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Engineering of High-Density Thin-Layer Graphite Foam-based Composite Architectures with Superior Compressibility and Excellent Electromagnetic Interference Shielding Performance

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ABSTRACT

Three-dimensional (3D) graphene architectures with well-controlled structure and excellent physiochemical properties have attracted considerable interest due to their potential applications in flexible electronic devices. However, the majority of the existing 3D graphene still encounter several drawbacks such as brittleness, non-uniform building units and limited scale (millimeter or even micrometer), which severely limit their practical applications. Herein, we demonstrate a new scalable technique for preparation of thin-layer graphite foam (GF) with controllable densities ($27.2 \sim 69.2 \text{ mg}\cdot\text{cm}^{-3}$) by carbonization of polyacrylonitrile using a template-directed thermal annealing approach. By integrating the GF with polydimethylsiloxane (PDMS), macroscopic porous GF@PDMS with variable thin-layer GF contents ranging from 15.9% to 31.7% were further fabricated. Owing to the robust interconnected porous network of the GF and the synergistic effect between it and PDMS, GF@PDMS with a 15.9% thin-layer GF content exhibited an impressive 254% increase in compressive strength over the bare GF. In addition, such 15.9% GF@PDMS can totally recover after first compression cycle at a 95% strain and maintains ~88% recovery even after 1000 compression cycles at an 80% strain, demonstrating its superior compressibility. Moreover, all the as-prepared GF@PDMS possessed high electrical conductivity (up to $34.3 \text{ S}\cdot\text{m}^{-1}$), relatively low thermal conductivity ($0.062\sim 0.076 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and excellent electromagnetic interference shielding effectiveness (up to 36.1 dB) over a broad frequency range of 8.2~18 GHz, indicating their great potential as promising candidates for high-performance electromagnetic waves absorption in flexible electronic devices.

KEYWORDS: thin-layer graphite foam, GF@PDMS, mechanical property, electrical conductivity, thermal conductivity, electromagnetic interference shielding effectiveness

1. INTRODUCTION

Graphene, as a two-dimensional (2D) semimetal has shown various unique properties such as superior chemical stability, extreme mechanical strength, exceptionally high electrical and thermal conductivities.¹⁻³ Owing to these advantages, its three-dimensional (3D) counterpart, thin-layer graphite/graphene foam (GF) as well as its macroscopic polymeric composites are expected to be promising candidates as flexible conductors,⁴⁻⁷ as heat spreader or electromagnetic interference (EMI) shielding materials in various electronic instruments,⁸⁻¹¹ and as high-performance electrode materials in flexible energy storage devices.¹²⁻¹⁵ In contrast to traditional metal-based composite materials that usually suffer from intrinsic high density and poor corrosion resistance in harsh environments,¹⁶ light-weight GF and their polymeric composites with large specific surface area, unique thermal and chemical stabilities are particularly attractive as wide-band EMI shielding candidate materials in harsh environments.^{8, 11}

To date, two major manufacturing strategies have been developed¹⁷ to achieve GF either by template-directed chemical vapor deposition (CVD) growth^{5, 18} or assembly of 2D graphene oxide (GO) sheets with/without a foam-like template.^{6-7, 9-10, 19-21} Among them, template-directed CVD has been demonstrated as one of the most commonly used technology to scalable fabrication of high quality GF with extreme low density.⁵ However, this technique inevitably involves highly flammable methane and hydrogen gases for high temperature growth and protective polymer coating for subsequent template removal process. In addition, the resulting GF are usually found to exhibit poor mechanical strength and collapse irreversibly, which significantly hinder their practical applications. On the other hand, assembly of 2D GO sheets into their 3D macroscopic counterparts by freeze-drying^{9, 20-21} and hydrothermal/solvothermal processes^{10, 15} have been considered as alternative approaches to fabricate GF with enhanced compressibility. Despite these

progresses, the resulting macroscopic architectures generally remain largely random, which are unfavorable for various practical applications where 3D macro-assemblies with well-controlled structure and superior physicochemical properties are necessary. Although assembly of GO sheets by 3D printing is an attractive template-free method to meet the abovementioned requirements, these printed GF are still restricted with only a limited scale (millimeter or even micrometer) due to the complex colloidal behavior of GO dispersion.¹⁹ Moreover, it is difficult to totally remove the oxygen-containing groups and defects from the resulting GF, which is detrimental to their overall mechanical and electrical properties.¹⁸ Therefore, development of an alternative approach for scalable fabrication of GF and graphene-based composite materials with well-controlled macroscopic structure and physicochemical properties to further broaden their practical applications remains an urgent need.

