose carbonization-induced volume expansion.

The experimental thermal conductivity values of the preforms are presented in Figure 8A as a function of the volume fraction of graphite flakes (Gf), with the thermal conductivities in the z-direction measuring in the range of 5-13 Wm$^{-1}$K$^{-1}$. A clear correlation is observed between thermal conductivity and Gf content, with PX-3 preforms showing the highest thermal conductivity, followed by PX-2 and PX-1. This finding aligns with previous studies on metal foams containing graphite flakes as thermal inclusions [23]. Among the preforms with comparable Gf volume fractions, PC-i preforms consistently exhibit the lowest thermal conductivity. The addition of small sucrose particles between flakes increases interfacial resistivity, resulting in lower thermal conductivity values compared to PA-i or PB-i preforms. Two upper and lower limits for thermal conductivity are shown in Figure 8A, calculated using Equation (12) and considering specific interfacial resistivity values, which encompass the experimentally measured thermal conductivity values ($R_k=5.4\times10^{-7}$ m$^2$KW$^{-1}$ and $R_k=1.0\times10^{-6}$ m$^2$KW$^{-1}$ for upper and lower limits, respectively, $k_r=1000$ Wm$^{-1}$K$^{-1}$ and $L=420$ μm). Comparable interfacial resistivities of graphite-based thermal inclusions have been reported by Mahanta et al. [30], suggesting that the values obtained in this study align with the existing literature. As the preforms progress from PX-1 to PX-3 (decreasing Gf content), their thermal conductivity gradually approaches the calculated lower limit, potentially due to the decreased likelihood of flakes making contact and forming thermal conduction paths.

In Figure 8B, experimental thermal conductivity values in the x-y plane for composite foam materials are shown, along with theoretical upper and lower limits calculated using Equation (12) and the same parameters as for the preforms. Thermal conductivity in the z-direction ranges from 3 to 12 Wm$^{-1}$K$^{-1}$. A similar trend of higher thermal conductivities with higher Gf contents is observed in the foam materials. C-i foams exhibit the highest thermal conductivity as they experience minimal expansion during carbonization, maintaining high Gf volume fractions. Both preforms and foams display thermal conductivities bounded by limits calculated from the same interfacial resistivity values, indicating that sucrose carbonization-induced expansion does not significantly alter the flake-flake interfaces, thus preserving percolative thermal conduction paths defined by flake-flake contacts in the preforms. Polarized light optical micrographs of A-3 foam in Figure 8C illustrate thermal percolation paths defined by physical flake-flake contacts in the direction of the thermal gradient (x or y direction of the x-y plane). This figure displays a nearly 2 mm-long percolation path passing through seven consecutive flakes, while the zoomed image provides an enlargement of flakes 2-5, showing overlapping that defines physical contacts allowing thermal conduction through percolating interfaces. Furthermore, the distinctive flake-flake physical contact structure is supported by additional characterization involving the assessment of the electrical conductivity of the fabricated materials (Figure S3 in the Supplementary Material section). This figure unmistakably reveals a correlation between materials with superior thermal conductivity and those exhibiting enhanced percolative thermal conductivity.
electrical conductivity. This correlation suggests the effective charge transport facilitated by the inter-flake contacts.

3.7. Compressive strength

Figure 9A presents the compressive strength test results for the composite foam materials. It's important to highlight that the carbon volume fraction, responsible for providing self-standing properties, remains consistent in all foams. Therefore, variations in mechanical behavior are primarily attributed to differences in overall pore and Gf volume fractions. The former tends to reduce mechanical properties, while the latter enhances them. Remarkably, specimens C-i exhibit the highest compressive strength values. This could be attributed to the smaller size of sucrose particles in PC-i preforms, which, after carbonization, create numerous bonding bridges between the graphite flakes (as small sucrose particles interpose between Gf). As a result, composite foam materials gain significant resistance to mechanical stresses. Characteristic stress-strain curves and primary mechanical properties of the prepared materials are presented in the Supplementary Materials section. Overall, the compressive strength values meet the requirements for heat sink applications in electronic devices and are up to six times higher than other Gf foams developed through similar means reported in the literature [17].

