

Thermally Conductive 3D Aerogels Based on Carbon Nanofillers

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Aerogels are perfect 3D interconnected designs with unique properties provided by tenuous networks of nanosheets or filaments; they are typically fabricated via sol–gel, freeze drying, and other phase-separating and drying techniques and possess remarkable properties, such as an extraordinarily high specific surface area, great flexibility, low density, variable tunable porosity, low dielectric constant, and low TC. Due to the abovementioned advantageous physical features, they present a large amount of promise for applications as adaptable absorbent materials and for their uses in EM shielding, thermal insulation, and wearable pressure-sensing materials, to be employed as a multifunctional aerogel material.

3D framework

nanofillers

graphene

1. Introduction

Carbon nanofillers have sparked a lot of attention because of their unique features, including improved thermal and electrical conductivity, high mechanical strength, and ease of processing ^{[1][2][3][4]}. One viable technique for maximizing the benefits of carbon nanofillers is to segregate them into a strong three-dimensional (3D) structure for greatly improved properties relative to one-dimensional (1D) and two-dimensional (2D) structures. Such a 3D structure could now be attained by 3D frameworks/foams or aerogels-based composites or polymer-composite systems. Specific methods, such as chemical functionalization ^[5], orientation ^[6], preferential localization ^[7], and application of high-aspect-ratio nanofillers ^[8], have been developed to reduce thermal contact resistance accompanied by low filler fractions and excellent TC. Since thermal contact resistance is inversely related to contact area, filler thermal transfer efficiency should follow the rule of $0D < 1D < 2D < 3D$, as the surface area grows with the filler dimensions (D). However, achieving high TC, while maintaining excellent electrical insulation performance, remains a significant challenge for these materials, due to the high electrical conductance of the 1D and 2D nanofiller particles. This section focuses on the TCs of carbon-based 3D framework structures composed of 1D and 2D nanofillers.

2. Thermally Conductive Three-Dimensional Aerogels Based on Two-Dimensional Carbon Nanofillers

In recent years, the most prevalent 3D aerogels are carbon-based structures with hierarchical anisotropic architectures, where the nanofiller is segregated into a 3D framework, elements of which are made up of

interconnecting nanosheets or nanofibers, often aligned or oriented. This targets unique properties such as low density, high porosity, and super elasticity [9][10][11]. The self-organized 3D structuring is typically created by a phase-separation process, such as freeze drying, or by other means of segregation. The 3D architecture could be created as anisotropic, if the process is directed, for example, by thermal gradient. Other methods to introduce directed self-assembly process include application of an external force field or pressure, such as a gravitational, magnetic field, or electrical field, acting in a specified direction [12][13]. The structuring is followed by the self-orientation and aligning of 2D particles at the formation of walls of the resulting 3D architecture, e.g., by surface tension, van der Waals, or other forces. The result is a sort of highly directed graphene aerogel with a hierarchical structure and specific direction. The highly aligned graphene sheets might fully leverage their high intrinsic in-plane TC, generating a highly efficient thermal conduction network, as opposed to randomly scattered graphene sheets in isotropic aerogels. For this purpose of self-assembly, several techniques such as the freeze-drying method, followed by resin impregnation, have been used in recent years for the fabrication of vertically aligned graphene-based 3D networks [11][12][14]. For example, hydrothermal reduction, aligning graphene oxide (GO) nanosheets by freeze drying, and a subsequent 2800 °C graphitization were used by Wenya and coworkers [11] to create 3D graphene networks, impregnated later with silicone rubber. Instead of van der Waals forces, they assumed the nearby graphene sheets in their work were joined by chemical covalent bonding, and, using vacuum impregnation and a high-pressure treatment process, graphene was thoroughly reduced, and the defects were totally eradicated. Meanwhile, prior studies on the graphitization of graphene mainly focused on removing the oxygen-containing functional groups from graphene and the use of van der Waals forces for the connection of adjacent graphene sheets [15]. For instance, a heat treatment process was used to create vertically aligned graphene hybrid foams/epoxy composites with a high out-of-plane TC, and the effects of the graphitization were studied [15]. The application of the graphitization is a very vital step to produce high-quality graphene, as it can eliminate most of the remaining oxygen functional groups in the reduced GO unit and correct defects. Hence, by following these steps, the out-of-plane thermal conductivity of the obtained thermal interface's materials (TIMs) reached ~1.26 W/mK, when the graphene filler concentration was only 0.5 wt.%.

