



Bidirectional shear-flow preparing lamellar graphene skeletons for tough and conductive nacre-like nanocomposites

Yicong Qin¹, Gangfeng Cai¹, Songhan Shi, Haodong Yang, Zihao Deng, Chendong Ge, Peng Li^{*}, Chao Gao, Zhen Xu^{*}

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, International Research Centre for X polymers, Department of Polymer Science and Engineering, Zhejiang Key Laboratory of Advanced Organic Materials and Technologies, Research Center for Advanced Fibers, Zhejiang University, 866 Yuhangtang Rd, Hangzhou, 310058, China

ARTICLE INFO

Keywords:

Bidirectional shear-flow
Lamellar graphene skeleton
Nacre-like nanocomposite
Fracture toughness
Electromagnetic interference shielding

ABSTRACT

Achieving structural nanocomposites that combine high fracture toughness with excellent electrical conductivity for electromagnetic interference (EMI) shielding is urgently required in engineering applications; however, this remains a significant challenge. Inspired by the nacre's "brick-and-mortar" architecture, we report a nacre-like epoxy bulk nanocomposite reinforced by a neat graphene lamellar skeleton, which exhibits significantly improved fracture toughness and electrical conductivity. The neat lamellar graphene skeleton is facilely prepared by bidirectional shear-flow field in an expanded extrusion, which effectively reorients graphene oxide sheets to be highly aligned, followed by ambient drying and thermal reduction. At an ultralow graphene loading of 1.04 wt %, the resulting nacre-inspired epoxy nanocomposite achieves a 3.84-fold increase in fracture toughness compared to pure epoxy. The electrical conductivity reaches 74.34 S/m, which results in an outstanding EMI shielding effectiveness (66.80 dB) in 8.2–12.4 GHz. The bidirectional shear-flow methodology enables the effective preparation of ordered lamellar graphene skeletons with highly restored graphene lattices, promoting the applications of nacre-like epoxy nanocomposites with high toughness and conductivity for advanced structural materials with EMI shielding performance.

1. Introduction

Nacre features a typical "brick-and-mortar" lamellar structure that exhibits high fracture toughness [1–3]. These remarkable characteristics make nacre an important model for the design and preparation of high-toughness nanocomposites [4–7]. Epoxy resin is an engineering material with high strength, stiffness, and chemical resistance, which is widely used in advanced fields including aerospace, automotive, and electronics [8–11]. However, the highly cross-linked structure results in inherent brittleness and low fracture toughness [12]. To enhance the toughness of epoxy resin, nanofillers, such as graphene, carbon nanotubes (CNTs), and nanofibers, are usually introduced into the epoxy matrix via simple blending methods [13–19]. Nevertheless, such nanofillers tend to agglomerate, preventing the stable and homogeneous dispersion in the epoxy matrix, limiting further enhancement in mechanical properties [20–23]. The agglomeration of nanofillers hinders the construction of continuous conductive networks, thereby limiting

the further enhancement of nanocomposites' electrical conductivity [24–27]. Natural nacre with brick-and-mortar structures provides an inspiration for constructing tough and conductive nanocomposites incorporating an ordered lamellar skeleton of nanofillers [28–30]. Nevertheless, it remains a challenge to precisely tailor the nanofillers' arrangement to form an ordered lamellar skeleton.

Previous efforts have highlighted the bidirectional freezing, also known as ice templating that fabricates three-dimensional (3D) graphene-based lamellar structures [31–36]. For example, Peng et al. [34] fabricated lamellar carboxymethyl cellulose sodium (CMC)/graphene oxide (GO) hybrid skeletons by bidirectionally freezing to toughen nanocomposites. Liu et al. [35] prepared polyamic acid salt (PAAS) and GO aerogels via bidirectional freezing to develop nanocomposites with high through-plane thermal conductivity. Although the bidirectional freezing effectively prepares such graphene-based lamellar structures, polymer additives are usually incorporated to maintain the structural stability owing to the powerful van der Waals interactions

^{*} Corresponding authors.

E-mail addresses: pengli512@zju.edu.cn (P. Li), zhenxu@zju.edu.cn (Z. Xu).

¹ These authors contributed equally to this work.

between GO sheets and ice crystals [37–39]. The polymer additives inevitably limit electrical conductivity [34,40]. Moreover, such direction-specific freezing critically requires precise a temperature gradient to achieve the long-range lamellar order [41]. Flow-assisted assembly has emerged as another effective strategy for tailoring the alignment of nanosheets in 3D space and constructing macroscopic hierarchical architectures [42–44]. A typical instance is that graphene fibers with the transversely concentric and axially aligned structure were prepared via a multiple shear-flow methodology [45]. Therefore, it is promising for designing the shear field to achieve such neat lamellar graphene skeletons with significant electrical conductivity [46].

Here, we propose a facile bidirectional shear-flow methodology that employs an expanded extrusion process to align GO sheets horizontally. This process enables the fabrication of lamellar graphene aerogels (LGAs) with long-range order, which serve as skeletons for nacre-like nanocomposites. Subsequent thermal reduction at 1500 °C and epoxy infiltration endow the nanocomposite with exceptional fracture toughness and electrical performance. Specifically, at an ultralow graphene content of 1.04 wt%, the nanocomposite exhibits a fracture toughness of 2.57 MPa·m^{1/2}, which is almost four times that of pure epoxy, alongside a high electrical conductivity of 74.34 S/m. Furthermore, the nanocomposite exhibits an outstanding electromagnetic interference (EMI) shielding effectiveness (SE) of 66.80 dB in the X-band frequency range (8.2–12.4 GHz). This bidirectional shear-flow methodology provides an efficient route for constructing long-range ordered lamellar structures and fabricating tough and conductive nacre-like nanocomposites.

2. Experimental section

2.1. Materials

Aqueous GO dispersion was purchased from Hangzhou Gaoxi Technology Co. Ltd. (www.gaoxitech.com). The epoxy matrix (E51) was obtained from Nantong Xingchen Synthetic Materials Co., Ltd. Hardener (methyltetrahydrophthalic anhydride, MTHPA), and accelerator (*N,N*-dimethylbenzylamine, DMBA) were obtained from Chuzhou Hui-Sheng Electronic Materials Co., Ltd. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals and reagents were used as received.

2.2. Fabrication of lamellar graphene aerogels

Aqueous GO suspensions (5, 10, 20 mg/g), with an average lateral size of ~12.50 μm (Fig. S1), were injected into a coagulation bath (5 wt % CaCl₂) through a custom-designed channel under bidirectional shear-flow to form lamellar GO hydrogels. The hydrogels were washed three times with deionized water to remove residual Ca²⁺, then immersed in a reduction bath (4 wt% sodium ascorbate) at 70 °C for 5 h, followed by washing with deionized water for 8 h to remove the residual sodium ascorbate. Subsequent processing included freezing and drying at ambient temperature to obtain chemically reduced LGAs.

The aerogels were thermally reduced under an argon atmosphere using a programmed heating procedure. First, the samples were heated to 400 °C at a rate of 0.5 °C/min and held for 1 h. Subsequently, the temperature was increased at 5 °C/min to the final temperatures of 500, 1000, or 1500 °C, and maintained for 2 h. For clarity, the resulting materials are labeled as LGAx-y, where x = 5, 10, and 20 correspond to initial GO concentrations of 5, 10, and 20 mg/g, respectively, and y = i, ii, and iii indicate the thermal reduction temperatures of 500 °C, 1000 °C, and 1500 °C, respectively.

For the fabrication of GO/sodium alginate (SA) hybrid aerogels, 1 wt % SA solution was mixed with 20 mg/g GO suspension at variable mass ratios. The mixtures were homogenized and degassed. The resulting chemically reduced LGA/SA aerogels with a mass ratio of 5:5 are designated as LGA-S.

2.3. Fabrication of nacre-like graphene/epoxy nanocomposites

Nacre-like graphene/epoxy nanocomposites (E-LGAs) were fabricated via vacuum-assisted impregnation and thermal curing. The epoxy resin, hardener, and curing accelerator were thoroughly mixed at a mass ratio of 100:85:1.05, and the LGAs were vacuum-infiltrated with the mixture at 70 °C for 4 h. The curing protocol consisted of sequential stages: 2 h at 100 °C, 2 h at 140 °C, and 90 min at 160 °C. For clarity, the resulting nanocomposites are designated E-LGAx-y and E-LGA-S.

2.4. Characterization

Scanning electron micrographs (SEM) was performed using a Hitachi S4800 with an accelerating voltage at 5.0 kV. The SAXS experiments were carried out at the beamline BL16B1 at the Shanghai Synchrotron Radiation Facility, with a sample-to-detector distance of 2000 mm. The Raman test was operated by Renishaw inVia Reflex Raman microscopy (excitation wavelength, 532 nm).