In a previous study [17], materials analogous to those synthesized in the present investigation were developed, featuring biphasic compositions where the two distinct phases, graphite and sucrose-derived carbon, were non-continuous. The carbon phase served as a binding agent for natural graphite. Notably, one of the materials in [17] shares a similar manufacturing process with those employed in our study, except for the exclusion of a uniaxial pressure densification step. This specific material, denoted as sample T1 in [17], possessed an apparent porosity of 61.4% and demonstrated a compressive strength of approximately 1.2 MPa. This strength is comparable to that of sample A-3 in our current study, which exhibits the lowest compressive strength due to its high porosity of around 81%. Comparing sample T1 from [17] with a similar porosity counterpart, such as B-2 (porosity of 62%) in our study, it is evident that T-1 in [17] displays a compressive strength that is approximately half. Several factors contribute to these differences, including the combined effects of the absence of graphite flake orientation in [17], likely stemming from the omission of the uniaxial compression step in its processing, and the smaller size of the graphite flakes used (in [17], natural graphite flakes with an average diameter of approximately 100 μm were utilized).

3.8. Thermal performance comparison of newly developed and reference materials

Thermal conductivity and compressive strength of various graphite and carbon foams fabricated using different methods (blowing method, templating method, and assembly/compression of graphitic units) are summarized in Figure 9B, indicating that our materials exhibit competitive properties similar to foams prepared using more expensive graphitization techniques.

To assess dissipative thermal behavior, the heat transfer coefficient (h) of the newly developed materials is compared to reference materials under equivalent energy consumption. The pumping power, representing the energy involved in fluid flow through porous material, is calculated with the following expression:

$$\Omega = \frac{\Delta P}{\Delta L \nu A L}$$  \hspace{1cm} (13)

where A is the cross-sectional area of the sample through which fluid flows and L is the sample length. Based on the data in Figure 10A, showing the relationship between relative pumping power (Ωr or Ω divided by A and L) and superficial velocity (ν), an optimal value for Ωr has been determined. This allows for the selection of an appropriate Ωr value for various samples, ensuring that ν falls within a plausible experimental range. The chosen value is Ωr = 6×10⁶ Wm⁻³, corresponding to Ω = 6 W (volume of the samples is 10⁶ m³). Figure 10A also includes evaluation of two reference materials: (i) a replicated aluminum foam (Al, k = 57 Wm⁻¹K⁻¹, K = 9.06×10¹² m², and Cᵖ = 5.56×10⁵ m⁻¹) and (ii) a commercially available POCO graphite foam (evaluated in two orientations: POCO-1, with kₓ = 245 Wm⁻¹K⁻¹, kᵧ = kᵧ =
70 Wm⁻¹K⁻¹, $K_x = 1.7 \times 10^{-11}$ m², $K_y = 6.4 \times 10^{-12}$ m², $C_{f_x} = 6.23 \times 10^6$ m⁻¹, $C_{f_y} = CF_x = 2.93 \times 10^7$ m⁻¹, and POCO-2, with $k_x = k_y = 70$ Wm⁻¹K⁻¹, $v_y = 245$ Wm⁻¹K⁻¹, $K_x = K_y = 6.4 \times 10^{-12}$ m², $K_z = 1.7 \times 10^{-11}$ m², $C_{f_x} = C_{f_y} = 2.93 \times 10^7$ m⁻¹, $C_{f_y} = 6.23 \times 10^6$ m⁻¹). Since the samples developed in this study are anisotropic and permit different orientations relative to the heated base, only the $h$ values corresponding to the sample arrangement in which the graphite flakes present their orientation plane perpendicular to it are reported. For POCO graphite foam, which also exhibits anisotropy, the values of $h$ for the two possible configurations are reported as well. The representative thermal conductivity for this configuration is presented in Figure 10B. This figure illustrates a trend of decreasing $h$ (heat transfer coefficient) with increasing thermal conductivity, which may appear contrary to the current literature [35,36]. However, it is important to consider that Figure 10B evaluates heating efficiency at constant pumping power, where pressure drop across the material becomes a significant factor. The composite foams with higher thermal conductivity in Figure 10B are generally less porous, leading to lower fluid permeability and consequently, higher pressure drop. Among the evaluated materials, sample B-3, with maximum permeability, exhibits the highest $h$ value, indicating superior efficiency compared to other samples, including the two reference materials. Therefore, B-3 Gf/C composite foam emerges as a promising candidate for active heat dissipation.