Herein, a facile and effective strategy is demonstrated for the fabrication of GF by carbonization of polyacrylonitrile (PAN) using template-directed thermal annealing method. By simply varying the concentration of PAN in N, N-dimethylformamide (DMF) solvent, GF with controllable density ranging from 27.2 to 69.2 mg·cm⁻³ can be successfully prepared. Owing to the relatively larger density of the GF, no extra protective polymer coating is needed for template removal process. Subsequently, macroscopic GF@PDMS porous architectures with high thin-layer GF contents of up to 31.7% can be fabricated by incorporation of polydimethylsiloxane (PDMS) into GF. Notably, the GF@PDMS with a 15.9% thin-layer GF content exhibited an impressive 254% increase in compressive strength as compared to the bare GF and excellent shape recovery, demonstrating its superior compressibility. Moreover, all the as-prepared GF@PDMS showed high electrical conductivity, low thermal conductivity and excellent EMI shielding effectiveness

(up to 36.1 dB) over a broad frequency range of 8.2~18 GHz, indicating their great potential as promising candidates for efficient microwave absorption in flexible electronic devices.

2. EXPERIMENTAL SECTION

2.1. Materials. Ni foam (150 x 40 x 5 mm; 110 PPI) was purchased from Hexiial Technologies, Singapore and was cut into pieces with a typical dimension of 40 x 40 x 5 mm. N, N-dimethylformamide (DMF, ACS, 99.8+%) was purchased from Alfa Aesar. Polyacrylonitrile (PAN, average $M_w = 150,000$) and hydrochloric acid (HCl, ACS reagent, 37%) were purchased from Sigma-Aldrich. Polydimethylsiloxane (PDMS, Sylgard 184 Silicone Elastomer Kit with components of PDMS base part A and curing agent part B) was purchased from Dow Corning. All chemicals were used as received without any further purification.

2.2. Fabrication of Thin-Layer Graphite Foam (GF). First, PAN solution with three different concentrations of 5.0 wt%, 7.5 wt% and 10 wt% in DMF were prepared. Ni foam pieces with dimension of 40 x 40 x 5 mm were then immersed into the respective PAN solution and kept at room temperature overnight. Next, Ni foams were taken out from the PAN solution and stabilized at 210 °C for 2 h in air. The resulting foams were loaded into a horizontal quartz tube and heated to 210 °C in argon atmosphere and kept at this temperature for 1 h, followed by heating to 1010 °C with a heating rate of 13.3 °C·min⁻¹ to obtain thin-layer graphite coated Ni foams (thin-layer graphite@Ni). Finally, the Ni template was totally removed by immersing the thin-layer graphite @Ni into HCl/H₂O (V: V = 1: 3) solution at 85 °C for a certain period to obtain free-standing GF. The resulting GF samples were defined as GF-X, where X (mg·cm⁻³) represents the density of GF.

2.3. Fabrication of GF@PDMS. PDMS solution with a concentration of 7 wt% in ethyl acetate was prepared by first mixing PDMS base part A and curing agent part B with an A/B ratio of 10:

1 and then certain amount of ethyl acetate was added, followed by bath ultrasonication for 10 min. Then, the GF-X was immersed into the above mixture at room temperature and taken out after 2 h, followed by curing at 100 °C overnight to obtain macroscopic porous GF@PDMS. The resulting GF@PDMS samples were defined as Y GF@PDMS, where Y represents the thin-layer GF content in the resulting GF@PDMS. For comparison, bare PDMS foam was also prepared with similar process by directly dipping Ni Foam into the above mixture for 2 h and curing at 100 °C overnight, followed by etching away the Ni template using HCl/H₂O (V: V = 1: 3) solution at 85 °C for a certain period.