The mechanical properties were evaluated using distinct setups tailored to different loading modes and all mechanical data reported represent the average values obtained from at least three valid specimens for each testing condition. Fracture and flexural tests were performed on an RGWT-4000-20 universal testing machine (REGER). Specifically, SENB tests were conducted via three-point bending tests on rectangular specimens (30 × ~2.5 × ~2.5 mm³). For these specimens, a notch was introduced perpendicular to the lamellar direction using a diamond blade and sharpened with a razor blade to a depth of approximately half the specimen width (0.45 ≤ a/W ≤ 0.55). The SENB tests were then performed with a span length of 12 mm and a crosshead speed of 0.1 mm/min. The flexural strength was determined by testing unnotched three-point bending specimens (30 × ~2.5 × ~2.5 mm³) under identical conditions. Tensile properties were characterized for both the E-LGAs and the original graphene skeletons. For the E-LGAs, tensile tests were carried out on a C45.103 universal testing machine using rectangular specimens (30 × ~2.5 × ~2.5 mm³) at a crosshead speed of 10 mm/min. For the original graphene skeletons, the gauge length in tensile tests was 5 mm on the RGWT-4000-20 machine at a speed of 1 mm/min.

The evolution of strain fields during crack propagation was monitored with a digital image correlation (DIC) system. A random speckle pattern was prepared on the sample surface by first applying a matte white base coat, followed by the deposition of matte black dots. Throughout mechanical testing, a CCD camera recorded sequential images of this pattern at 2 Hz. Full-field strain data were subsequently processed and computed using VIC-3D software.

Electrical conductivity was measured along the directions parallel and perpendicular to the lamellar plane using a standard two-probe method with a Keithley 2460 multimeter. Specimens with dimensions of 25.0 × ~2.5 × ~2.5 mm³ were connected at both ends with copper tape and conductive silver paste. The self-monitoring capability was evaluated using notched beam specimens (30.0 × ~2.5 × ~2.5 mm³) under three-point bending at a crosshead speed of 0.05 mm/min. Electrical resistance was simultaneously recorded using a Keithley 2460 multimeter. The testing protocol consisted of an initial loading-unloading cycle with concurrent stress and resistance monitoring, followed by a second loading test under identical conditions. The EMI SE was tested in the X-band frequency range with the waveguide method on a vector network analyzer (ZNB-40, Rohde & Schwarz, Germany). The thickness of each test sample was about 3 mm.

2.5. Calculation

According to ASTM D5045–14, the initial fracture toughness, K_{IC} , was calculated by the following equation:

$$K_{IC} = \frac{P_{IC}S}{BW^2} f\left(\frac{a}{W}\right) \cdot f\left(\frac{a}{W}\right) = \frac{3\left(\frac{a}{W}\right)^{\frac{1}{2}} \left[1.99 - \frac{a}{W} \left(1 - \frac{a}{W} \right) \left(2.15 - 3.93 \frac{a}{W} + 2.7 \left(\frac{a}{W} \right)^2 \right) \right]}{2 \left(1 + 2 \frac{a}{W} \right) \left(1 - \frac{a}{W} \right)^{\frac{3}{2}}} \quad (1)$$

where P_{IC} is the maximum load at crack initiation; S , B , and W are the span, width, and thickness of the specimen; and a is the notch size.

According to ASTM E1820-13e1, the fracture toughness, K_J , was calculated as the following equation:

$$K_J = \sqrt{\frac{EJ_{pl}}{1 - \nu^2} + K_{IC}^2}, J_{pl} = \frac{2A_{pl}}{B(W - a)} \quad (2)$$

where A_{pl} is the plastic area under the load-displacement curve, E is the Young's modulus, and ν is the Poisson's ratio.

The crack extension (Δa) was computed indirectly through a recursive method:

$$\Delta a = a_n - a, a_n = a_{n-1} + \frac{W - a_{n-1}}{2} \frac{C_n - C_{n-1}}{C_n}, C_n = \frac{u_n}{f_n} \quad (3)$$

where a_n is the crack length; u_n and f_n represent the measured displacement and load at each point after crack departure, respectively; and C_n is the corresponding compliance calculated at these points.

According to ASTM D790-17, the stress (σ) and strain (ϵ) were calculated from the three-point bending force-displacement curves using the following equations

$$\sigma = \frac{3FS}{2bd^2} \quad (4)$$

$$\epsilon = \frac{6Dd}{S^2} \quad (5)$$

Here, F is the force; D is the displacement; S is the support span length; b and d are the specimen width and thickness, respectively. Flexural strength and fracture strain were computed from the peak F and D values at failure.

The conductivity ($\sigma = 1/\rho$) were computed using the equation below

$$\frac{1}{\rho} = \frac{L}{bdR} \quad (6)$$

where b , d and L denote the width, thickness, and length of the specimen, respectively, and R represents the electrical resistance.

The EMI SE was determined from the scattering parameters (S_{11} , S_{22} , S_{12} , S_{21}) acquired by a vector network analyzer.

$$R = |S_{11}|^2 \quad (7)$$

$$T = |S_{21}|^2 \quad (8)$$

$$A = 1 - R - T \quad (9)$$

$$SE_R = -10 \log(1 - R) \quad (10)$$

$$SE_A = -10 \log[T/(1 - R)] \quad (11)$$

$$SE_T = SE_R + SE_A \quad (12)$$

Where R , T and A represent the reflection, transmission and absorption power coefficients, respectively. SE_T , SE_R , and SE_A represent the total, reflective, and absorptive SE, respectively.

To comprehensively evaluate the alignment of the graphene lamellae, the orientation order was quantified via both SAXS patterns and SEM image analysis. For the SAXS measurements, the azimuthal intensity distribution $I(\phi)$, was extracted from the characteristic

scattering arc, where ϕ denotes the azimuthal angle. The full width at half maximum ($FWHM$ in degrees) was obtained by fitting the $I(\phi)$ profile with a Gaussian function. Consequently, the SAXS-based orientation order parameter (f_{SAXS}) was calculated using the empirical formula:

$$f_{SAXS} = (180^\circ - FWHM)/180^\circ \quad (13)$$

Alternatively, the orientation was analyzed from the SEM images by applying a Fast Fourier Transform (FFT) using ImageJ software. The resulting FFT power spectra allowed for the calculation of the order parameter f_{FFT} , according to Herman's orientation function:

$$f_{FFT} = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (14)$$

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (15)$$

Where ϕ represents the azimuthal angle. $I(\phi)$ denotes the azimuthal intensity distribution derived from the FFT frequency map and $\langle \cos^2 \phi \rangle$ is the mean-square cosine of the angle. An f_{FFT} value of 1 indicates perfect alignment parallel to the reference direction, while a value of 0 implies a completely random orientation.

3. Results and discussion

3.1. Bidirectional shear-flow for nacre-like graphene/epoxy nanocomposites

The fabrication process of nacre-like E-LGAs prepared via bidirectional shear-flow methodology is illustrated in Fig. 1a and Video S1. First, GO suspension was extruded through a custom-designed channel with specific expansion ratio into CaCl_2 solution for gelation (Fig. S2), forming lamellar GO hydrogels. These hydrogels were then chemically reduced with sodium ascorbate. Subsequent steps included freezing and ambient drying, yielding chemically reduced LGAs. The resulting skeletons were thermally reduced at various temperatures without significant shrinkage (Fig. S3). Finally, vacuum infiltration with epoxy prepolymer and curing were carried out to produce the nacre-like E-LGAs.

To elucidate the alignment process of GO nanosheets in the bidirectional shear-flow field, we investigated the structural evolution during the expanded extrusion process by SEM (Fig. 1b). In Stage I, GO nanosheets became almost aligned parallel to the flow direction under strong shear forces within the confined channel [43,47]. In the bidirectional shear-flow region (Stage II), the combined action of vertical flow (u) and horizontal flow (v) synergistically reoriented GO nanosheets to align perpendicular to the flow, forming a parabolic arrangement due to the significant velocity gradient from the center to the sides [48–50]. The parabolic GO nanosheets finally stabilized into a horizontal long-range ordered lamellar structure in Stage III under a uniform velocity profile of plug flow within the vertical section (Fig. S4) [51]. Based on the bidirectional shear-flow field, LGAs were successfully prepared with highly ordered lamellar structure (Fig. S5), in contrast to the random structure formed without bidirectional shear-flow (Fig. S6).

We directly observed the liquid crystalline texture in the bidirectional shear-flow field under polarized light and investigated the effect of expansion ratios on the liquid crystalline texture. As shown in Fig. 1c, the liquid crystalline texture was in accordance with SEM images (Fig. 1b) from the expanded extrusion process, exhibiting a parabolic GO texture in the bidirectional shear-flow region [52]. The liquid crystalline textures observed at variable expansion ratios spanning from 300% to 1000% demonstrated that the bidirectional shear-flow methodology could fabricate lamellar structures across a wide range of expansion ratios (Fig. S7). Accordingly, we prepared LGAs with their lateral dimensions enlarged from $1 \times 1 \text{ cm}^2$ to $15 \times 15 \text{ cm}^2$ (Fig. 1d).