3.9. Heat dissipation performance in simulated operating conditions

We utilized CFD simulations to evaluate the thermal performance of different materials acting as heat sinks in power electronic modules. For this analysis, we selected samples C-1 and B-3 with the highest thermal conductivity and heat transfer coefficient, respectively, at constant pumping power (see Figures 8B and 10B). Additionally, we included two reference samples: a replicated aluminum foam and a commercial POCO graphite foam, both with a pore volume fraction of 0.61. The simulations were conducted on a conventional power electronic module with dimensions shown in Figure 2, featuring four hot spots in the chip domain. Each hot spot generated a power density of 200 kWcm⁻³, based on [37] which suggests localized heat fluxes above 1 kWcm⁻² for submillimeter areas. The porous material in the bottom packaged layer allowed heat dissipation through an active exchange mechanism (conduction + convection). To ensure fair comparisons, the simulations were performed with constant pumping power. The new pumping power value ($\Omega$) was calculated as 192 W by multiplying the relative pumping power ($\Omega r = 6 \times 10^6$ Wm⁻³) from the previous section by the simulated module values of $A$ and $L$. Figure 10C illustrates the temperature profiles in two planes of the simulated module. Impressively, material B-3 demonstrated the highest thermal performance in both the chip and porous domains. Under the specified conditions, this material kept the on-chip temperatures within a safe operating range, with the maximum temperature not exceeding 62 ºC and the minimum temperature near 49 ºC (Figure 10D). On the other hand, other materials showed significantly higher temperatures. For instance, the chip temperatures in the aluminum foam, a standard for active heat dissipation, were approximately 10 ºC higher than those recorded for material B-3. Material C-1 showed a temperature distribution comparable to the graphite foam in its optimal configuration. These results indicate that the materials developed in this study exhibit exceptional thermal properties, making them highly promising for heat dissipation applications.

4. Conclusions

In this study, we propose a novel, simple, and sustainable method for producing graphite/carbon composite foams with exceptionally high thermal conductivity using natural graphite flakes. The key conclusions drawn from our findings are as follows:

- By employing a variant of the replication method, we successfully prepared graphite/carbon composite foam materials. The method involves uniaxial pressing of a mixture of natural graphite flakes, templating agent (NaCl particles), and blowing/binder agent (solid sucrose) to form self-standing preforms. The properties of the preforms are determined by the proportions of the components and the average size of sucrose particles.
- Preforms containing large sucrose particles (150-200 μm) exhibit the highest thermal conductivity due to a greater number of flake-flake contacts, despite a lower degree of graphite flake orientation. In contrast, preforms with small sucrose particles (38-45 μm) show lower thermal conductivities, as NaCl particles do not effectively interpose between graphite flakes in these cases.

- Heat treatment up to 600 ºC under vacuum converts sucrose into a carbonaceous phase. The interaction between sucrose and NaCl particles influences the foaming of the preforms, as NaCl particles catalyze sucrose degradation, leading to additional material expansion.

- Interestingly, the most thermally conductive composite foam materials originate from preforms with small sucrose particles. The stronger interaction between NaCl and small sucrose particles limits volumetric expansion, resulting in higher volume fractions of graphite flakes and denser physical flake-flake percolative interfaces that enhance thermal conduction paths.

- The composite foam materials achieved thermal conductivities of up to 91 Wm⁻¹K⁻¹, surpassing previous measurements by 18 times compared to foams produced through densification of graphitic units. Additionally, these materials exhibit competitive mechanical properties when compared to those obtained from expensive and complex graphitization processes.