2.4. Mechanical Test. The mechanical properties of the GF, PDMS foam and GF@PDMS were measured using an Instron 5567 Mechanical Tester system at room temperature. Typically, square-shaped samples (10 x 10 x 4.5 mm) was firstly loaded on the centre of the lower platen. Then, a compression rod with diameter of 50 mm was applied onto the sample with a controlled speed. To comprehensively investigate compressive behaviors of the foam samples, strains of 20, 40, 60, 80 and 95% were applied at a strain rate of 100%/min. Compressive strain was calculated from the displacement of the compression rod divided by original height of the foam samples. Compressive stress was extracted from the applied compressive force over cross-sectional area of the sample. Recoverability of the foam samples is defined as the displacement recovered over the applied displacement. For 15.9% GF@PDMS sample, the cyclic uniaxial compression data was acquired at a loading-unloading rate of 0.04 mm/min at a strain of 80%. All the measurements were repeated at least three times to extract average values.

2.5. Characterization. The morphologies and microstructures of the as-prepared foam samples were characterized by scanning electron microscopy (SEM, JEOL, JSM-IT100 and JSM-7600F). The elemental composition of the GF samples was studied by SEM/energy dispersive X-ray

electron microscopy (EDX) analysis. The microstructure and crystallinity of the GF were investigated by low- and high-resolution transmission electron microscopy (TEM, Tecnai G2 F20 X-Twin) together with selected area electron diffraction (SAED), as well as Raman spectroscopy (WITEC CRM200 Raman system). The thermal stability of all the as-prepared foams and the thin-layer GF content in the GF@PDMS were evaluated by thermogravimetric (TGA, Shimadzu DTG-600H thermal analyzer) analysis under air atmosphere with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Electrical and thermal conductivities of the bare PDMS foam and GF@PDMS were measured by a two-probe method using SC-200-mm probe station and a ThermTest transient plane source (TPS) 2200 thermal constants analyzer at $23\text{ }^{\circ}\text{C}$ according with TPS standard analysis module, respectively. For all the samples, TPS sensor RTK5465 (3.189 mm radius) was used and a 10 second test time, and a power output of 0.005 Watt were determined as the optimal measurement parameters. The average electrical conductivity and corresponding errors of each sample were determined by three measured values. The average thermal conductivity and corresponding errors of each sample were determined by five measured values. The EMI shielding effectiveness of the PDMS foam and GF@PDMS were tested with N9917A FieldFox microwave analyzer (Agilent Technologies) measurement system in the frequencies of 8.2-12.4 GHz (X-band) and 12.4-18 GHz (Ku-band). The EMI shielding effectiveness measurements were repeated three times for each sample to confirm the reproducibility. The dimensions of the foam samples for the measurements in the X-band and Ku-band were $22.9 \times 10.2 \times 4.5\text{ mm}$ and $15.8 \times 8.0 \times 4.5\text{ mm}$, respectively. From the measured scattering parameters (S_{11} and S_{21}), the power coefficients of reflectivity (R) and transmissivity (T) can be obtained. R and T can be calculated from the following equations:

$$R = |S_{11}|^2 \quad (1)$$

$$T = |S_{21}|^2 \quad (2)$$

The EMI SE_R , SE_A and SE_{Total} can be calculated as follows:

$$SE_R = -10 \log (1 - R) \text{ dB} \quad (3)$$

$$SE_A = -10 \log \left(\frac{T}{1-R} \right) \text{ dB} \quad (4)$$

$$SE_{Total} = SE_R + SE_A + SE_M \quad (5)$$

where SE_M is the microwave multiple internal reflections, which can be negligible when $SE_{Total} \geq 15 \text{ dB}$.²²

3. RESULTS AND DISCUSSION

3.1. Morphology and Microstructure Analysis. The preparation process for GF and GF@PDMS were illustrated in Figure 1a. Briefly, PAN was first infused into Ni foam (PAN@Ni) by a dip-coating method. Stabilization and carbonization of the infused PAN were then performed at 210 °C for 2 h in air and at 1010 °C for 1 h in argon atmosphere, respectively. After thin graphite layers have been successfully introduced onto the Ni foam surface (thin-layer graphite@Ni), free-standing GF was obtained by etching away the Ni foam template. Subsequently, GF@PDMS was prepared by integrating a thin layer of PDMS into the as-prepared GF. The density of the GF and the thin-layer GF content in the resulting GF@PDMS were controllably tuned by varying the concentration of the PAN solution. As a result, GF with three different densities of 27.2, 51.9 and 69.2 mg·cm⁻³ were achieved, and which were competitive to those of the high-density CVD-grown multilayer graphene webs (MGW) prepared by using a compressed Ni foam as a template²³ and were generated as GF-27.2, GF-51.9, and GF-69.2, respectively. Such GF with different densities thus led to the resulting GF@PDMS with three different thin-layer GF contents of 15.9 wt%, 26.8 wt% and 31.7 wt%, which were defined as 15.9% GF@PDMS, 26.8% GF@PDMS and 31.7%

GF@PDMS, respectively. Figure 1b shows a typical piece of free-standing GF-27.2 with a dimension of $\sim 5.7\text{ cm} \times 4\text{ cm} \times 4.5\text{ mm}$. This GF-27.2 is observed to display well-connected porous structure (Figure 1c) and consist of wrinkled cell walls with in-plane size of tens to hundreds of microns (Figure 1d). Such cell walls of GF-27.2 are mainly composed of large area thin-layer graphite (13~19 layers, Figure 1e,f), and which exhibits typical six-fold symmetry hexagonal lattice and high crystallinity as shown in the SAED pattern (inset of Figure 1e).

The composition and elemental distributions within the GF-27.2 are illustrated in the SEM/EDX and corresponding elemental mapping images. It is observed that the GF-27.2 is mainly composed of carbon (C), nitrogen (N) and Oxygen (O) elements with an atomic ratio of 90.26: 5.46: 4.28 (Figure S1a), and all of which are homogeneously distributed throughout the interconnected porous network (Figure 1g). For comparison, GF with another two different densities (GF-51.9 and GF-69.2) have also been systematically characterized and both of which exhibit similar morphologies and microstructures with those of GF-27.2 (Figure S1-S3), while the average numbers of the graphite layer gradually increase with increasing density of GF. It is interesting to note that the macroporous morphology of the GF is well preserved after PDMS coating process (Figure 1h,i) and the C, O, N and silicon elements are homogeneously distributed on the cell walls as identified by the corresponding EDX elemental mapping analysis (Figure 1j).

The crystalline structure of the as-prepared GF, PDMS foam and GF@PDMS are further evaluated by Raman characterization. As shown in Figure 2a, all the GF and GF@PDMS show characteristic D, G and 2D peaks of multilayer graphene located at ~ 1355 , 1584 and 2698 cm^{-1} , respectively,⁵ while all the GF@PDMS exhibit additional three peaks at 2965 , 2905 and 1412 cm^{-1} , corresponding to typical peaks of the bare PDMS,²⁴ indicating the successful integration of the PDMS layers. Meanwhile, a small shoulder peak D' at 1619 cm^{-1} assigned to N-doping in the

graphene can be observed for all the GF and GF@PDMS.^{3,25} The intensity ratio of D- and G-band (I_D/I_G) for the GF-27.2 and GF-51.9 are 0.37 and 0.41, respectively, while a much higher value of 0.84 was observed for the GF-69.2 with a relatively higher thin-layer graphite content, which is attributed to more sp^3 carbon atoms or defects are introduced as compared to those of GF-27.2 and GF-51.9 during the carbonization stage. It is known that the I_G/I_{2D} ratio is very sensitive to the number of graphene layers.³ With the increase of the GF density from 27.2 to 69.2 $\text{mg}\cdot\text{cm}^{-3}$, the I_G/I_{2D} ratio gradually increases from 2.33 to 3.09, indicating the gradually increased graphite layer numbers of GF, which corroborates the abovementioned HRTEM characterization. After integration of PDMS, no obvious changes in their respective I_G/I_{2D} ratio can be detected, confirming the crystallinity of GF within the GF@PDMS is well preserved. The thermal stability of all the as-prepared foam samples and the thin-layer GF content in the GF@PDMS were further evaluated by TGA analysis under air atmosphere (Figure 2b). For all the GF, the weight loss starts at $\sim 500^\circ\text{C}$, while the GF@PDMS shows slightly slower thermal degradation than that of bare PDMS foam at a temperature range of $300\sim 500^\circ\text{C}$, attributing to the successful integration of the GF with relatively high thermal stability. In addition, the weight loss over temperature range from $\sim 508^\circ\text{C}$ to 850°C is assigned for the decomposition of the GF in the GF@PDMS, which can be identified as the respective thin-layer GF content in the composite foams (Detailed calculation process can be seen in the Supporting Information).

3.2. Mechanical Properties. Mechanical strength and elasticity are very important factors which will affect the overall performance of a macroscopic porous architecture in practical applications.^{2,9,19} Therefore, the mechanical properties of GF, PDMS foam and GF@PDMS were systematically assessed by uniaxial compression tests. As shown in Figure 3a, both the GF-27.2 and 15.9% GF@PDMS could be compressed to a strain up to 95% because of their abundant

porosities as observed in their respective SEM images (Figure 1c,i). It is noted that the bare GF-27.2 deforms almost plastically upon compression, which could be due to the weak van der Waals or π - π interactions between the graphene walls that could not support the reversible shape recovery of GF during unloading process.²⁶ As a result, only 10% of the original height was maintained after removal of the applied strain. On the other hand, the integration of PDMS dramatically improves the shape recoverability of the GF-27.2, leading to its full recovery to original dimension without any residual deformation after the loading-unloading cycle at the same strain of 95%. Figure 3b shows the comparison of stress-strain curves for bare PDMS foam, various bare GF and corresponding GF@PDMS at an 80% compressive strain. All the bare GF deform plastically upon compression, while their compressive strength gradually increases with the GF density increase resulting from the increased concentration of PAN solution adopted for their synthesis. This is due to the fact that graphene sheets with higher thickness (thin-layer graphite) are able to provide substantial mechanical supports and strengthen the intersheet interactions as well.²⁷⁻²⁹ As comparison, although with slightly lower strength, the bare PDMS foam is highly elastic and exhibits 100% shape recovery after unloading of the compression. Combining the advantages of GF and PDMS, the as-prepared 15.9% GF@PDMS, 26.8% GF@PDMS and 31.7% GF@PDMS not only exhibit significantly enhanced compressive strength where respective 254%, 227% and 217% increases as compared to the bare GF can be achieved, but also fully recover after the loading-unloading of compression at an 80% strain. The robust GF porous network and its good interfacial compatibility with the PDMS intensify the interactions at the intersheet junctions and contribute to the effective load transfer, leading to the increased overall strength of the GF architectures.^{9, 30} Meanwhile, the PDMS segments also serve as lubricant between the graphene

sheets that prevents their agglomeration and restacking during the compressive loading-unloading processes, resulting in the remarkably improved shape recovery of GF@PDMS.

To comprehensively investigate the compressive behaviours of 15.9% GF@PDMS, uniaxial compressions at various strains of 20%, 40%, 60%, 80% and 95% were further carried out (Figure 3c). The stress-strain curves acquired during the loading process display typical three-regime mechanical responses of the open-cell foams:^{26, 31-32} a linear elastic region for strain $\leq 25\%$, where Young's modulus of 0.15 KPa is observed; a plateau regime (stacking of graphene sheets) at $25\% < \text{strain} < 80\%$; and a densification regime for strain $\geq 80\%$ with dramatically increasing stress. The stresses of unloading curves return to the original point after unloading of the applied strains, indicating the 15.9% GF@PDMS fully recovers to its original shape without permanent deformation. Long-term compressive behaviours are crucial in terms of their practical mechanical related applications. As such, cyclic compressions of the 15.9% GF@PDMS at strain of 80% were further conducted to investigate its cyclic behaviour. Figure 3d shows the representative stress-strain curves of the 15.9% GF@PDMS for the 1st, 2nd, 10th, 100th, 500th, and 1000th cycles. Preconditioning effect³³⁻³⁴ could be observed for both the shape recoverability and compressive strength with the increasing compression cycles, which were further extracted and summarized in Figure 3e. It is noted that the compressive strength is 0.098 MPa for the 15.9% GF@PDMS during the first compression cycle, which gradually decreases to ~ 0.050 MPa after the first 100 cycles of compression and keeps nearly constant upon further compression loading. As shown in Figure S4, the overall interconnected porous structure of the 15.9% GF@PDMS is well maintained with only slight surface cracks in the network can be observed after 100 uniaxial compressive cycles at 80% strain. These slight structure damages will contribute to the stress softening. Moreover, this stress softening phenomenon may also be caused by the weakening of intersheet van der Waals

interactions and the introduction of additional defects upon the continuous cyclic compression, while after which a new equilibrium status is reached to perform a stable mechanical response. Similar transient phenomenon is also observed for the shape recovery ratio of the 15.9% GF@PDMS, which evolves from 100% for the 1st cycle to ~88% after the initial 100 cycles, and is well maintained upon further 900 cycles of compression. In addition, the as-prepared 15.9% GF@PDMS is able to endure various shape deformations including bending and twisting (Figure S5), indicating their excellent toughness and flexibility that are beneficial for applications where complicated mechanical loadings are anticipated.

3.3. EMI Shielding Performance. In contrast to the bare PDMS foam that is highly electrically insulating, all the GF@PDMS exhibit high electrical conductivity and which gradually increases from 23.4 to 34.3 $\text{S}\cdot\text{m}^{-1}$ with the increase of thin-layer GF content in the GF@PDMS (Figure 4a). These values are much higher than the target electrical conductivity value ($\sim 1 \text{ S}\cdot\text{m}^{-1}$) required for EMI shielding application.²² Based on their high electrical conductivity, excellent mechanical properties and abundant interface resulting from continuous interconnected porous network, these as-prepared GF@PDMS are expected to meet the requirements for efficient EMI shielding application. As such, the total EMI shielding effectiveness (SE_{Total}) of the GF@PDMS with three different GF contents and electrical conductivities were further investigated in the frequencies ranging from 8.2-12.4 GHz (X-band, Figure 4b) and 12.4-18 GHz (Ku-band, Figure 4c). The average EMI SE_{Total} of the 15.9% GF@PDMS, 26.8% GF@PDMS and 31.7% GF@PDMS were found to be approximately 30.7, 33.2, 35.4 in the X-band and 31.5, 34.1, 36.1 in the Ku-band, respectively. It is observed that the average EMI SE_{Total} gradually increases with the increase of the thin-layer GF content in the GF@PDMS and all of which exceed the required value for commercial applications (20 dB).³⁵ As shown in Table S1, the electrical conductivity of the

GF@PDMS composite gradually increases with the increase of the density of the GF adopted, while the GF@PDMS with the lowest GF content of 15.9% exhibits the best EMI performance among the three as-prepared GF@PDMS composites. As the density of the GF is proportional to the graphene layer numbers, it is reasonable to propose that the resulting GF@PDMS composite incorporated by the GF with relative thinner graphene layers and proper electrical conductivity would possess better EMI performance. To more appropriately evaluate the EMI efficiency of the GF@PDMS, the EMI SE_{Total} divided by density (SSE) of the GF@PDMS, as well as their comparison with various materials have been listed in Table S1 as well.³⁵⁻⁵⁰ It is interesting to note that the SSE for GF@PDMS with respective electrical conductivity of 23.4, 29.1 and 34.3 $S \cdot m^{-1}$ are 183.0, 177.4 and 162.7 $dB \cdot cm^3 \cdot g^{-1}$, respectively. These values are lower than those of foam materials (333.3 $dB \cdot cm^3 \cdot g^{-1}$ for Graphene foam/PDMS,⁸ and 420 $dB \cdot cm^3 \cdot g^{-1}$ for G-foam³⁵), which can be attributed to their relatively lower densities than those of the GF@PDMS. Impressively, the SSE values of the GF@PDMS are much higher than those of typical metal (10 $dB \cdot cm^3 \cdot g^{-1}$ for solid copper³⁶) and several carbon-based foam materials (27.8 $dB \cdot cm^3 \cdot g^{-1}$ for SiC,²² 33.0 $dB \cdot cm^3 \cdot g^{-1}$ for SWCNT/PS,³⁷ 25.3 $dB \cdot cm^3 \cdot g^{-1}$ for graphene/PMMA,³⁸ 65.1 $dB \cdot cm^3 \cdot g^{-1}$ for FGS/PS,³⁹ 79.3 $dB \cdot cm^3 \cdot g^{-1}$ for graphene/PEI,⁴⁰ 139.31 $dB \cdot cm^3 \cdot g^{-1}$ for SF-EP-CNT2,⁴¹ and 71.8 $dB \cdot cm^3 \cdot g^{-1}$ for 3D porous P/MWCNTs composite⁴²), and comparable to other foam materials with similar density such as MWCNT/carbon (163 $dB \cdot cm^3 \cdot g^{-1}$)⁴³ and cMF-Au-G-IO/PDMS (157.4 $dB \cdot cm^3 \cdot g^{-1}$).⁴⁴ This excellent EMI shielding effectiveness makes the GF@PDMS promising alternative candidates for potential wide-band electromagnetic wave absorption applications.

To better understand the EMI shielding mechanism in the porous GF@PDMS, the microwave absorption (SE_A) and microwave reflection (SE_R) of the GF@PDMS with three different GF contents at a frequency of 12.4 GHz were further calculated and extracted. The SE_{Total} , SE_A and

SE_R for the 15.9% GF@PDMS were 31.0, 23.0, 8.0 dB, while the corresponding values for 26.8% GF@PDMS and 31.7% GF@PDMS were 33.4, 30.1, 3.3 dB, and 35.5, 32.0, 3.5 dB, respectively (Figure 4d). These results demonstrate that more microwave power is absorbed by the porous GF@PDMS rather than being reflected back from the surface of the composites, indicating absorption is the primary EMI shielding mechanism in the frequencies ranging from 8.2~18 GHz for such porous GF@PDMS architectures (Figure 4e). Furthermore, the changes in the electrical conductivity and EMI performance of the 15.9% GF@PDMS before and after repeated compression have been further measured as shown in Figure S6. As shown in Figure S6a, obvious decreases of ~24.9% and ~50.6% in the electrical conductivity of the 15.9% GF@PDMS after 100 and 1000 compression cycles can be found, respectively. This phenomenon is mainly attributed to the slight structure damages, the weakening of intersheet van der Waals interactions and the introduction of additional defects upon the continuous cyclic compression. On the other hand, compared to its fresh counterpart, a higher EMI shielding effectiveness value of the 15.9% GF@PDMS after 100 compression cycles in both the X-band and Ku band is observed, while which with only slight decrease can be observed for the the 15.9% GF@PDMS after 1000 compression cycles (Figure 6Sb). Moreover, it is noted from Figure 6Sc that only slight changes in the SE_R, SE_A, and SE_{Total} are observed, indicating the absorption dominant EMI shielding mechanism of the 15.9% GF@PDMS is not affected after repeated compression. These absorption dominant EMI shielding mechanism can be attributed to the abundant interconnected porous network of the GF@PDMS, which will benefit the multiple internal reflection within the composite foams, leading to absorption and energy dissipation of the electromagnetic waves.

Owing to the exceptional mechanical strength and superior physical properties, the as-prepared GF@PDMS are particularly attractive as EMI shielding materials for aviation and aerospace

applications in harsh environments.¹¹ It should be mentioned that EMI shielding materials with lower thermal conductivity is desirable for such kind of applications. Therefore, thermal conductivities of the bare PDMS foam and GF@PDMS with different thin-layer GF contents at room temperature were further explored. As a result, the thermal conductivities of the GF@PDMS with thin-layer GF contents of 15.9%, 26.8% and 31.7% are found to be 76.34 ± 0.9 , 62.13 ± 0.2 and $69.38 \pm 0.2 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively, all of which are ~ 1 -fold higher than bare PDMS foam ($37.77 \pm 0.08 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), attributing to the integration of GF with relatively high thermal conductivity (Figure 4f).⁴⁰ With all these intrinsic features and controllable characteristics, the as-prepared GF@PDMS with well-controlled macroscopic porous network are promising EMI shielding candidates for use in aircraft and spacecraft systems.

CONCLUSIONS

In summary, we have successfully fabricated macroscopic GF by carbonation of PAN using template-directed thermal annealing method. The density of the resulting GF can be controllably tuned from 27.2 to 69.2 $\text{mg} \cdot \text{cm}^{-3}$ by simply varying the concentration of PAN in DMF solvent. By integration of PDMS thin layer with these GF, GF@PDMS with three different thin-layer GF contents of 15.9%, 26.8% and 31.7% have been further prepared. The morphology and microstructure of the GF and GF@PDMS have been comprehensively characterized and analyzed. Owing to the robust interconnected porous network of GF and its good interfacial compatibility with PDMS, all the as-prepared GF@PDMS exhibit an impressive increase (up to 254%) in compressive strength as compared to their respective bare GF. It is noteworthy that the 15.9% GF@PDMS can totally recover after first compression cycle at a 95% strain and retains $\sim 88\%$ recovery even after 1000 compression cycles at an 80% strain, indicating its superior compressibility. Moreover, all the as-prepared GF@PDMS exhibit an absorption dominant EMI

shielding mechanism with excellent EMI shielding effectiveness of up to 36.1 dB over the broad frequency range of 8.2~18 GHz, attributing to the abundant interconnected porous network of the GF@PDMS. The simple processing feature, together with their abundant porous structure, high electrical conductivity (up to $34.3 \text{ S} \cdot \text{m}^{-1}$), low thermal conductivity, excellent mechanical and EMI shielding performances make the as-prepared GF@PDMS promising as efficient microwave absorption candidates for flexible electronic applications.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

SUPPORTING INFORMATION

SEM/EDX element analysis of the GF and GF@PDMS (Figure S1); Morphology and structure of the GF-51.9 and 26.8% GF@PDMS (Figure S2); Morphology and structure of the GF-69.2 and 31.7% GF@PDMS (Figure S3); SEM images of the 15.9% GF@PDMS after 100 uniaxial compressive cycles at 80% strain (Figure S4); Digital images of the 15.9% GF@PDMS which can withstand various applied mechanical deformations (Figure S5); Comparisons of electrical conductivity and EMI shielding effectiveness for the 15.9% GF@PDMS before and after 100 and 1000 compression cycles; Comparison of EMI shielding performance of the GF@PDMS with other materials (Table S1); Video regarding the bending and twisting of the 15.9% GF@PDMS composite (Supporting Information 1).

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FIGURE CAPTIONS

Figure 1. Preparation process, morphology and microstructure of the GF-27.2 and 15.9% GF@PDMS. (a) Schematic illustration of the preparation process. Optical (b), SEM (c, d), TEM (e, f) images of the GF-27.2 and corresponding SEM/EDX elemental mapping (g) of C, O and N elements. Inset of (e) show the SAED image of the GF-27.2. Optical (h) and SEM image (i) of the 15.9% GF@PDMS and corresponding SEM/EDX elemental mapping (j) of C, O, N and Si elements for the selected area in (i).

Figure 2. Raman (a) and TGA spectra (b) of the as-prepared GF with three different densities, bare PDMS foam and GF@PDMS with three different GF contents.

Figure 3. Mechanical properties of the as-prepared GF, bare PDMS foam and GF@PDMS. (a) Digital display of GF-27.2 and 15.9% GF@PDMS compressed to a strain up to 95%. (b) Comparison of stress-strain curves for bare PDMS foam, various GF and corresponding GF@PDMS at an 80% compressive strain. (c) Stress-strain curves of 15.9% GF@PDMS at various strains of 20%, 40%, 60%, 80% and 95%. (d) Representative stress-strain curves of the 15.9% GF@PDMS for the 1st, 2nd, 10th, 100th, 500th, and 1000th cycles, and (e) the corresponding extracted shape recoverability ratio and compressive strength with the increasing compression cycles.

Figure 4. (a) Electrical conductivity variations of GF@PDMS as a function of thin-layer GF content. EMI shielding effectiveness of the as-prepared GF@PDMS with three different GF contents and electrical conductivities in the frequencies ranging from (b) 8.2-12.4 GHz and (c) 12.4-18 GHz. (d) Comparison of total EMI shielding effectiveness (SE_{Total}), microwave absorption (SE_A) and microwave reflection (SE_R) at a frequency of 12.4 GHz for the GF@PDMS with different GF contents. (e) Schematic illustration of electromagnetic waves with GF@PDMS. (f)

Thermal conductivity of the bare PDMS foam can be controllably enhanced with the integration of GF at 23 °C. Improvements of up to 196% can be achieved for the GF@PDMS with a GF content of 15.9%.

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Graphical Table of Contents