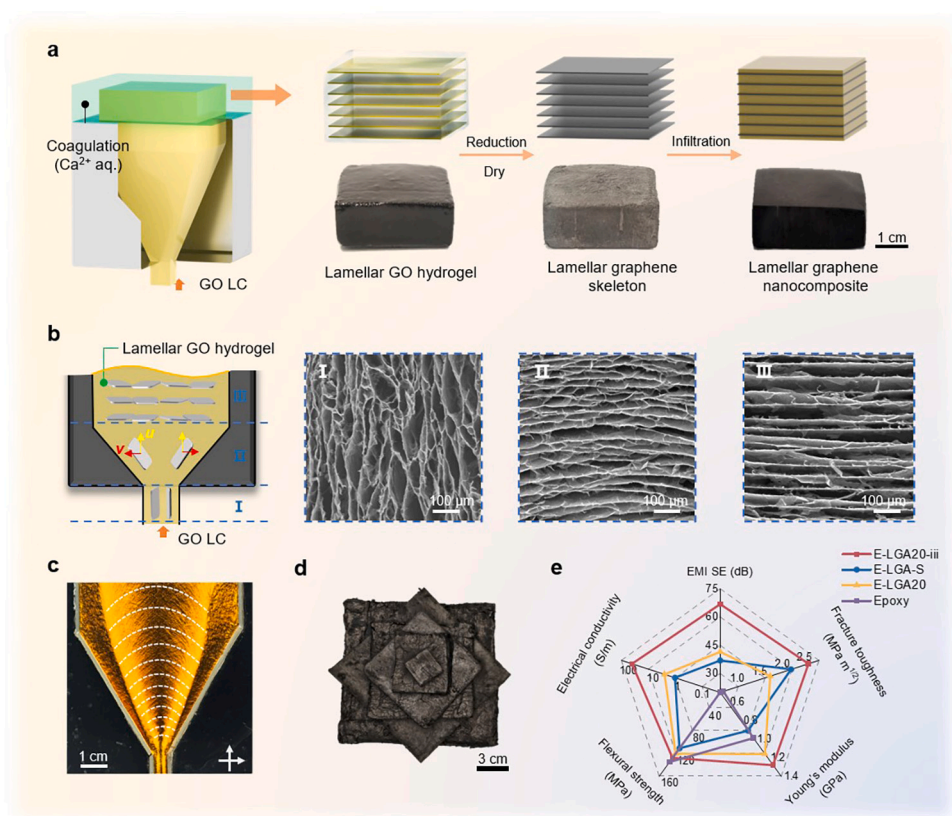


Fig. 1. Bidirectional shear-flow-assisted fabrication of LGAs and their nacre-like nanocomposites. a) Schematic illustration and corresponding photographs of the fabrication process. b) Schematic diagram and corresponding SEM images depicting the alignment evolution of GO sheets within the flow channel: (I) parallelly aligned GO nanosheets along the flow direction before entering the bidirectional shear-flow field; (II) gradual alignment under bidirectional shear-flow field, and (III) long-range ordered lamellar structure. c) Optical image of the GO liquid crystalline texture observed in the bidirectional shear-flow channel under polarized light. d) Photographs of LGA samples with various sizes. e) Radar plot comparing the EMI SE, fracture toughness, Young's modulus, flexural strength, and electrical conductivity of E-LGA20, E-LGA-S, and E-LGA20-iii.

Furthermore, this methodology can also be extended to prepare lamellar skeletons composed of SA and GO (Fig. S8). Our bidirectional shear-flow methodology, combined with ambient drying, enables the preparation of LGAs without the precise temperature gradient required in conventional bidirectional freezing. Furthermore, this methodology also offers excellent reproducibility and structural stability (Fig. S9). We investigated nacre-like nanocomposites based on two types of skeletons: neat lamellar graphene (E-LGA20-iii, E-LGA20) and SA-hybrid lamellar graphene (E-LGA-S). All nanocomposites exhibit significantly enhanced fracture toughness compared to pure epoxy resin. Moreover, they simultaneously demonstrated superior electrical conductivity and EMI shielding performance (Fig. 1e), achieving an exceptional balance of fracture toughness and conductivity that outperforms many previously reported carbon-based and graphene skeleton-structured systems (Fig. S10).

We systematically investigated the influence of GO concentration on the formation of the lamellar structure (Fig. 2). At low concentrations, GO sheets lacked sufficient overlapping to form a robust, continuous network, resulting in a fragile structure. As the concentration of the GO precursor solution increased, we sequentially prepared lamellar GO aerogels. We observed that increasing the GO concentration led to a narrowing of lamella spacing (Figs. 2a₁–c₁), which defined as the distance between adjacent lamellae. The lamella spacing of the prepared chemically reduced LGAs decreased from 59.07 μm to 21.05 μm as the GO concentration was increased from 5 mg/g to 20 mg/g (Figs. 2a₄–c₄). Thermal reduction effectively removed the decorated oxygen functional groups on the GO nanosheets with decreased intensity ratio of D band and G band (I_D/I_G) characterized by Raman spectroscopy, thereby

providing LGAs with restored graphene lattices (Fig. S11) [53]. We found that the lamella spacing remained essentially constant during both thermal reduction and vacuum infiltration of epoxy into the LGAs (Figs. 2a₂–c₂ and S12), resulting in a stable and uniform lamellar structure in the nanocomposites (Figs. 2a₃–c₃ and S13).

3.2. Mechanical properties of nacre-like graphene/epoxy nanocomposites

The ordered “brick-and-mortar” architecture of E-LGAs is crucial to their enhanced fracture toughness [54], as evaluated by SENB tests. As shown in Fig. 3a, the E-LGAs show a yield behavior at the end of the linear elastic region, in which the load on the sample decreases in a stepwise manner. In contrast, epoxy resin displays a brittle fracture in its force–displacement curve, indicating a catastrophic failure. Specifically, to validate the enhancement in intrinsic mechanical properties, we conducted tensile tests on the pure graphene skeletons (Fig. S14). The results demonstrate that the LGA20-iii skeleton, thermally reduced at 1500 $^{\circ}\text{C}$, simultaneously exhibits superior strength and toughness compared to the chemically reduced LGA20. This improvement is attributed to the restoration of the sp^2 lattice and enhanced interactions between graphene sheets at higher annealing temperatures, leading to an intrinsically robust framework. Consequently, this strengthening translates to the composite performance, where the yield load is improved with increasing thermal reduction temperature (Fig. S15a) [55]. The load-bearing capacity of E-LGAs increases with the decreasing lamella spacing (Fig. S15c). Additionally, the improved interfacial interaction between SA and epoxy resin also reinforces the nacre-like nanocomposites [56,57]. E-LGA-S exhibits a force–displacement curve