- The active heat dissipation capacity of the developed materials was assessed through heat transfer coefficient measurements and computational simulations under realistic conditions, both at constant pumping power. Permeability of the materials played a crucial role, with the material exhibiting the highest permeability demonstrating superior thermal dissipation behavior compared to reference materials like graphite or aluminum foams.

- Considering their remarkable thermal and mechanical properties, as well as the improved microstructural control achieved through the replication method, these materials hold immense promise as the next-generation heat dissipators for thermal management applications.

**ACKNOWLEDGMENT**

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**REFERENCES**


Figure 1. Scanning electron microscopy (SEM) images of the raw materials (upper); schematic diagram of the fabrication process for Gf/C composite foams (lower).
Figure 2. Dimensions of the 3D power module considered for simulations (A), cross-sectional view of the computational domains (B) and bottom view of the chip domain identifying four hot spots (C).
Figure 3. Polarized light optical micrographs of the preforms PA-3 (A) and PC-3 (B); volume increase ($\Delta V$) of preforms after heat treatment (C) and instantaneous relative dimensional change ($\Delta L/L_0$) measured by thermomechanical analysis of preforms PC-1 (D), PC-2 (E) and PC-3 (F); thermogravimetry-differential scanning calorimetry (TG-DSC) (G) and differential thermogravimetry-differential scanning calorimetry (DTG-DSC) (H) for sucrose powder; differential thermogravimetry (DTG) for PA-1, PB-1 and PC-1 preforms (I) and PB-1 preforms compacted at various pressures (J), all compared to the sucrose DTG; (K) is a photograph of heat-treated NaCl:sucrose mixtures (samples S-i) and graphite-coated NaCl:sucrose mixtures (samples T-i); (L) is a bar graph depicting the volume expansions (to ±4% in accuracy) of the samples shown in (K).
Figure 4. Mass of carbonized-preforms PA-i, PB-i and PC-i as a function of NaCl template dissolution time (A); bar graph depicting the time required to dissolve 50% of the total mass of NaCl (B).
Figure 5. Photographs of composite foams A-i, B-i and C-i (left); scanning electron microscopy (SEM) micrographs displaying the fracture surfaces of A-1, B-1 and C-1 composite foams (arranged in center and right panels, from top to bottom).
Figure 6. Two-dimensional pore size distribution of composite foams and particle size distribution of NaCl embedded in resin (A), mercury intrusion curves with applied pressure for some fabricated composite foams (B), (C) is a double logarithmic representation of results from (B), (D) is the pore size distribution derived from mercury porosimetry, (E) are nitrogen adsorption/desorption isotherms at 77 K and (F) is the pore size distribution (PDS) calculated with the NLDFT model from the data in (E).
Figure 7. Relative pressure drop ($\Delta P(\Delta L)^{-1}$) as a function of superficial air velocity for composite foams A-i, B-i and C-i (A); (B) is a bar graph that summarizes the composite foam permeabilities derived from the second-degree fitting of curves according to Equation (3).
Figure 8. Thermal conductivity ($k_x=k_y$) as a function of the Gf volume fraction for all preforms (A) and composite foams (B); (C-D) are polarized light optical micrographs of the A-3 foam displaying thermal conductive paths due to flake-flake contacts.

Figure 9. Compressive strength ($\sigma_s$) of prepared composite foam materials (A); thermal conductivity as a function of compressive strength (B) for carbon and graphite foam materials (black symbols: graphite foams
prepared by the blowing method; unfilled symbols: carbon foams; red symbols: foams prepared by assembly of graphitic units).

**Figure 10.** Relative pumping power ($\Omega_r$) versus superficial air velocity (A); heat transfer coefficient (h) versus thermal conductivity (k) for a pumping power of 6 W (B); temperature profiles in two planes, one at the base of the chip domain and the other representing a cross section of the heat spreader and porous domains (C); minimum, maximum, and volume average temperatures encountered in the chip domain (D).