Qiu et al. [12] applied the freeze-casting method to create an interconnected graphene monolith with a honeycomb-like segregated structure, mimicking cork. The structure is unique for its kind and unprecedented, with the graphene foam exhibiting good flexibility, a light weight, and good mechanical strength rather than brittleness, without the need of infiltration by a polymer. When a well-distributed partially reduced graphene oxide (pr-GO) dispersion freezes, pr-GO sheets are condensed at the forming ice crystals' boundaries and, subsequently, are aligned along the ice's development direction due to the squeezing action; a continuous segregated honeycomb-like network emerges, as a result. When the ice is thawed, the framework particles remain inter-connected, preserving the structure. The findings suggest that such a robust structure could pave the way for the future scientific research of segregated carbonaceous fillers, to achieve good TC and other thermal properties. At present, various carbon-based aerogels with 2D nanofillers are being developed for numerous applications including wastewater treatment, energy storage and conversion, flame retardance, carbon dioxide capture, and catalyst supports and sensors; however, at the present time, they are now able to be employed to pertinent industrial applications, specifically related to TIMs.

Various strategies for obtaining continuous 3D networks have been proposed in the literature [16][17]. In particular, substantial study has been done on the structure of graphene aerogels, and many studies on the production and engineering of aerogels with regard to the improvement of TC can be discovered [15][18][19][20][21][22][23][24][25][26][27][28]. Highly thermally conductive 3D structures were subsequently infiltrated with an epoxy resin to generate polymeric nanocomposites with increased phonons transport characteristics, due to the strong connectivity of graphene planes with the chains of polymers. Weng et al., for example, used a simple process to create highly thermally conductive paths: thermal-shock exfoliation of a graphene oxide sheet, followed by the self-polymerization of silanol inside graphene frameworks (GF), was executed [29]. The self-polymerization of silanol with graphene resulted in the surface modification of graphene by the silanol group. This chemical reaction further converted silanol into siloxane, with the cross-linking of graphene frameworks with siloxane networks (SGF) with a --Si--O--Si-- molecular network structure formed by self-polymerization. The GF were then compressed, and the films, with tightly packed sheets, generated a microporous honeycomb structure with pore sizes varying from several to tens of micrometers. This porous structure was made up of horizontally aligned and locally attached graphene sheets, allowing it to function as a highly anisotropic, continuous network for phonon and electron transport. The epoxy (EP) resin was then infiltrated into GF to form the EP/SGF composite. After the impregnation by epoxy, a compression procedure was used on the GF sample to eradicate the voids and create a denser structure for enhanced TC, followed by thermal curing. Siloxane molecules, which were able to immobilize the graphene sheets in the epoxy matrix system, reduced the thermal resistances in the composite with the construction of siloxane molecular bridges inside the GF structure. Thus, the in-plane and through-plane TC values of EP/SGF composites with a GF loading concentration of 20.2 wt.% reached 54.2 and 1.62 W/mK, respectively, due to improved GF quality and significantly decreased intersheet and interfacial resistances. As another important consequence of the achieved results, researchers can state that these aerogels' porosity can be altered, resulting in a different structural density and, consequently, in a variable amount of filler in the final 3D composite material.

The skeleton walls of the 3D graphene aerogels/foams used in thermally conductive polymer composites can be thought of as ultrathin graphene-based films. The quality of nanosheets and their aligned dense compaction are critical for heat conduction along the aerogel's continuous skeletons. In reality, several approaches are developed to derive graphene aerogels/foams from GO sheets, and high temperature annealing is used to eliminate the GO sheets' residual oxygen-containing groups and regenerate their lattices to heal defects in order to reduce phonon scattering [15][22][30]. However, the gases produced during the heat treatments and trapped at the skeleton walls may lead to thermally inert pores between the oriented graphene sheets, reducing the TC of the skeleton walls. For instance, Ruoff et al. used a chemical vapor deposition (CVD) technique to fabricate a three-dimensional (3D) graphene foam as the continuous thermal paths for the phase-change material. Nickel foam was employed as a template to deposit ultrathin graphite foam (UGF) with several graphene layers CVD-grown on the substrate, followed by the removal of nickel by the chemical etching process. The thin graphite hollow struts were then filled with hydrophobic paraffin wax, by immersing the foam in hot liquid wax. The fabricated composite of UGF/paraffin wax displayed the ideal phase change material, with a high TC of 3.44 W/mK at a very low graphene-loading concentration of 1.23 vol.% [31]. The TC increase can reach up to 1800%, relative to paraffin wax, as a matrix polymer with a specific TC enhancement of 1500% per 1 vol.% of graphene content. Thus, the construction of

continuous graphene heat-transfer channels becomes an effective approach to improve the TCs of the polymer/graphene composite materials, due to the effective decreases in both the contact thermal resistance among the graphene sheets and the interface thermal resistance between the graphene and polymeric matrix [27][32].

TIMs based on graphene offer a lot of potential for eliminating surplus heat created by electrical devices; however, their actual uses are frequently hampered by their poor TC, which is mostly caused by poor graphene-sheet dispersion and distribution. The TC-enhancement efficiency is still significantly below the theoretical value. The effectiveness of the 3D graphene network's TC improvements remains a significant hurdle to attain a high through-plane TC of more than 10 W/mK, with a quite low graphene-loading concentration as a filler material in a polymeric matrix. Therefore, alternative approaches are constantly being tested for their efficiency. Fei et al. studied the hydrothermal reduction of reduced graphene oxide (rGO) in the presence of high-quality graphene nanoplatelets, followed by air drying and annealing, which created vertically aligned graphene hybrid foams (GHF) with high densities [15]. The resulting vertically aligned high-quality graphene porous structure with high density, as an ideal thermal conductance network of TIMs, is extremely effective in improving the TC of its composite; when impregnated with epoxy, it attains an extremely high through-plane thermal conductivity of 35.5 W/mK at a graphene loading of 19.0 vol.%. The enhancement in the TC was mainly associated with an increase in the annealing temperature, in an ascending order ranging from 1000 °C till 2800 °C. The increasing trend of temperature exhibited the removal of defects inside the graphene structure, as observed in the Raman mapping and XPS spectrum, resulting in a higher TC. Raw (not annealed) GHF5 (the 5 comes from the mass ratio of graphene oxide:graphene = 1:5) and its thermally annealed equivalent GHF-2800 (GHF annealed at 2800 °C) are characterized using ID/IG Raman mapping. A large blue region surrounds the yellow and green sections in GHF5. The blue regions correspond to high-quality GNPs with an I_D/I_G value of less than 0.2, whereas the yellow and green regions, which have larger I_D/I_G values >0.5, are caused by rGO sheets with residual oxygen functional groups and defects. GNPs are interconnected by rGO sheets, according to this I_D/I_G distribution. The Raman mapping of GHF-2800, a GHF annealed at 2800 °C, is full of dark blue, and most I_D/I_G values remain below 0.025, because this temperature is high enough to entirely eliminate the leftover oxygen functional groups and repair the lattice defects. In support of these findings, XPS spectrum shows a decrease in the oxygen content, with a complete reduction in the oxygen peaks for GHF-2800. Hence, augmentation in TC of polymer composites can be directly linked to the annealing temperatures of their graphene structures for the removal of phonon-scattering defects and decreasing contact thermal resistance. The annealed graphene hybrid-foams-based epoxy composites are, thus, well-suited for TMA due to their outstanding TC characteristics, especially when the annealing is conducted at extremely high or ultrahigh temperatures, as supported by several authors [33][34]. Typically, graphene porous structures are made up of chemically or thermally reduced graphene sheets, which often have residual oxygen-containing groups and lattice defects that can produce phonon scattering [35]. The high-temperature annealing process, fortunately, has been shown to be effective in eliminating these functional groups and repairing the defects. For illustration, the preparation of thermally annealed defect-free graphene sheets was reported by Lian et al. [36], in which phonon-scattering centers and defects were greatly minimized, for the effective thermal transport of phonons by high temperature annealing, at around 2200 °C for thermally conductive phase-change

materials, which displayed a high TC of 3.55 W/mK at a 10 wt.% of graphene-loading concentration. Similarly, in support of the aforementioned statements, Gao et al. employed a high-temperature annealing and mechanical pressing to create a high-quality graphene sheet with an ultrahigh TC of approximately 1940 W/mK and good flexibility for high-power electronic devices [37].

Most carbon-based aerogels have high intrinsic electrical conductivities, limiting their usage in electronic packaging materials' systems due to issues such as short circuiting and other complications. As a result, converting carbon-based aerogels from electrically conductive to electrically insulating, while maintaining their outstanding mechanical and thermal qualities, may prove to be highly desirable and essential. Developing such carbon-based aerogels with a high electrical resistivity and heat dissipation capability, as well as strong structural stability, is now a major issue. Among several developed approaches, the nanohybridization of thermally conductive boron nitride with synergy with carbon-based materials such as graphene, graphene oxide, and reduced graphene oxide seems to be one of the most promising solutions to solve this problem [38][39][40]. For instance, the fabrication of 3D hybrid boron nitride graphene oxide nanosheets as aerogels with epoxy impregnation was explored, and the results showed an excellent TC of 4.53 W/mK (11.6 vol.% loading fraction) and good electrical insulation, with electrical conductivity reaching a low scale of 10^{-11} S/m, almost equaling the electrical conductivity of pure epoxy [40]. Moreover, for another different approach [18], a hydrothermal procedure aided by hydrofluoric acid produced highly compressible and thermally conductive, though electrically insulating, fluorinated graphene aerogels (FGAs). The introduction of fluorine to fluorinated graphene aerogels via the hydrothermal process results in a substantial reduction in charge-carrier density and changes the band gap of the inherent graphene. These aerogels have been shown to be very insulating, with the lowest electrical conductivity measured at 4×10^{-9} S/m, with the tunable band gap as reported [18], which allows for the modification of their electrical insulating performance. Moreover, the electrical resistance of these FGAs varies depending on the deformation condition.

3. Thermally Conductive Tree-Dimensional Aerogels Based on One-Dimensional Carbon Nanofillers

Carbon nanotubes (CNTs) have been reported extensively for their usage as 1D carbon materials for 3D-based frameworks. Since their first discovery more than three decades ago, CNTs have drawn a lot of attention due to their exceptional physical, thermal, and mechanical properties [41][42][43]. In order to improve materials' performance, CNTs are used as nanofillers in polymeric materials, such as epoxy resin, polyimide, and poly (methyl methacrylate), for achieving high TC. Due to their inherent high TC, of around 6600 W/mK (via MD simulation) and ~3000 W/mK (experimentally) [44], CNTs exhibit a vital role in TIMs for the dissipation of heat energy in electronic devices, with important factors including alignment/orientation, loading percentages, dispersion, density, aspect ratio, presence of topological and inherent structural defects, and chemical interaction of polymer matrix materials with CNTs [45][46]. In the case of a 3D framework aerogel structure [1][47], vertically aligned carbon nanotubes (VACNTs) are an ideal material for achieving a high TC with good mechanical characteristics [48]. By improving the contact at the interface or densifying the CNTs, the thermal interface resistance is decreased, resulting in an increased TC. Moreover, the heat transport can also be improved

immensely by using high-temperature annealing to reduce defect density [49], utilizing mechanical densification to increase the volume percentage of CNTs [50], and enhancing the CNT alignment through processing with strong magnetic fields [51]. In thermally conductive aerogels with a polymer matrix, CNTs work in synergy with other carbon fillers to create a hybrid filler composite [43][52]. For instance, a unique class of paraffin-based shape-stable phase-change materials was fabricated by vacuum-assisted impregnation of paraffin into an aerogel comprised of reduced graphene oxide (rGO) and carbon nanotubes (CNTs). Investigations were done into how the morphology, structure, and properties of the paraffin composite were affected by the ratio of rGO to CNTs in the 3D-network structure. The 3D-network topology of rGO/CNTs possessed a high TC and acted as a single thermally conductive skeleton with good stability.

Other than carbon nanotubes, carbon fibers have been used as 1D fillers in 3D polymer composites for TMAs [53][54][55][56][57]. These carbon fiber composites are typically fabricated by the combination of several steps, including carbonization, graphitization, and high-temperature hot-press molding techniques, and possess high TCs in both the axial and radial directions, with in-plane TC exceeding 900 W/mK [58][59]. Little work has been done on the thermally conductive 3D-based aerogels based on carbon fibers, but, nevertheless, 3D-based fabricated structures of 1D carbon fiber have been reported with increased interest, in recent years. For instance, in their experimental study, Yao et al. first created porous carbon-fiber (C/C) composites using low-temperature hot-press molding [60]. Following that, a chemical vapor infiltration (CVI) technique, precursor impregnation, and pyrolysis were used to densify the porous C/C composites. Finally, carbon bulks with a density of 1.90 g cm³ and in-plane TC of 667 W/mK were produced, following the graphitization process at 3000 °C. Similarly, in a study conducted by Zhang et al., the researchers densified large-diameter graphite fiber bundles and developed a method to synthesize two types of carbon rods without the use of hot pressing [53]. One kind was fabricated by injecting phenolic resin into the bundles of carbon fiber, followed by curing, carbonization, graphitization, and densification with a CVI technique, while another type was created by subjecting the carbon bundles to CVI treatment, with further densification of both types of carbon rods finally. After graphitization, these kinds of carbon rods achieved TCs of around 569 and 675 W/mK, respectively. Moreover, in another study conducted by Nan Sheng et.al, the role of wrapped graphene on the vertically aligned hollow carbon fiber was investigated with impregnation by Paraffin wax [57]. Biomass cotton was used to fabricate porous carbon scaffolds as the supporting framework for creating high-performance phase-change materials (PCMs), in order to address the issues of the leakage and poor heat conductivity of the composite materials based on paraffin. The phase-change composite (PCC) with an 8.5 wt% filler concentration demonstrated a high TC along the axial fiber direction of 2.68 W/mK, which is 10 times greater than that of paraffin. The segregated carbon fibers are connected by the porous carbon frameworks produced by the introduction of urea, which are tightly coiled around the fibers and filled in where there are gaps. Hollow carbon fibers and porous graphene frameworks are part of a three-dimensionally connected and crosslinked carbon network that can provide various, continuous pathways for the thermal-conduction phenomenon. Particularly, the high TC of graphene type carbon is projected to significantly improve the PCC's ability to conduct heat and to be used in applications related to TMA.

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