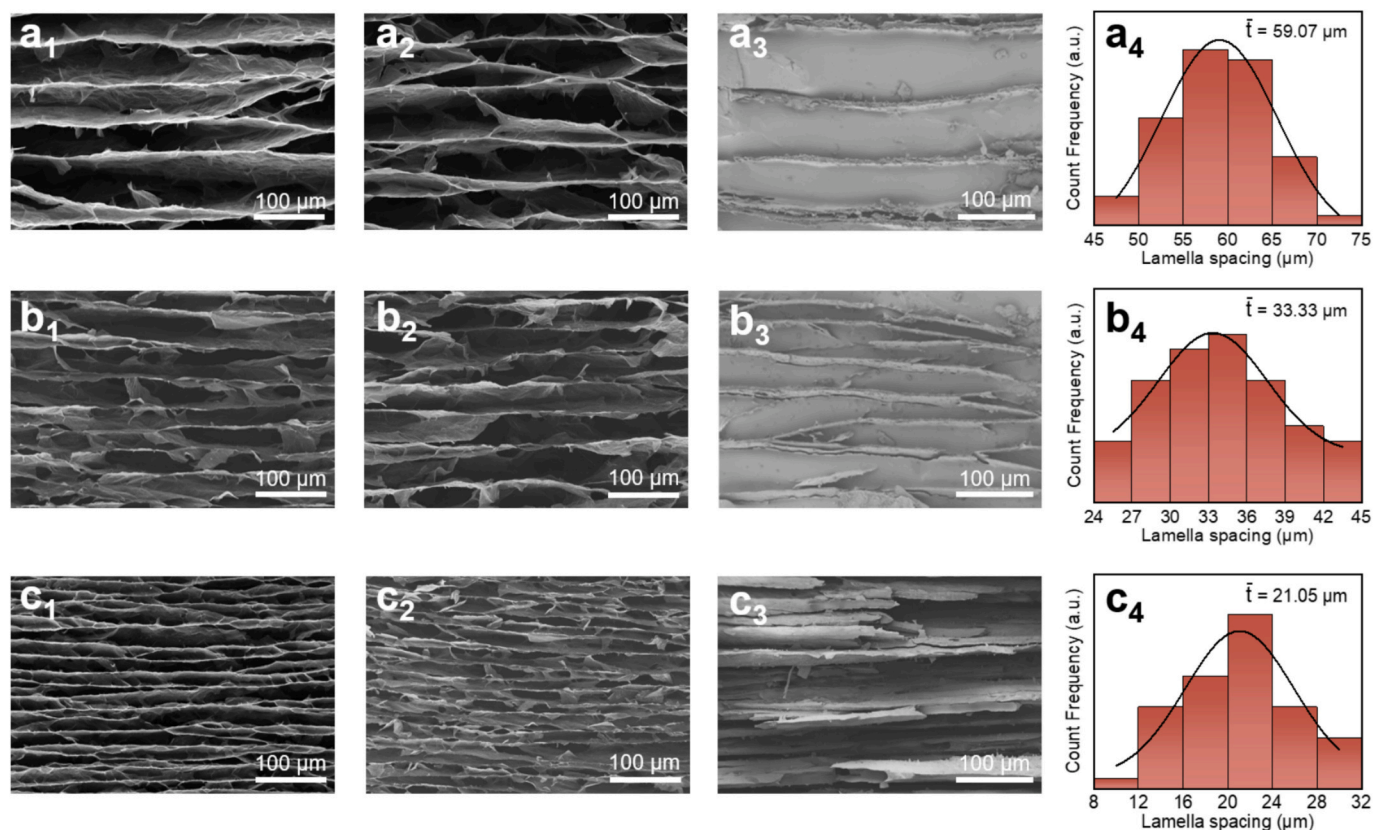


Fig. 2. Structure of the lamellar skeletons and composites with different GO concentrations. a₁-c₁) Cross-sectional SEM images of LGA5, LGA10, and LGA20 skeletons, respectively. a₂-c₂) Cross-sectional SEM images of LGA5-iii, LGA10-iii, and LGA20-iii skeletons, respectively. a₃-c₃) Cross-sectional SEM images of E-LGA5-iii, E-LGA10-iii, and E-LGA20-iii nanocomposites, respectively. a₄-c₄) Statistical distribution of lamella spacing in the LGA skeletons.

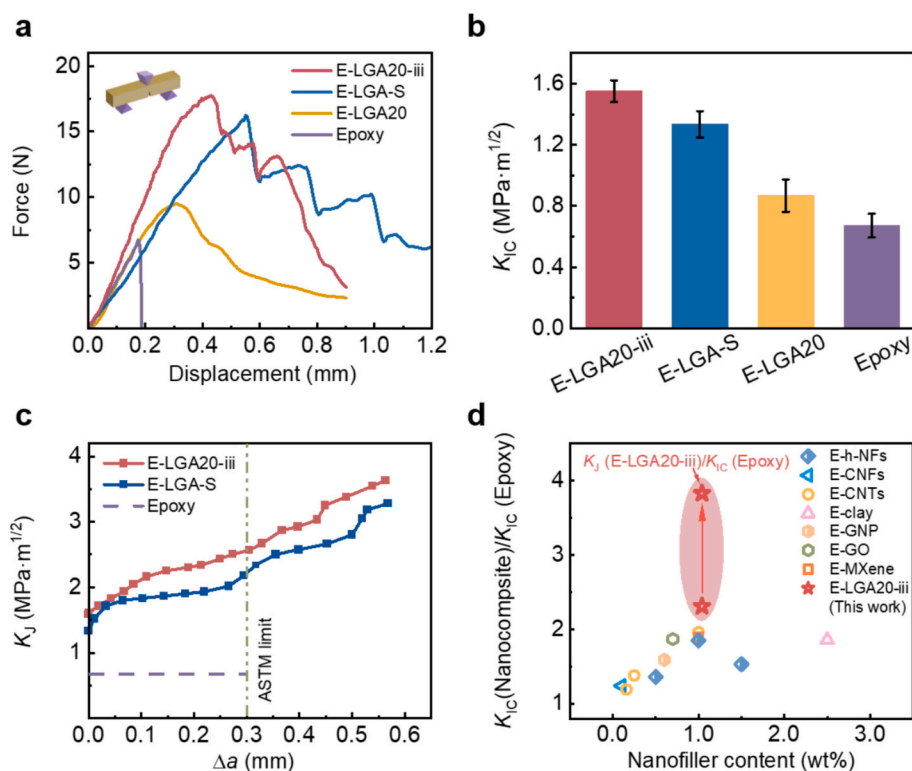


Fig. 3. Fracture performance of E-LGAs. a) Force-displacement curves of epoxy, E-LGA20, E-LGA-S, E-LGA20-iii. b) K_{IC} comparison of E-LGAs and epoxy. c) R-curve of E-LGA-S and E-LGA20-iii. d) Comparison of K_{IC} (Nanocomposite)/ K_{IC} (Epoxy) of the E-LGA20-iii with previously reported homogeneous epoxy nanocomposites.

comparable to that of E-LGA20-iii, which is composed of an LGA reduced at a high temperature. Notably, the initial fracture toughness, K_{IC} , is dramatically enhanced in the E-LGAs as shown in Fig. 3b and Table S1. Owing to its intrinsic brittleness, the K_{IC} of epoxy resin is only $0.67 \text{ MPa}\cdot\text{m}^{1/2}$. When loaded perpendicular to the lamellar direction, E-LGA20, E-LGA-S, and E-LGA20-iii exhibited K_{IC} values of 0.87, 1.33, and $1.55 \text{ MPa}\cdot\text{m}^{1/2}$, which are 1.30, 1.99, and 2.31 times the value of pure epoxy, respectively. For the E-LGAs, K_{IC} increases with higher GO concentration and annealing temperature, a trend that is correspondingly reflected in the force–displacement curves (Figs. S15b and d).

In addition to the K_{IC} , which serves as a valid parameter for evaluating resistance to crack initiation, we measured the maximum fracture toughness, K_J , to capture the extrinsic toughening mechanisms activated during the crack propagation stage [58]. Mechanisms such as crack deflection at low-stiffness interfaces contribute significantly to energy dissipation. By effectively impeding crack propagation, these extrinsic toughening pathways enhance the growth resistance of cracks, leading to a characteristic rising resistance curve, commonly known as the R-curve effect [59]. As the crack extended, the fracture toughness of E-LGA20-iii increased at a higher rate than that of E-LGA-S (Fig. 3c). The maximum fracture toughness, K_J , values for E-LGA20-iii and E-LGA-S reached $2.57 \text{ MPa}\cdot\text{m}^{1/2}$ and $2.17 \text{ MPa}\cdot\text{m}^{1/2}$, respectively, within the American Society for Testing and Materials (ASTM) limit (E1820-13e1). In contrast, brittle fracture occurred in epoxy resin with a constant value of $0.67 \text{ MPa}\cdot\text{m}^{1/2}$.

Fig. 3d compares the fracture toughness of the nacre-like E-LGA20-iii with that of epoxy nanocomposites toughened by conventional blending methods. Even with improved dispersion through modification or compounding, agglomeration inevitably hinders greater enhancement in fracture toughness. Thus, the K_{IC} (nanocomposite)/ K_{IC} (epoxy) ratio for homogeneous nanocomposites typically ranges between 1.19 and 1.96 (Table S2). More significantly, the graphene lamellar skeleton prepared via the bidirectional shear-flow methodology addresses key challenges including nanofiller aggregation and low toughening efficiency. With a GO content of only 1.04 wt%, the E-LGA20-iii exhibits a fracture toughness that significantly surpasses that of homogeneous

epoxy nanocomposites. Notably, the K_J of E-LGA20-iii measured perpendicular to the lamellar direction reaches $2.57 \text{ MPa}\cdot\text{m}^{1/2}$, 3.84 times that of pure epoxy, demonstrating exceptionally high fracture resistance. The anisotropic skeletons lead to mechanical anisotropy of the E-LGAs (Fig. S16). Although the weak interfaces were introduced to improve fracture toughness, the nanocomposites preserved mechanical strength nearly comparable to that of pure epoxy (Figs. S17, S18 and Table S3).

To gain further insight into the toughening mechanisms of the E-LGA20-iii, the fracture surfaces and crack propagation paths of the SENB specimens were examined using SEM and DIC. Multi-scale analysis reveals that the extrinsic toughening is governed by hierarchical mechanisms across different length scales. At the macroscopic scale, the crack in the nacre-like E-LGA20-iii propagates in a highly tortuous, non-linear manner (Figs. 4b, S19 and Video S2), contrasting with the straight, brittle fracture path of pure epoxy (Fig. 4a). This macroscopic tortuosity indicates that the alternating epoxy/graphene lamellar structure acts as an effective barrier, forcing the crack to deviate from its nominal growth plane and extending the energy-dissipation path. At the microscopic scale, the synergistic action of crack branching, local deflection, and frictional pull-out prevents catastrophic failure and dramatically enhances the fracture toughness of the nanocomposite [52,55,56], as shown in Figs. 4c and d. The rigid graphene skeleton obstructs the crack tip, triggering local crack deflection (yellow arrows in Figs. 4c and d) and crack branching (green arrows in Figs. 4c and d), which significantly multiplies the fracture surface area. Furthermore, unlike the smooth fracture surface of pure epoxy (Fig. S20b), the E-LGAs exhibit prominent graphene sheet pull-out (Fig. S20a). This pull-out process is intrinsically accompanied by interfacial friction, as evidenced by the smooth sliding traces on the lamellae surfaces (pink arrows in Figs. 4c and d). This frictional sliding dissipates considerable strain energy, thereby impeding crack propagation.

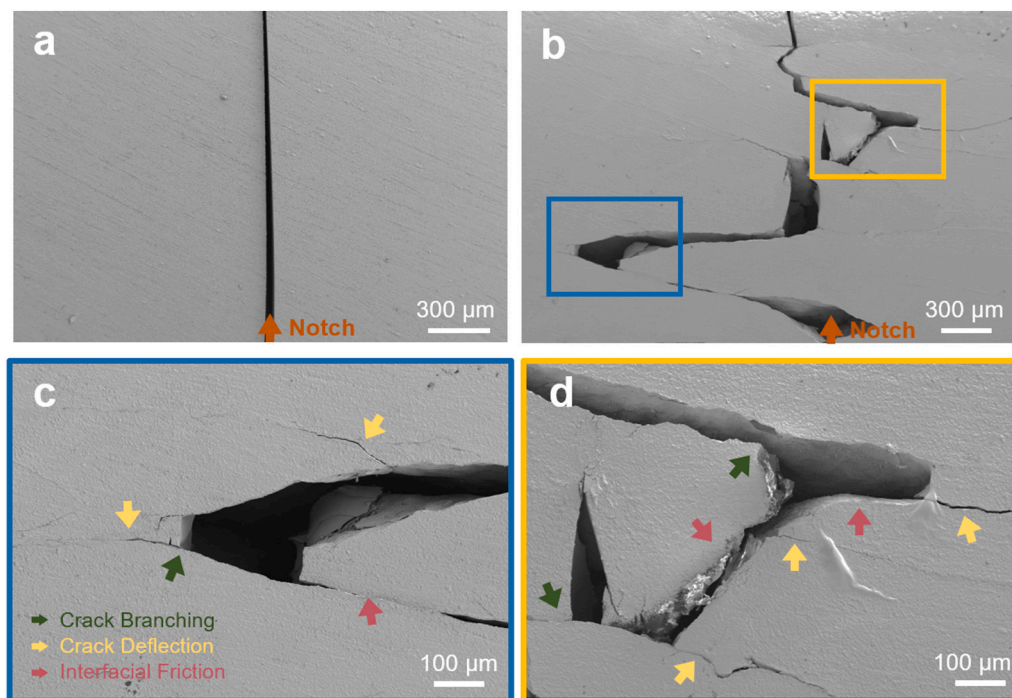


Fig. 4. Crack paths and fracture mechanisms of E-LGAs and epoxy. a) SEM image of crack propagation in epoxy resin. b) SEM image of the fracture surface of E-LGA20-iii. c, d) Enlarged SEM images of the regions highlighted by the blue and yellow boxes in (b), respectively. The main toughening mechanisms are indicated: crack branching (green arrows), crack deflection (yellow arrows), and interfacial friction (pink arrows).

3.3. Nacre-like graphene/epoxy nanocomposites for self-monitoring and EMI shielding applications

The lamellar structure renders the graphene skeleton intrinsically anisotropic, thereby forming continuous in-plane conductive pathways. Consequently, the in-plane conductivity of E-LGAs is an order of magnitude higher than the through-plane conductivity (Fig. S21). As shown in Fig. 5a, the E-LGA20-iii composed of thermally reduced LGAs achieved an electrical conductivity of 74.34 S/m, nearly two orders of magnitude higher than that of E-LGA20 (1.35 S/m), whose skeleton was only chemically reduced by sodium ascorbate. Such a high electrical conductivity is also significantly superior to that of previously reported nacre-like nanocomposites using graphene/polymer hybrid lamellar skeletons [34,57]. The outstanding electrical performance of E-LGA20-iii facilitates the monitoring of crack propagation for the assessment of structural integrity [60]. During the first loading cycle of the notched E-LGA20-iii specimen, the electrical resistance increased steadily in tandem with the load, as the crack initiated and propagated (Fig. 5b). When the load peaked, the normalized resistance change ($\Delta R/R_0$) increased to 9.97%, indicating the formation of an internal crack. In the second loading cycle, the load initially rose to a peak value and then decreased gradually (Fig. 5c). Correspondingly, $\Delta R/R_0$ first increased steadily and then surged sharply to 22.70%, suggesting the opening and stable growth of the pre-existing crack. These results confirm that the structural integrity of E-LGAs can be effectively monitored by tracking the electrical resistance change.

The significantly improved electrical conductivity allows our E-LGAs to achieve excellent EMI shielding performance. The corresponding conductivity and EMI shielding values for all samples are listed in Table S3. Over the X-band frequency range, the EMI SE of E-LGA20-iii, fabricated from thermally reduced LGAs at 1500 °C, reaches 66.80 dB, which is 1.81 and 1.61 times higher than those of E-LGA-S (36.93 dB) and E-LGA20 (41.49 dB), both of which are based on chemically reduced LGA skeletons (Fig. 5d). Notably, these electrical and shielding properties exhibit excellent long-term stability and environmental durability (Fig. S22). In contrast, epoxy resin is insulating, leading to a low EMI SE

of only 2.70 dB at a thickness of 3 mm. As the annealing temperature increases from E-LGA20 to E-LGA20-iii, the SE_T rises progressively (Figs. S23a and b), attributed to the effective restoration of the conjugated carbon lattice and the removal of oxygen-containing groups [61]. The resulting highly conductive network facilitates electron transport and enhances conduction loss [62,63]. Simultaneously, increasing the GO concentration from 5 to 20 mg/g significantly boosts the SE_T from 51.20 dB to 66.80 dB (Figs. S23d and e). The corresponding evolution of power coefficients (Figs. S23c and f) further corroborates the intensified interaction between the EMWs and the material network. This enhancement arises from the denser lamellar spacing in high-concentration composites, which creates more physical barriers per unit volume to intercept electromagnetic waves (EMWs) [64,65].

To elucidate the dominant shielding mechanism, the contributions of reflection and absorption were analyzed based on the S-parameters. As shown in Fig. 5e, the absorbed EMI SE (SE_A , 52.98 dB) of E-LGA20-iii significantly exceeds its reflected EMI SE (SE_R , 13.83 dB) indicating that E-LGA20-iii primarily attenuates EMWs through strong internal absorption. Based on this high internal attenuation, we proposed the synergistic shielding mechanism illustrated in Fig. 5f. First, the macroscopic conductivity provided by the graphene skeleton induces ohmic losses, dissipating energy into heat. This mechanism accounts for the superior EMI shielding of E-LGA20-iii compared to E-LGA20 and E-LGA-S. Second, the lamellar graphene skeleton plays a critical role in internal attenuation. The high SE_A represents the multiple reflections and scattering of incident EMWs at interfaces of lamellae, which significantly extends the propagation path and effectively attenuates the energy [66]. Furthermore, the abundant heterogeneous interfaces between the graphene sheets and the epoxy matrix act as capacitor-like structures. Under the alternating electromagnetic field, these interfaces generate interfacial polarization and dipole relaxation (Maxwell–Wagner–Sillars effect), further contributing to dielectric loss [67]. Therefore, the lamellar structure of E-LGA20-iii contributes significantly to its shielding performance.

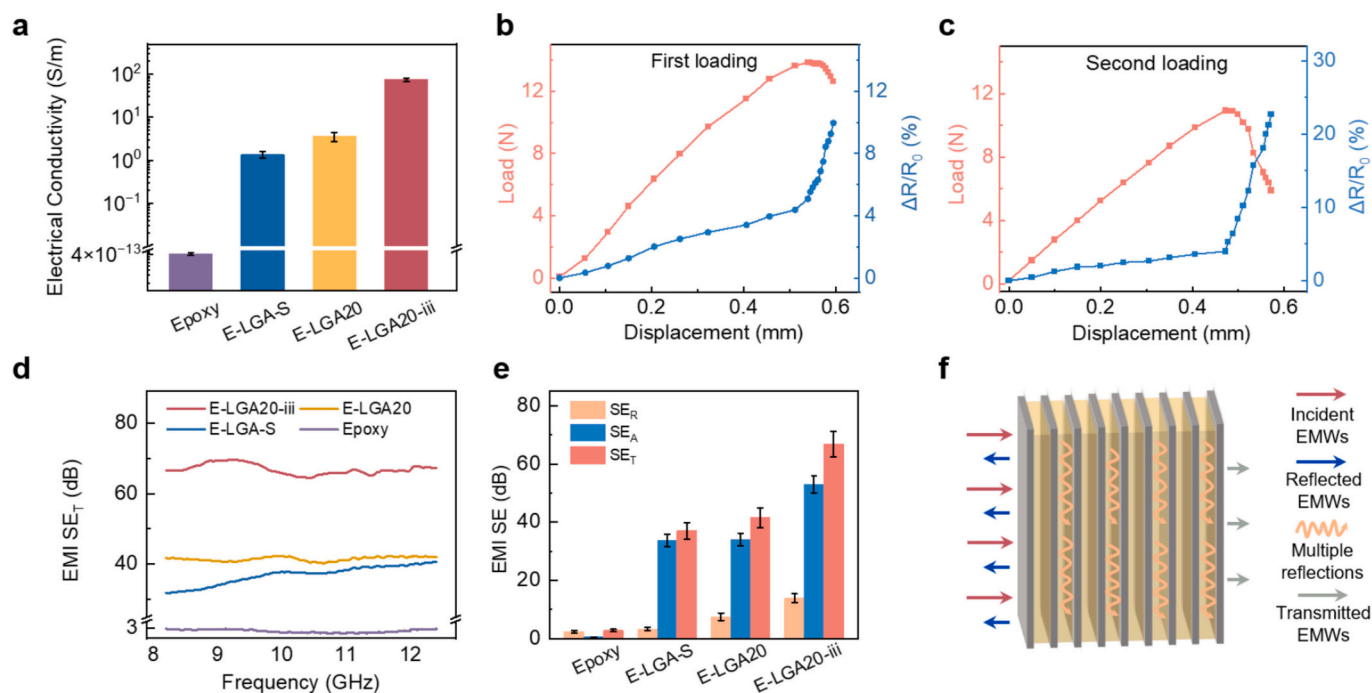


Fig. 5. Electrical conductivity and EMI shielding performance of E-LGAs and epoxy resin. a) Electrical conductivity of the E-LGAs and epoxy. b, c) Self-monitoring of structural integrity in E-LGA20-iii during the first and second loading cycles. d) EMI SE_T of E-LGAs and epoxy. e) Average SE_R , SE_A , SE_T values of E-LGAs and epoxy in the X-band frequency range. f) Schematic illustration of the enhanced EMI shielding mechanism of E-LGAs.

4. Conclusion

In summary, we have successfully fabricated a nacre-inspired epoxy nanocomposite featuring a highly ordered, long-range lamellar graphene skeleton via a scalable bidirectional shear-flow strategy. With an ultralow graphene loading of 1.04 wt%, the resultant nanocomposites achieve a fracture toughness of $2.57 \text{ MPa}\cdot\text{m}^{1/2}$ (3.84-fold enhancement over pure epoxy) and a high electrical conductivity of 74.34 S/m . These enhancements are attributed to the effective extrinsic toughening mechanisms and the formation of continuous conductive networks along the lamellae. Furthermore, the nanocomposites demonstrate superior performance in EMI shielding and reliable crack self-monitoring. This work not only validates the efficacy of the bidirectional shear-flow technique but also highlights its potential for the scalable production of macroscopic nanocomposites with tailored structural skeletons and integrated multifunctional properties.

CRedit authorship contribution statement

Yicong Qin: Writing – review & editing, Writing – original draft, Visualization, Validation, Data curation. **Gangfeng Cai:** Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Formal analysis, Conceptualization. **Songhan Shi:** Writing – review & editing, Visualization. **Haodong Yang:** Visualization, Investigation. **Zihao Deng:** Visualization, Formal analysis. **Chendong Ge:** Visualization, Resources. **Peng Li:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Chao Gao:** Supervision, Project administration, Funding acquisition. **Zhen Xu:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. 52403051, 52272046), the Natural Science Foundation of Zhejiang Province (LQN25E030008), National Key Research and Development Program of China (NO.2022YFA1205300, 2022YFA1205301), Shanxi-Zheda Institute of New Materials and Chemical Engineering (2022SZ-TD011, 2022SZ-TD012), Hundred Talents Program of Zhejiang University (188020*194231701/113), Fundamental Research Funds for the Central Universities (226-2024-00074 and 226-2025-00219), “Pioneer” and “Leading Goose” R&D Program of Zhejiang (2026C02A1055, 2023C01190).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.175349>.

Data availability

Data will be made available on request.

References

- [1] M. Grossman, F. Bouville, F. Erni, K. Masania, R. Libanori, A.R. Studart, Mineral nano-interconnectivity stiffens and toughens nacre-like composite materials, *Adv. Mater.* 29 (2017) 1605039, <https://doi.org/10.1002/adma.201605039>.
- [2] H.C. Loh, T. Divoux, B. Gludovatz, P.U.P.A. Gilbert, R.O. Ritchie, F.J. Ulm, A. Masic, Nacre toughening due to cooperative plastic deformation of stacks of co-oriented aragonite platelets, *Commun. Mater.* 1 (2020) 77, <https://doi.org/10.1038/s43246-020-00078-y>.
- [3] U.G.K. Wegst, H. Bai, E. Saiz, A.P. Tomsia, R.O. Ritchie, Bioinspired structural materials, *Nat. Mater.* 14 (2015) 23–36, <https://doi.org/10.1038/nmat4089>.
- [4] S.M. Chen, Z.B. Zhang, H.L. Gao, S.H. Yu, Bottom-up film-to-bulk assembly toward bioinspired bulk structural nanocomposites, *Adv. Mater.* 36 (2024) 2313443, <https://doi.org/10.1002/adma.202313443>.
- [5] Z. Ding, T. Klein, C. Barner Kowollik, M. Mirkhalaf, Multifunctional nacre-like materials, *Mater. Horiz.* 10 (2023) 5371–5390, <https://doi.org/10.1039/D3MH01015E>.
- [6] L. Wang, B. Wang, Z. Wang, J. Huang, K. Li, S. Liu, J. Lu, Z. Han, Y. Gao, G. Cai, Y. Liu, Y. Chen, Y. Lin, Y. Liu, C. Gao, Z. Xu, Superior strong and tough nacre-inspired materials by interlayer entanglement, *Nano Lett.* 23 (2023) 3352–3361, <https://doi.org/10.1021/acs.nanolett.3c00332>.
- [7] H. Zhao, Z. Yang, L. Guo, Nacre-inspired composites with different macroscopic dimensions: strategies for improved mechanical performance and applications, *NPG Asia Mater.* 10 (2018) 1–22, <https://doi.org/10.1038/s41427-018-0009-6>.
- [8] Y. Wen, C. Chen, Y. Ye, Z. Xue, H. Liu, X. Zhou, Y. Zhang, D. Li, X. Xie, Y.W. Mai, Advances on thermally conductive epoxy-based composites as electronic packaging underfill materials—a review, *Adv. Mater.* 34 (2022) 2201023, <https://doi.org/10.1002/adma.202201023>.
- [9] W. Wu, H. Feng, L. Xie, A. Zhang, F. Liu, Z. Liu, N. Zheng, T. Xie, Reprocessable and ultratough epoxy thermosetting plastic, *Nat. Sustainability* 7 (2024) 804–811, <https://doi.org/10.1038/s41893-024-01331-9>.
- [10] F. Van Lijsebetten, T. Maiheu, J.M. Winne, F.E. Du Prez, Epoxy adhesives with reversible hardeners: controllable thermal debonding in bulk and at interfaces, *Adv. Mater.* 35 (2023) 2300802, <https://doi.org/10.1002/adma.202300802>.
- [11] N. Li, Y. Zhang, Y. Xu, J. Li, Graphene/epoxy coating with radiation heat dissipation properties for spacecraft thermal management, *Chem. Eng. J.* 519 (2025) 165105, <https://doi.org/10.1016/j.cej.2025.165105>.
- [12] G. Levita, S. De Petris, A. Marchetti, A. Lazzeri, Crosslink density and fracture toughness of epoxy resins, *J. Mater. Sci.* 26 (1991) 2348–2352, <https://doi.org/10.1007/BF01130180>.
- [13] N. Shirodkar, S. Cheng, G.D. Seidel, Enhancement of mode I fracture toughness properties of epoxy reinforced with graphene nanoplatelets and carbon nanotubes, *Compos. Part B Eng.* 224 (2021) 109177, <https://doi.org/10.1016/j.compositesb.2021.109177>.
- [14] R. Jin, B. Xu, D. Guo, L. Qu, Constructing a novel controllable interface structure through the anchoring effect of α -cyclodextrin at cryogenics to enhance and toughen the mechanical properties of epoxy resin, *Chem. Eng. J.* 503 (2025) 158062, <https://doi.org/10.1016/j.cej.2024.158062>.
- [15] Y. Bo, A. Guo, H. Zhao, D. Liu, Enhancing thixotropic properties of epoxy resin and mechanical properties of epoxy resin thermosets by polyethyleneimine functionalized carbon nanotubes, *Prog. Org. Coat.* 196 (2024) 108721, <https://doi.org/10.1016/j.porgcoat.2024.108721>.
- [16] Q. Tang, Y. Li, J. Liu, H. Li, Q. Peng, M. Kang, T. Kang, G. Chang, Constructing high-performance composite epoxy resins: interfacial π - π stacking interactions-driven physical rolling behavior of silica microspheres, *Adv. Mater.* 37 (2025) 2415485, <https://doi.org/10.1002/adma.202415485>.
- [17] M.D. Ali, A. Starczewska, T.K. Das, M. Jesionek, Exploration of sp^2 carbon networks: advances in graphyne research and its role in next-generation technologies, *Int. J. Mol. Sci.* 26 (2025), <https://doi.org/10.3390/ijms26115140>.
- [18] S. Ghosh, P. Das, S. Ganguly, S. Remanan, T.K. Das, S.K. Bhattacharyya, J. Baral, A. K. Das, T. Laha, N.Ch. Das, 3D-enhanced, high-performing, super-hydrophobic and electromagnetic-interference shielding fabrics based on silver paint and their use in antibacterial applications, *ChemistrySelect* 4 (2019) 11748–11754, <https://doi.org/10.1002/slct.201901738>.
- [19] P. Bhawal, S. Ganguly, T.K. Das, S. Mondal, N.c. Das, Mechanically robust conductive carbon clusters confined ethylene methyl acrylate-based flexible composites for superior shielding effectiveness, *Polym. Adv. Technol.* 29 (2018) 95–110, <https://doi.org/10.1002/pat.4092>.
- [20] V.S. Romanov, S.V. Lomov, I. Verpoest, L. Gorbatikh, Stress magnification due to carbon nanotube agglomeration in composites, *Compos. Struct.* 133 (2015) 246–256, <https://doi.org/10.1016/j.compstruct.2015.07.069>.
- [21] G. Zhou, H. Yao, Y. Zhou, W. Wang, M. Peng, Self-assembled complexes of graphene oxide and oxidized vapor-grown carbon fibers for simultaneously enhancing the strength and toughness of epoxy and multi-scale carbon fiber/epoxy composites, *Carbon* 137 (2018) 6–18, <https://doi.org/10.1016/j.carbon.2018.05.014>.
- [22] M. Zhu, L. Liu, Z. Wang, Iron-phosphorus-nitrogen functionalized reduced graphene oxide for epoxy resin with reduced fire hazards and improved impact toughness, *Compos. Part B Eng.* 199 (2020) 108283, <https://doi.org/10.1016/j.compositesb.2020.108283>.
- [23] S.K. Ghosh, K. Nath, S.S. Ganguly, T.K. Das, S. Paul, T. Ghosh, A.K. Das, N.Ch. Das, Improved rheological, barrier, antibacterial, and electromagnetic interference shielding properties of graphene and graphene derivatives based linear low density polyethylene nanocomposites, *Polym. Compos.* 44 (2023) 5702–5720, <https://doi.org/10.1002/pc.27520>.
- [24] M. Haghighi, R. Ansari, M.K. Hassanzadeh-Aghdam, Prediction of electrical conductivity of carbon fiber-carbon nanotube-reinforced polymer hybrid composites, *Compos. Part B Eng.* 167 (2019) 728–735, <https://doi.org/10.1016/j.compositesb.2019.03.046>.
- [25] H. Gu, H. Zhang, C. Ma, X. Xu, Y. Wang, Z. Wang, R. Wei, H. Liu, C. Liu, Q. Shao, X. Mai, Z. Guo, Trace electrosprayed nanopolystyrene facilitated dispersion of

- multiwalled carbon nanotubes: simultaneously strengthening and toughening epoxy, *Carbon* 142 (2019) 131–140, <https://doi.org/10.1016/j.carbon.2018.10.029>.
- [26] S.Y. Kim, Y.J. Noh, J. Yu, Prediction and experimental validation of electrical percolation by applying a modified micromechanics model considering multiple heterogeneous inclusions, *Compos. Sci. Technol.* 106 (2015) 156–162, <https://doi.org/10.1016/j.compscitech.2014.11.015>.
- [27] S.K. Ghosh, S. Paul, T. Ghosh, N.Ch. Das, Design of interconnected graphene loaded thermoplastic elastomeric blend composite films for minimizing electromagnetic radiation and efficient heat management, *Polym. Adv. Technol.* 35 (2024) e6510, <https://doi.org/10.1002/pat.6510>.
- [28] R. Han, J. Ren, Z. Zhou, G.X. Chen, Q. Li, Preparation of high-k polymeric composites based on low-k boron nitride nanosheets with high-connectivity lamellar structure, *ACS Appl. Mater. Interfaces* 15 (2023) 34064–34074, <https://doi.org/10.1021/acsami.3c06143>.
- [29] H. Wang, R. Lu, J. Yan, J. Peng, A.P. Tomsia, R. Liang, G. Sun, M. Liu, L. Jiang, Q. Cheng, Tough and conductive nacre-inspired MXene/epoxy layered bulk nanocomposites, *Angew. Chem. Int. Ed.* 62 (2023) e202216874, <https://doi.org/10.1002/anie.202216874>.
- [30] D. Li, E. Peng, F. Lu, B. Wang, Y. Shen, P. Liu, L. Liu, Y. Huang, Z. Hu, Toughening epoxy nanocomposites with graphene-encapsulated liquid metal framework, *Chem. Eng. J.* 455 (2023) 140887, <https://doi.org/10.1016/j.cej.2022.140887>.
- [31] M. Yang, N. Zhao, Y. Cui, W. Gao, Q. Zhao, C. Gao, H. Bai, T. Xie, Biomimetic architected graphene aerogel with exceptional strength and resilience, *ACS Nano* 11 (2017) 6817–6824, <https://doi.org/10.1021/acs.nano.7b01815>.
- [32] H.L. Gao, Z.Y. Wang, C. Cui, J.Z. Bao, Y.B. Zhu, J. Xia, S.M. Wen, H.A. Wu, S.H. Yu, A highly compressible and stretchable carbon spring for smart vibration and magnetism sensors, *Adv. Mater.* 33 (2021) 2102724, <https://doi.org/10.1002/adma.202102724>.
- [33] Z. Dong, J. Wang, J. Li, J. Lu, S. Tan, Q. Feng, Z. Xu, Three-dimensional layered multifunctional carbon aerogel for energy storage and pressure sensors, *Chem. Eng. J.* 491 (2024) 151797, <https://doi.org/10.1016/j.cej.2024.151797>.
- [34] J. Peng, C. Huang, C. Cao, E. Saiz, Y. Du, S. Dou, A.P. Tomsia, H.D. Wagner, L. Jiang, Q. Cheng, Inverse nacre-like epoxy-graphene layered nanocomposites with integration of high toughness and self-monitoring, *Matter* 2 (2020) 220–232, <https://doi.org/10.1016/j.matt.2019.08.013>.
- [35] P. Liu, X. Li, P. Min, X. Chang, C. Shu, Y. Ding, Z.Z. Yu, 3D lamellar-structured graphene aerogels for thermal interface composites with high through-plane thermal conductivity and fracture toughness, *Nano Micro Lett.* 13 (2020) 22, <https://doi.org/10.1007/s40820-020-00548-5>.
- [36] W. Gao, N. Zhao, T. Yu, J. Xi, A. Mao, M. Yuan, H. Bai, C. Gao, High-efficiency electromagnetic interference shielding realized in nacre-mimetic graphene/polymer composite with extremely low graphene loading, *Carbon* 157 (2020) 570–577, <https://doi.org/10.1016/j.carbon.2019.10.051>.
- [37] C. Wang, X. Chen, B. Wang, M. Huang, B. Wang, Y. Jiang, R.S. Ruoff, Freeze-casting produces a graphene oxide aerogel with a radial and centrosymmetric structure, *ACS Nano* 12 (2018) 5816–5825, <https://doi.org/10.1021/acs.nano.8b01747>.
- [38] P. Liu, X. Li, X. Chang, P. Min, C. Shu, Y. Li, Y. Kang, Z. Yu, Highly anisotropic graphene aerogels fabricated by calcium ion-assisted unidirectional freezing for highly sensitive sensors and efficient cleanup of crude oil spills, *Carbon* 178 (2021) 301–309, <https://doi.org/10.1016/j.carbon.2021.03.014>.
- [39] H. Geng, X. Liu, G. Shi, G. Bai, J. Ma, J. Chen, Z. Wu, Y. Song, H. Fang, J. Wang, Graphene oxide restricts growth and recrystallization of ice crystals, *Angew. Chem. Int. Ed.* 56 (2017) 997–1001, <https://doi.org/10.1002/anie.201609230>.
- [40] H.L. Gao, Y.B. Zhu, L.B. Mao, F.C. Wang, X.S. Luo, Y.Y. Liu, Y. Lu, Z. Pan, J. Ge, W. Shen, Y.R. Zheng, L. Xu, L.J. Wang, W.H. Xu, H.A. Wu, S.H. Yu, Super-elastic and fatigue resistant carbon material with lamellar multi-arch microstructure, *Nat. Commun.* 7 (2016) 12920, <https://doi.org/10.1038/ncomms12920>.
- [41] B. Zhou, Q. Cheng, Z. Chen, Z. Chen, D. Liang, E.A. Munro, G. Yun, Y. Kawai, J. Chen, T. Bhowmick, K.K. Padmanathan, L.G. Occhipinti, H. Matsumoto, J. W. Gardner, B.L. Su, T. Hasan, Universal Murray's law for optimised fluid transport in synthetic structures, *Nat. Commun.* 15 (2024) 3652, <https://doi.org/10.1038/s41467-024-47833-0>.
- [42] C. Zhao, P. Zhang, J. Zhou, S. Qi, Y. Yamauchi, R. Shi, R. Fang, Y. Ishida, S. Wang, A.P. Tomsia, M. Liu, L. Jiang, Layered nanocomposites by shear-flow-induced alignment of nanosheets, *Nature* 580 (2020) 210–215, <https://doi.org/10.1038/s41586-020-2161-8>.
- [43] G. Xin, W. Zhu, Y. Deng, J. Cheng, L.T. Zhang, A.J. Chung, S. De, J. Lian, Microfluidics-enabled orientation and microstructure control of macroscopic graphene fibres, *Nat. Nanotechnol.* 14 (2019) 168–175, <https://doi.org/10.1038/s41565-018-0330-9>.
- [44] X. Zhu, Y. Zhang, Z. Man, W. Lu, W. Chen, J. Xu, N. Bao, W. Chen, G. Wu, Microfluidic-assembled covalent organic frameworks@Ti₃C₂T_x MXene vertical fibers for high-performance electrochemical supercapacitors, *Adv. Mater.* 35 (2023) 2307186, <https://doi.org/10.1002/adma.202307186>.
- [45] P. Li, Z. Wang, Y. Qi, G. Cai, Y. Zhao, X. Ming, Z. Lin, W. Ma, J. Lin, H. Li, K. Shen, Y. Liu, Z. Xu, Z. Xu, C. Gao, Bidirectionally promoting assembly order for ultrastiff and highly thermally conductive graphene fibres, *Nat. Commun.* 15 (2024) 409, <https://doi.org/10.1038/s41467-024-44692-7>.
- [46] G. Cai, Z. Wang, P. Li, K. Shen, Q. Yin, X. Ye, Y. Liu, D. Chang, Y. Liu, H. Qin, Z. Xu, C. Gao, Simultaneously enhancing plasticity and load-bearing capacity by ionic crosslink for strong and conductive wet-spun graphene fibers, *Matter* 9 (2026), <https://doi.org/10.1016/j.matt.2025.102517>.
- [47] S.C. Zhang, Y. Hou, S.M. Chen, Z. He, Z.Y. Wang, Y. Zhu, H. Wu, H.L. Gao, S.H. Yu, Highly rationally-confined alignment of nanosheets enables high-performance nanocomposites, *Adv. Mater.* 36 (2024) 2405682, <https://doi.org/10.1002/adma.202405682>.
- [48] M. Trebbin, D. Steinhäuser, J. Perlich, A. Buffet, S.V. Roth, W. Zimmermann, J. Thiele, S. Förster, Anisotropic particles align perpendicular to the flow direction in narrow microchannels, *Proc. Natl. Acad. Sci.* 110 (2013) 6706–6711, <https://doi.org/10.1073/pnas.1219340110>.
- [49] P. Poulin, R. Jalili, W. Neri, F. Nallet, T. Divoux, A. Colin, S.H. Aboutaleb, G. Wallace, C. Zakri, Superflexibility of graphene oxide, *Proc. Natl. Acad. Sci.* 113 (2016) 11088–11093, <https://doi.org/10.1073/pnas.1605121113>.
- [50] H. Niu, H. Guo, L. Kang, L. Ren, R. Lv, S. Bai, Vertical alignment of anisotropic fillers assisted by expansion flow in polymer composites, *Nano Micro Lett.* 14 (2022) 153, <https://doi.org/10.1007/s40820-022-00909-2>.
- [51] T. Guan, W. Hu, S. Shen, Y. Han, G. Wu, L. Chu, Z. Huang, L. Zhang, N. Bao, Flow-regime-controlled fabrication of CNT-bridged vertically aligned rGO/MXene fibers for high-performance fiber supercapacitors, *Adv. Mater.* (n.d.) e16561, doi: <https://doi.org/10.1002/adma.202516561>.
- [52] Z. Xu, C. Gao, Graphene in macroscopic order: liquid crystals and wet-spun fibers, *Acc. Chem. Res.* 47 (2014) 1267–1276, <https://doi.org/10.1021/ar4002813>.
- [53] S. Pei, H.M. Cheng, The reduction of graphene oxide, *Carbon* 50 (2012) 3210–3228, <https://doi.org/10.1016/j.carbon.2011.11.010>.
- [54] M. Grossman, D. Pivovarov, F. Bouville, C. Dransfeld, K. Masania, A.R. Studart, Hierarchical toughening of nacre-like composites, *Adv. Funct. Mater.* 29 (2019) 1806800, <https://doi.org/10.1002/adfm.201806800>.
- [55] Y. Wang, Y. Chen, S.D. Lacey, L. Xu, H. Xie, T. Li, V.A. Danner, L. Hu, Reduced graphene oxide film with record-high conductivity and mobility, *Mater. Today* 21 (2018) 186–192, <https://doi.org/10.1016/j.mattod.2017.10.008>.
- [56] K. Chen, B. Shi, Y. Yue, J. Qi, L. Guo, Binary synergy strengthening and toughening of bio-inspired nacre-like graphene oxide/sodium alginate composite paper, *ACS Nano* 9 (2015) 8165–8175, <https://doi.org/10.1021/acs.nano.5b02333>.
- [57] C. Huang, J. Peng, S. Wan, Y. Du, S. Dou, H.D. Wagner, A.P. Tomsia, L. Jiang, Q. Cheng, Ultra-tough inverse artificial nacre based on epoxy-graphene by freeze-casting, *Angew. Chem. Int. Ed.* 58 (2019) 7636–7640, <https://doi.org/10.1002/anie.201902410>.
- [58] F. Bouville, E. Maire, S. Meille, B. Van de Moortèle, A.J. Stevenson, S. Deville, Strong, tough and stiff bioinspired ceramics from brittle constituents, *Nat. Mater.* 13 (2014) 508–514, <https://doi.org/10.1038/nmat3915>.
- [59] Z. Zhu, Y. Liu, Y. Qin, F. Gu, L. Zhuang, H. Yu, Y. Chu, Tough and strong bioinspired high-entropy all-ceramics with a contiguous network structure, *Nat. Commun.* 16 (2025) 4587, <https://doi.org/10.1038/s41467-025-59914-9>.
- [60] X. Chen, Y. Hui, J. Zhang, Y. Wang, J. Zhang, X. Wang, S. Cheng, K. Wen, Z. Li, C. Yi, J. Shao, Single multifunctional MXene-coated glass fiber for interfacial strengthening, damage self-monitoring, and self-recovery in fiber-reinforced composites, *Compos. Part B Eng.* 259 (2023) 110713, <https://doi.org/10.1016/j.compositesb.2023.110713>.
- [61] L. Dong, J. Yang, M. Chhowalla, K.P. Loh, Synthesis and reduction of large sized graphene oxide sheets, *Chem. Soc. Rev.* 46 (2017) 7306–7316, <https://doi.org/10.1039/C7CS00485K>.
- [62] X. Yan, J. Yang, C. Huang, Z. Yu, H.-X. Zhang, L. Fang, K.-B. Yoon, Ultra-fast, cost-effective and scale-up preparation of lightweight electromagnetic interference shielding graphite worm-based aerogel, *Chem. Eng. J.* 504 (2025) 158793, <https://doi.org/10.1016/j.cej.2024.158793>.
- [63] C. Huang, X. Yan, S. Wang, H. Zhang, L. Fang, K.B. Yoon, Preparation of self-healing thermoplastic polyurethane/carbon nanotube nanocomposites for electromagnetic shielding, *Polym. Compos.* 46 (2025) S965–S972, <https://doi.org/10.1002/pc.30143>.
- [64] X. Yan, H. Zhang, W. Gu, K. Yoon, Construction of self-healing polycaprolactone composite foams with segregated structure for superior electromagnetic interference shielding, *J. Mater. Sci. Technol.* 227 (2025) 96–107, <https://doi.org/10.1016/j.jmst.2024.12.019>.
- [65] W. He, S. Wang, H. Zhang, L. Fang, Y. Wan, Lightweight multifunctional poly (dimethylsiloxane)/hollow microsphere/carbon nanotube composite foam for electromagnetic interference shielding and thermal management, *ACS Appl. Polym. Mater.* 7 (2025) 10293–10303, <https://doi.org/10.1021/acscpm.5c02302>.
- [66] S. Wang, X. Xiao, X. Yan, W. He, C. Huang, L. Chen, H. Zhang, L. Fang, K. Yoon, Multifunctional PDMS/coal gasification fine slag composites for enhanced electromagnetic shielding and thermal management, *Fuel* 395 (2025) 135195, <https://doi.org/10.1016/j.fuel.2025.135195>.
- [67] W. He, S. Li, S. Wang, H. Zhang, M. Liu, K. Yoon, Facile fabrication of ultralight magnetic graphene/hollow microsphere aerogels for high performance shielding of electromagnetic wave, heat, and sound, *Adv. Funct. Mater.* 36 (2026) e20123, <https://doi.org/10.1002/adfm.202520123>.