**Table 1.** Volume percentages of Gf, NaCl and sucrose in mixtures used for the preparation of self-standing preforms. $d_{Gf}$, $d_{NaCl}$ and $d_{suc}$ represent the diameters of the graphite flakes, NaCl and sucrose particles, respectively.

<table>
<thead>
<tr>
<th>Preform code</th>
<th>$d_{Gf}$ (µm)</th>
<th>$d_{NaCl}$ (µm)</th>
<th>$d_{suc}$ (µm)</th>
<th>Gf:NaCl:sucrose (%)</th>
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</thead>
<tbody>
<tr>
<td>PA-1</td>
<td>400</td>
<td>355-500</td>
<td>150-200</td>
<td>60:20:20</td>
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<tr>
<td>PA-2</td>
<td></td>
<td></td>
<td></td>
<td>50:25:25</td>
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### Table 2. Solid and fluid properties at 25 ºC used for computational simulations.

<table>
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<th>Material</th>
<th>Chip domain and hot spots</th>
<th>Heat spreader</th>
<th>Fluid</th>
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<tr>
<td>Thermal conductivity (Wm⁻¹K⁻¹)</td>
<td>148 [19]</td>
<td>600 [19]</td>
<td>0.025</td>
</tr>
<tr>
<td>Heat capacity (Jkg⁻¹K⁻¹)</td>
<td>705 [19]</td>
<td>725 [19]</td>
<td>1007</td>
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</table>

### Table 3. Composition and main properties of the prepared preforms. \( V_{Gf}, V_{NaCl}, V_{suc} \) and \( V_{pore} \) represent the volume fraction of Gf, NaCl, sucrose and porosity of preforms (with an estimated error of 1%). \( V_0 \) and \( V_f \)
are the volumes of the preforms before and after heat treatment (with an associated error of 1%). $\rho$ is the density of the preforms (with an estimated error of 3%) and $k$ their thermal conductivity measured in the $x$ or $y$ direction (Gf are oriented in the $x$-$y$ plane). The estimated error in $k$ is 10%.

<table>
<thead>
<tr>
<th>Preform code</th>
<th>$V_{Gf}$</th>
<th>$V_{NaCl}$</th>
<th>$V_{suc}$</th>
<th>$V_{pore}$</th>
<th>$V_0$</th>
<th>$V_f$</th>
<th>$\rho$</th>
<th>$k_x=k_y$</th>
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<td>2.89</td>
<td>3.50</td>
<td>1.82</td>
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Table 4. Material density ($\delta_m$, with an associated error of 3%), skeletal density ($\delta_{sk}$, with an estimated error <0.5%), solid body density ($\delta_b$, with an associated error of 3%) and volume fractions (with an associated error of 1%) of each phase in composite foam materials. $V'_{Gf}$, $V'_c$, $V'_t$, $V'_{ccp}$ and $V'_{ocp}$ represent the volume fractions of graphite flakes, carbon, template-generated (open) porosity, closed carbonization-generated porosity and open carbonization-generated porosity, respectively. $k$ is the thermal conductivity of the
composite foams measured in the x or y direction (Gf are oriented in the x-y plane). The estimated error in k is 10%.

<table>
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<th>δ_k</th>
<th>δ_b</th>
<th>V'_Gf</th>
<th>V'_c</th>
<th>V'_vp</th>
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<td>(gcm⁻³)</td>
<td>(Wm⁻¹K⁻¹)</td>
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<tr>
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<td>2.16</td>
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<td>0.02</td>
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<tr>
<td>A-3</td>
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<tr>
<td>B-1</td>
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Table 5. Second-degree fitting parameters obtained from the relative pressure drop versus superficial velocity curves of air at 25 ºC following Equation (3): ΔP/ΔL=av + bv², where a=μ/K and b=pc_f.

<table>
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<td>B-1</td>
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<td>9.67×10^{-1}</td>
<td>9.99×10^{-1}</td>
<td>9.90×10^{-1}</td>
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</table>

Declaration of interests

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

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: